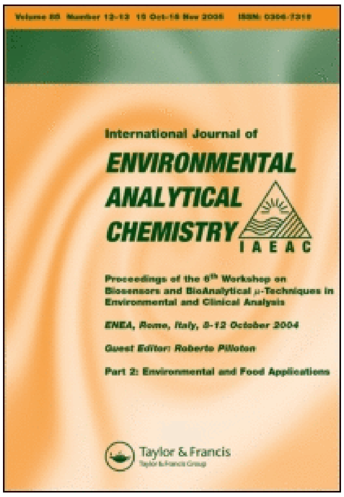

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Caroline Gommy[a]; Esperanza Perdrix[a]; Jean-Claude Galloo[a]; René Guillermo[a]
[a] Departement Chimie et Environnement, Ecole des Mines de Douai, Douai, France

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METAL SPECIATION IN SOIL: EXTRACTION OF EXCHANGEABLE CATIONS FROM A CALCAREOUS SOIL WITH A MAGNESIUM NITRATE SOLUTION

CAROLINE GOMMY*, ESPERANZA PERDRIX, JEAN-CLAUDE GALLOO
and RENÉ GUILLERMO

Ecole des Mines de Douai, Departement Chimie et Environnement, 941 rue C. Bourseul, BP838, 59508 Douai, France

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The exchangeable fraction of metals in a calcareous soil was studied with a magnesium nitrate solution and its extraction procedure was optimised. Parameters like extraction time, pH and concentration of the extractant solution, number of extractions or soil/solution ratio were examined. Experiments showed that after a 1-hour extraction, an equilibrium was established between extracted and re-sorbed metal. Moreover, carrying-out successive extractions re-sorbed quantities and maximum extracted ones could be estimated. Initial pH was fixed at 7 to avoid carbonates dissolution or hydroxides precipitation. A concentration of 0.5 mol/L and a soil/solution ratio of 1/20 were chosen. Leachate analyses showed a good selectivity of the extraction toward other soil fractions.

Keywords: Speciation; soil; metals; exchangeable fraction

INTRODUCTION

The single knowledge of the total amount of a metal in a soil does not predict its behaviour nor especially its impact on the environment. A quantitative determination of the physico-chemical forms of this metal by a speciation scheme becomes necessary for the real assessment of its mobility and toxicity in the soil. The first step of a speciation scheme consists in the determination of the exchangeable fraction.

This exchangeable fraction was studied by several authors in order to value the metal distribution and its association with soils[1–2], to predict the metal availability to plants[3–6] and the metal mobility from sludge-amended soils[7–8] or

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* Corresponding author. Fax: +33–3–27–712525. E-mail: guillermo@ensm–douai.fr.

composted ones[9]. Exchangeable metals are fixed on exchange surfaces which are developed by negatively charged colloids, mainly clays[10–11] and organic matter[10,12].

Fixation of cations on negative surfaces may be reversible[13] and several factors have been identified to affect the metal desorption : types and amounts of soil colloids, physico-chemical parameters like pH, ionic strength of the soil solution, metallic cation concentration[13–14] or presence of ligands[10].

Several salt solutions have been employed to remove metals from exchangeable surfaces (Table I). Their actions are determined both by properties of the cation and the anion present in solution.

The efficiency of the exchange reaction is due to the cation. Commonly studied exchangeable cations are divalent like magnesium, calcium or barium or monovalent such as ammonium, potassium or sodium. Divalent cations are better exchangers than monovalent ones (Ca^{2+}>Na^+) and, for the same valence, less hydrated cations are better fixed. Exchangeable cations can be classified in terms of efficiency in the following order : $Ba^{2+}>Ca^{2+}>Mg^{2+}>NH_4^+>K^+>Na^+$[11,15–16]. However, although Ba^{2+} is a good exchanger cation, it is not naturally present in soils and consequently is not a component giving information about the real soil exchange capacity. Moreover given that our soil contains carbonates and that an addition of Ca^{2+} ions can displace calcocarbonic equilibria, we therefore decided to use among the most efficient exchanger cations Mg^{2+}.

The anion has an important role as it is likely to react with desorbed metals and other soil constituents. Usually employed anions are acetate, chloride and nitrate. The buffer capacity of ammonium acetate is used to avoid the decrease in the pH[38]. However, sodium acetate can increase the pH which involves the precipitation of metallic hydroxides[39]. Generally, the more important extraction rates are obtained with these reagents[21,40].

Some authors used the complexing power of some anions like acetate or chloride to prevent readsorption or precipitation of released metal ions[41]. However, in natural soil conditions and specially in topsoils, dissolved organic matter (fulvic acid) is a strong natural complexant. Moreover by preventing the readsorption of cations on to soil particles, acetate and chloride ions may hide soil natural phenomena. Then, to limit this cation overestimation due to excessive complexation, different ways have been investigated like the application of a dilute acetate solution at 0.01 mol/L[42] or the use of the less complexing nitrate anions[5,35].

Although magnesium nitrate is applied in some speciation schemes as the reagent of the exchangeable fraction, its use is not free from questions or problems and requires further optimisations.

TABLE I Some reagents used for the extraction of the exchangeable fraction in speciation schemes

Reagents	*Environmental Samples*	*Ref.*
Ammonium acetate, 1 mol/L, pH=7	Sediments	17
	Sediments	18
	Sediments	19
Sodium acetate, 1 mol/L, pH=8.2	Soil	20
	Sediments	21
Ammonium chloride, 1 mol/L	Sediment	22
Calcium chloride, 0.05 mol/L	Soil	23
Magnesium chloride, 1 mol/L, pH=7	Sediments	21
	Soil	24
	Ash and soil	1
	Soil	25
Barium chloride, 0.1 mol/L and triethanolamine pH=8.1	Sediments	26
Barium chloride, 1 mol/L	Sediments	27
Ammonium nitrate, 1 mol/L pH=7	Soil	28
Potassium nitrate :		
0.5 mol/L	Sludge-amended soil	29
	Sludge-amended soil	30
1 mol/L	Sludges	31
Calcium nitrate :		
0.01 mol/L	Sludge-amended soil	32
0.1 mol/L	Soil	33
	Soil	34
Magnesium nitrate :		
-	Organic matter-amended soil	35
1 mol/L, pH=7	Soil	5
1 mol/L, pH=7	Soil	36
0.25 mol/L	Soil and sludge	37

The objectives of this research were to examine 1) the efficiency of $Mg(NO_3)_2$, to extract exchangeable metals at varying pH, extraction times, concentrations and soil/solution ratios and 2) the selectivity of this extraction.

This optimised procedure will permit to really value the amount of exchangeable metals and therefore assess their real mobility or bioavailability considering soil organic matter influence.

MATERIAL AND METHODS

Soil sampling

The soil sample was collected from a calcareous soil located in Northern France. This soil was selected for its location under dominant winds at 1 km from a lead-producing factory established since the beginning of the century. The top-soil 0–30 cm was used for analysis. The soil was dried at 35°C and gently ground to pass a 2 mm sieve. In order to characterise the soil, the total content of each element studied in the exchangeable fraction was measured. For Si and Al, the solid was digested by alkaline fusion and for other elements the French standard procedure NF X31–151[43] (HF and $HClO_4$), was used. Element concentrations were determined by flame atomic absorption spectrometry (FAAS). Organic matter (OM) was determined with the French standard procedure NF X31–109(44) ($K_2Cr_2O_7/H_2SO_4$). The cation exchange capacity (CEC) was obtained by the cobaltihexamine method. The main characteristics of the soil are given in Table II.

TABLE II Soil properties

Soil type	Clay silt
pH (in KCl 1:2.5)	7.4
OM (%)	4.21
CEC (meq/100g)	29.8
Element	**mg/kg of dry soil**
Cadmium	17.4
Lead	1060
Zinc	965
Aluminium	41000
Calcium	24400
Iron	51300
Manganese	350
Silicon	251500

Initial Extraction procedure

Extraction experiments were performed in triplicate using 500 mL Teflon bottles. Experimental parameters were initially chosen in accordance with the bibliography (Table I) and then successively optimised. Concurrently, several complementary studies were carried out about phenomena brought into play during reactions.

The sample-to-solution ratio was 1/20, i.e. 10 g of soil with 200 mL of 0.5 mol/L magnesium nitrate aqueous solution. Soil samples were obtained using an automatic-sampler-divider (Retsch PT 1000). A preliminary study has shown that the weight of the sample (from 2 g to 10 g) has no effect on the results obtained for metal extraction. The pH of the $Mg(NO_3)_2$, solution was previously adjusted to 7 with potassium hydroxide. Soil suspension was shaken for 2 hours at room temperature (23°C), with end-over-end continuous agitation and then, equilibrium pH (pHeq) was measured. Afterwards, soil suspension was centrifuged for 5 min at 2000 rpm. The supernatant was filtered at 0.45µm, acidified with nitric acid (1% v/v) and stored at 6°C in the dark prior to analysis. Zinc, lead and cadmium quantities were determined by FAAS with an air-acetylene flame. The results were expressed in mg of extracted metal per kg of dried soil.

The same centrifugation/filtration technique was used after each extraction. The procedure for optimisation was conducted as described in Table III.

TABLE III Procedure for optimisation of $Mg(NO_3)_2$ extraction parameters

		Experimental Conditions			
		Extraction time(hour)	*Initial pH*	*$Mg(NO_3)_2$ concentration (mol/L)*	*Soil/ solution ratio*
Parameter under study	Reaction time	1 to 4	7	0.5	1/20
	pH	2	2 to 9	0.5	1/20
	Concentration	2	7	0.02 to 1	1/20
	Soil/solution ratio	2	7	0.5	1/5 to 1/100

Kinetics, successive extractions and re-sorption

A preliminary kinetic experiment was performed to determine the equilibrium time of the exchange reaction. 75 g of soil and 1.5 L of magnesium nitrate solution were mixed under continuous agitation, 10 mL aliquots were taken at different time intervals up to 240 minutes.

Following the results of this kinetic experiment a complementary study was made about the re-sorption of cations. It had 2 parts:

1. the determination of the quantity of re-sorbed metals using 3 successive extractions (this also permits the characterisation of the efficiency of each extraction),

2. the comparison of extraction results made with or without a complexing anion (respectively Cl^- and NO_3^-) while the exchanger cation remains Mg^{2+}.

The same 10 g soil sample was extracted 3 times successively for 2 hours. Each extraction was made with a new 200 mL volume of 0.5 mol/L $Mg(NO_3)_2$ or magnesium chloride solution both adjusted at pH=7 with KOH.

Influence of pH

The determination of the exchangeable fraction has usually been made at pH 7 (Table I). However, knowing that the pH has an influence on metal adsorption[45–50], it was interesting to study the influence of the initial pH of the $Mg(NO_3)_2$ solution on metal desorption.

The initial pH range of the $Mg(NO_3)_2$ solution was adjusted from 2 to 9. For comparison the "natural" pH of a 0.5 mol/L $Mg(NO_3)_2$ solution is about 5. The pH was adjusted from 2 to 4 with nitric acid and over 5 with an alkaline solution which can modify some characteristics of the extracting solution. Three alkaline solutions, KOH, NaOH and $NaHCO_3$ were tested.

A complementary study refers to exchanger cations action in acidic conditions. This study enables the real action of Mg^{2+} in comparison with H^+ to be evaluated.

It was achieved with : 1) 0.5 mol/L of $Mg(NO_3)_2$ solution whose pH was adjusted from 2 to 5 with nitric acid (simultaneous action of Mg^{2+} and H^+) and 2) water acidified at the same pH range (action of H^+ only).

Influence of ionic concentration

The effect of ionic strength on metal desorption was measured for seven concentrations of $Mg(NO_3)_2$: 0.02, 0.05, 0.1, 0.25, 0.5, 0.75 and 1 mol/L.

Influence of soil/solution ratio

Weights of about 10 g of soil sample were mixed with different volumes of $Mg(NO_3)_2$ solution to obtain soil/solution ratio of 1/5, 1/10, 1/20, 1/50 and 1/100 (g/mL).

Selectivity

To assess the selectivity of this extraction, the concentrations of different elements were measured in the $Mg(NO_3)_2$ solution leachates : Ca, Mg, Fe, Mn, Al and Si. Although all these elements are present in several soil constituents, each one can be used as an indicator of the attack of a particular soil constituent. Thus Ca and Mg concentrations inform about carbonates dissolution. Fe and Mn are characteristic of Fe and Mn oxides. Al and Si concentrations represent alumino-silicate degradation. Dissolved organic carbon concentration inform about organic matter evolution and was determined with a Dohrmann Carbon Analyser.

RESULTS AND DISCUSSION

Influence of the extraction time, successive extractions and re-sorption

Influence of the extraction time

Concerning Zn desorption kinetics, the maximum rate of 3.5 mg/kg is reached during the first minute (Figure 1). This result agrees with the known duration of a cation exchange, which is a fast process lasting some µs or ms[51]. Then the quantity of Zn in solution decreases and after 45 minutes becomes constant, which accounts for the equilibrium between extracted and re-sorbed Zn. On this plateau, after a 2-hour extraction, the extracted Zn only represents 1.9 mg/kg or 0.2 % of soil total Zn. It means that about 50 % of the Zn extracted during the first minute is re-sorbed after 2 hours.

Cd extraction is also a fast-process (Figure 1). The maximum extracted Cd is reached in 5 minutes : 0.62 mg/kg or 3.6 % of soil total cadmium. Like for Zn kinetics, the Cd concentration decreases and reaches a plateau after 45 minutes, leading to values of 0.54 mg/kg or 3.1 % of total Cd after a 2-hour extraction. Cd re-sorption is less important than that of Zn and is estimated at 13 % of total cadmium in soil.

Concentrations of Pb extracted by the magnesium nitrate solution are less than the FAAS detection limit (0.1 mg/L), so studies on Pb desorption were stopped.

Extraction of zinc and cadmium from the soil by a $Mg(NO_3)_2$solution appears to take place rapidly, the maximum quantity of extracted cations being reached in less than 10 minutes. Both kinetics show a decrease in the concentration of metal remaining in solution and are characteristic of a cation re-sorption. After 45 minutes, stability is observed. In order to obtain comparable results, the determination of the exchangeable fraction must be carried out during the stabilisation time. We chose an extraction time of 2 hours for our investigations.

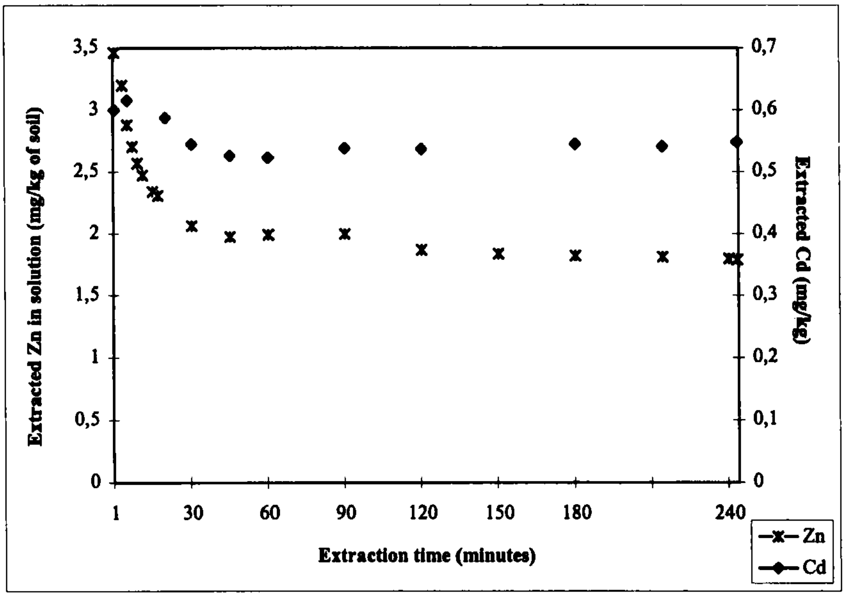

FIGURE 1 Zn and Cd extraction as a function of the extraction reaction time

Successive extractions

To further understand the re-sorption of cations observed in the kinetic study, we developed two other experiments. The first one consisted in carrying out 3 successive extractions with $Mg(NO_3)_2$. In the second one, we compared the results obtained by extractions made with or without a complexing inorganic anion.

Concerning Zn extraction, the most important quantity is measured in the first leachate, 61.2 % of the sum of the 3 extractions, and declines with the number of extractions : 23.4 % for the second and 15.4 % for the third extraction.

For each extraction i, the ratio α between the extracted Zn or Zn_i and the initially total extractable Zn or $(Zn_i+Zn_{i+1}+\ldots+Zn_N)$ where N is the total number of successive extractions, was found constant and equal to 0.6 (Equation 1) :

$$\alpha = \frac{(\mathrm{Zn})_1}{(\mathrm{Zn})_1 + (\mathrm{Zn})_2 + (\mathrm{Zn})_3} = \frac{(\mathrm{Zn})_2}{(\mathrm{Zn})_2 + (\mathrm{Zn})_3} = 0.6 \qquad (1)$$

Then, assuming that the total extractable zinc for the first extraction, $Zn_1+Zn_2+\ldots+Zn_N$, is approximately equal to the total exchangeable zinc of the soil, i.e. the cumulative quantity of zinc obtained after an infinite number of successive extractions, one may theoretically calculate the total exchangeable zinc of the soil by dividing Zn_1 by α. We found 3.75 mg/kg of soil, i.e. 0.4 % of the soil total zinc. This value is similar to the one measured after the first minute of the extraction (3.5 mg/kg see Figure 1).

Concerning Cd, this calculation can be applied too. The ratio α is calculated with the first two extractions (the third was less than the FAAS detection limit) (2) :

$$\alpha = \frac{Cd_1}{Cd_1 + Cd_2} = 0.75 \tag{2}$$

with Cd_1=0.46 mg/kg and Cd_2=0.15 mg/kg. The total exchangeable cadmium is thus estimated at 0.61 mg/kg of soil, about 3.5 % of total Cd, which is still comparable with the maximum of 0.62 mg/kg obtained after 5 minutes of extraction in the kinetic study.

Therefore knowing the constant ratio α and the amount of metal released during the first 2-hour extraction, the total quantity of exchangeable metal in the soil can theoretically be estimated. This quantity corresponds to the maximum value which can be reached during an extraction, before the establishment of the equilibrium with the re-sorption reactions. Then, this calculated quantity permits to value the amplitude of the metal re-sorption

Complexing anion

The use of complexing anions, like Cl^-, to maintain released metal in solution gives overestimated results, compared with what can happen in natural conditions. Extracted Cd is 11 times higher with $MgCl_2$ solution than with $Mg(NO_3)_2$ solution, respectively 5.18 mg/kg and 0.46 mg/kg. In fact, more than 99 % of the extracted Cd is complexed by the chloride anions. Moreover, the presence of complexing anions may favour the release of metals in solution by displacing the equilibrium towards an increase in the extracted quantities. However, we calculated with complexation constants of Cd and Cl^- that 16 % of complexed Cd is positively charged ($CdCl^+$), then it can be fixed on negative surfaces. This phenomenon is limited because $CdCl^+$ concentration is very low with respect to Mg^{2+} one, respectively 1.7 meq and about 1000 meq. The readsorption, principally on to sites of anionic exchange like the oxide ones is also possible for complexed forms negatively charged ($CdCl_3^-$ and $CdCl_4^{2-}$] which represent more than 50 % of complexed Cd.

Then, it seems better to use a non-complexing extractant. The advantage of using complexing anions to retain metals in solution becomes a problem as results are overestimated. With $Mg(NO_3)_2$ solution, the achievement of two successive extractions and a simple calculation allows to obtain the total exchangeable metal in soil and the amplitude of metal re-sorption (natural phenomenon in the soil).

Influence of the pH on desorption

Three alkaline solutions have been used to adjust the pH at 7 : NaOH, KOH and $NaHCO_3$. With NaOH the pH is unstable and decreases rapidly. With KOH, the pH remains constant at about 7 for several minutes, which is enough to set up extractions. Thanks to its buffer capacity, $NaHCO_3$ keeps the pH at 7 without any stability problem. However quantities of Zn and Cd extracted when the pH is fixed with $NaHCO_3$ are higher than those obtained with KOH, respectively 2.23 mg/kg and 0.72 mg/kg with $NaHCO_3$ and 1.86 mg/kg and 0.36 mg/kg with KOH. Equilibrium pH obtained after a 2-hour extraction are the same for both KOH and $NaHCO_3$ solutions. Finally, KOH solution has been chosen because it permits to fix the pH at 7 better than the NaOH solution without involving any perturbation on calcocarbonic equilibria due to the bicarbonate ions of the $NaHCO_3$ solution.

Figure 2 shows the evolution of the equilibrium pH of the soil depending on the initial pH of the $Mg(NO_3)_2$ solution. When the pHi is higher than 3.5, the soil buffer capacity allows to neutralise all the solution acidity reaching a pHeq at about 7.6–7.7. This results from the presence of carbonates in the soil. However, the soil buffer capacity does not entirely neutralise the acidity of a $Mg(NO_3)_2$ solution when its pHi varies between 2 and 3.5, so pHeq decreases up to 6.7.

The evolution of extracted Zn when the acidity of $Mg(NO_3)_2$ solution rises shows that when pHeq decreases by 1 pH unit from 7.7 to 6.7, extracted Zn increases more than 8 times from 1.5 to 13.2 mg/kg (Figure 3). This growth can be explained by the carbonates dissolution when pHeq is less than 7.6–7.7 and also by the decrease in the CEC through neutralisation or protonation of the exchange pH-dependent sites of clays or organic matter[48].

In order to distinguish the action of Mg^{2+} from the one of H^+ an additional experiment was carried out using acidified water instead of the acidified magnesium nitrate solution. Figure 4 shows that the quantities of Zn extracted by (Mg^{2+} + H^+) are always higher than those extracted by an acidified water (H^+ only).

In aqueous solutions with pHi $\geq$ 2.8 (or pHeq $\geq$ 7.5), H^+ ions seem to have no effect on Zn extraction.

As the pHi is smaller than the pHeq of the soil (7.4–7.5) the dissolution of the calcite goes on until reaching the pHeq. Then metals linked to calcite can be released. However, dissolution equilibrium constants of $ZnCO_3$ and $CaCO_3$ show that for the same dissolved carbonate CO_3^{2-} concentration, Ca concentra-

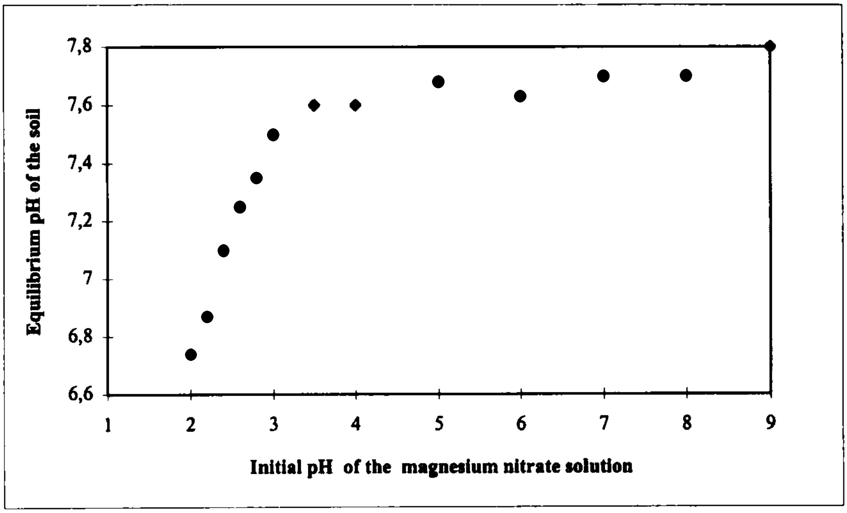

FIGURE 2 Evolution of the equilibrium pH of the soil suspension depending on the initial pH of the $Mg(NO_3)_2$ solution

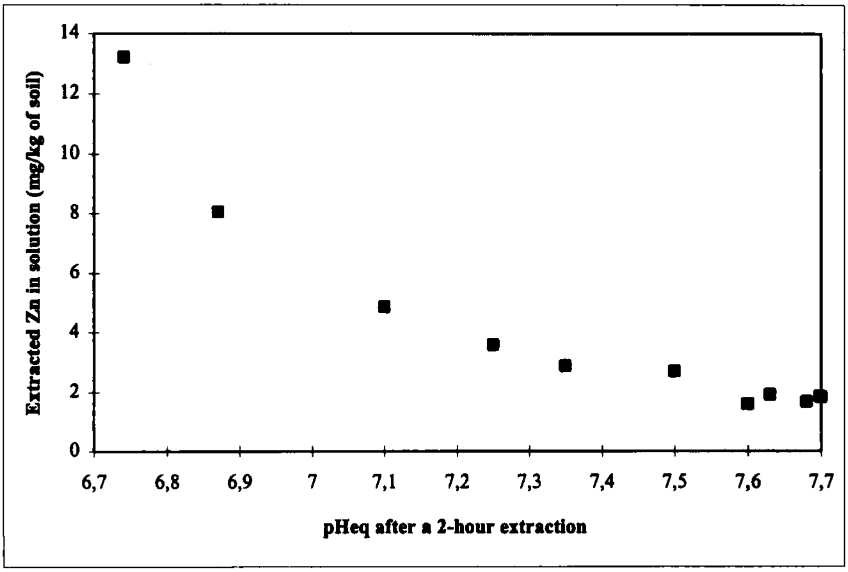

FIGURE 3 Influence of the equilibrium pH of the soil suspension on the amount of extracted Zn in solution

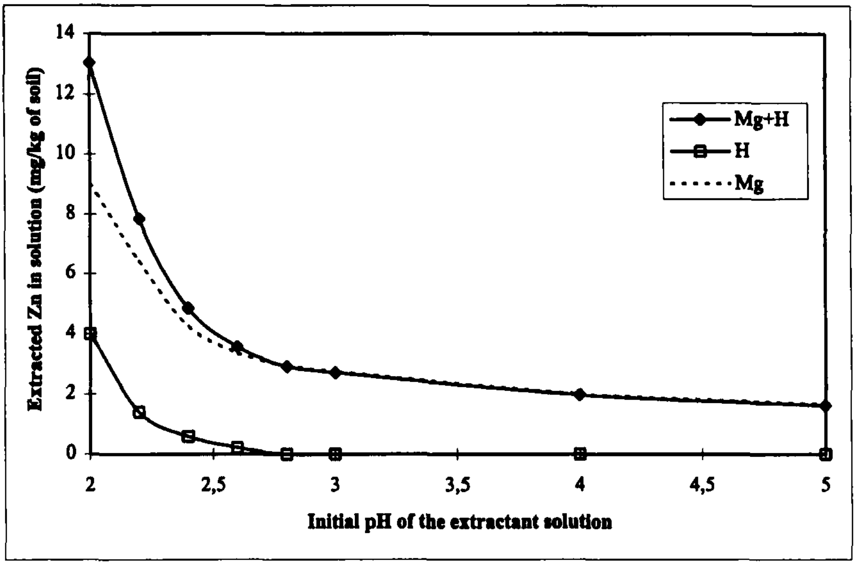

FIGURE 4 Extracted Zn as a function of initial pH for an acidified $Mg(NO_3)_2$ solution (Mg+H) or for acidifed water (H) (the dotted curve of "Mg only" is calculated and drawn by substraction of the two other curves)

tion is 400 times higher than the Zn one. This means that $ZnCO_3$ is less soluble than $CaCO_3$. Besides, as the CEC is high at alkaline pH, the Zn likely to be released by carbonates dissolution may be adsorbed on available exchange sites when Mg^{2+} is not in high quantity. On the contrary, when Mg^{2+} is present in high quantity, exchange sites will be in majority occupied by Mg^{2+} cations, which reduces the readsorption of Zn.

For an initial pH included between 2 and 2.8 (pHeq from 6.6 to 7.5), a part of the extracted Zn comes from the action of H^+ ions. For instance at pHi=2 about 30 % of the zinc extracted by the acidified magnesium nitrate solution derives from the action of the protons only. If a competition for exchange sites exists between Mg^{2+} and H^+, the quantity of Zn extracted by Mg^{2+} ions should decrease with the increase in H^+ ions but this is not the case. Moreover, the concentration of H^+ ions is at least 50 times smaller than the one of Mg^{2+} ions.

In addition to the dissolution of acido-soluble compounds like the calcite the most likely action of H^+ ions in this range of pH concerns the neutralisation of the pH-dependent sites, following the reaction (3) :

$$SO\text{-}Zn + 2\,H^+ \Leftrightarrow 2\,SO\text{-}H + Zn^{2+} \qquad (3)$$

where « SO » refers to a negative pH-dependent surface site.

Given that the number of pH-dependent sites in the form of SO-H increases with the diminution of the pH, there will be fewer sites available for metal readsorption.

In conclusion, for pHi ≥ 2.8 (pHeq ≥ 7.5), the extracted metal mainly comes from the cation exchange reaction with the magnesium ions. Extraction efficiencies are smaller than those obtained for acidic pHeq. pH-dependent sites are mainly in the dissociated form SO^-, which involves a strong probability of readsorption of the metal exchanged by magnesium ions. Moreover, the precipitation of carbonates which can imply the co-precipitation of metals is favoured.

When the initial pH of the solution is inferior to 2.8 (pHeq ≤ 7.5), the action of H^+ ions is added to the Mg^{2+} one. The solubilisation of acido-soluble compounds takes place as well as the neutralisation of the surface sites from the SO^- form to the SOH form.

The competition between protons and magnesium cations for exchange sites is not observed in the studied range of pHeq included between 6.6 and 8.4. Nevertheless, for more acidic pH the competition would become less negligible (Yousfi, 1995).

To sum up, when the acidity of the extraction solution increases, extracted quantities of Zn become bigger. Nevertheless these quantities remain insignificant and constitute a maximum of about 1.3 % of soil total zinc.

Influence of the concentration

Determination of the Mg/Zn exchange coefficient K

Thanks to the results obtained in the successive extractions experiments an experimental ratio α between the quantity of Zn in solution (Zn^{2+}) and the total exchangeable Zn (Zn_T) has been established (4) :

$$\alpha = \frac{(Zn^{2+})}{(Zn_T)} = 0.6 \qquad (4)$$

During the cation exchange reaction (5), Mg^{2+} ions introduced by the extractant replace the Zn ions fixed on the exchange sites of the soil constituents :

$$\overline{Zn} + Mg^{2+} \leftrightarrows \overline{Mg} + Zn^{2+} \qquad (5)$$

where $\overline{Zn}$, $\overline{Mg}$ represent the zinc and magnesium fixed on soil and Zn^{2+}, Mg^{2+} the cations in solution.

Applying the mass action law, an adimentional exchange coefficient K related to the reaction (5) can be written (6) :

$$K = \frac{(\overline{Mg})}{(\overline{Zn})} \times \frac{(Zn^{2+})}{(Mg^{2+})} \tag{6}$$

where $(\overline{Zn})$ and $(\overline{Mg})$ represent respectively the quantities of Zn and Mg fixed in soil in meq/L and (Zn^{2+}) and (Mg^{2+}) the quantities of cations in solution in the same units. Considering the mass balance equation for zinc (7),

$$(Zn_T) = (Zn^{2+}) + (\overline{Zn}) \tag{7}$$

the relation (6) may be written taking a into account (8) :

$$K = \frac{(Zn^{2+})/(Zn_T)}{1-(Zn^{2+})/(Zn_T)} \times \frac{(\overline{Mg})}{(Mg^{2+})} = \frac{\alpha}{1-\alpha} \times \frac{(\overline{Mg})}{(Mg^{2+})} \tag{8}$$

As Mg^{2+} cations are in very high concentration (0.5 mol/L) relative to pollutant metals, the CEC of the soil is considered as being in the majority occupied by Mg^{2+} ions, that is to say (9) :

$$CEC = (\overline{Mg}) + (\overline{Zn}) \sim (\overline{Mg}) \tag{9}$$

As the extraction is made with 10 g of soil in 200 mL of extractant and CEC equals 30 meq/100g, the quantity of fixed magnesium is therefore $(\overline{Mg})$=15 meq/L.

The determination of (Mg^{2+}) is achieved by the mass balance equation (10) :

$$(Mg^{2+}) = (Mg_T) - (\overline{Mg}) = 985 \text{ meq/L} \tag{10}$$

where (Mg_T) represents the magnesium brought by the magnesium nitrate solution, neglecting the magnesium that is likely coming from the soil : (Mg_T) = 1000 meq/L.

Thus the value of the exchange coefficient K can be easily calculated. This value of $K=2.28 \times 10^{-2}$ suggests a high affinity of the exchange sites towards zinc with respect to the magnesium.

Influence of the $Mg(NO_3)_2$ solution concentration on Zn extraction

Figure 5 shows that extracted Zn increases with the concentration of the $Mg(NO_3)_2$ solution. The effect of the salinity on the quantity of Zn in solution can be valued by the ratio α which depends on (Mg_T), as seen in (11).

$$\alpha = \frac{(Zn^{2+})}{(Zn_T)} = \frac{1}{1+\dfrac{1}{K\left(\dfrac{(Mg_T)}{CEC}-1\right)}} \tag{11}$$

The relation (11) allows the calculation of the theoretical quantity of Zn^{2+} in solution. This calculated amount of zinc is presented in Figure 5, where it can be noted that a good correlation exists between experimental and calculated results.

Finally, extractions will be made with a 0.5 mol/L $Mg(NO_3)_2$ solution, which permits a good extraction rate without involving any analytical problem due to the salinity.

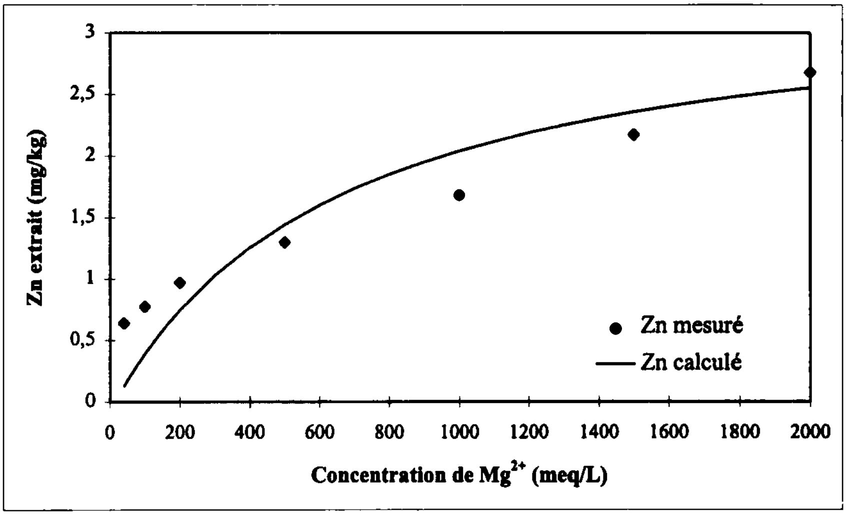

FIGURE 5 Influence of the $Mg(NO_3)_2$ concentration on Zn extraction (the calculated Zn derived from Equation 11 with K=2.28 × 10^{-2}, CEC=30 meq/100g, and Zn_T=3.4 mg/kg)

Influence of soil/solution ratio

As seen previously, theoretically released Zn can be calculated using the equation (11). However, in this case the evolution of the soil/solution ratio M/V leads to the variation of the CEC expressed in meq/L (12).

$$\mathrm{CEC(meq/L)} = \frac{\mathrm{CEC(meq/100g)}}{100} \times \frac{\mathrm{M(g)}}{\mathrm{V(L)}} \qquad (12)$$

where V is the volume of the magnesium nitrate solution and M=10 g corresponds to the mass of soil which is kept constant.

These calculations are made with the hypothesis that the concentration of fixed magnesium equals the CEC (9). Then, as the extractant volume varies, the value of the CEC, expressed in meq/L varies too (Table IV).

TABLE IV Variations of the CEC (meq/L) related to the soil solution ratio

Soil/Solution ratio (g/mL)	1/5	1/10	1/20	1/50	1/100
CEC (meq/L)	60	30	15	6	3

Figure 6 represents the decrease in the extracted Zn with the increase in the CEC (meq/L), that is with the decrease in the extractant volume. A good enough correlation can be seen between calculated and observed Zn values.

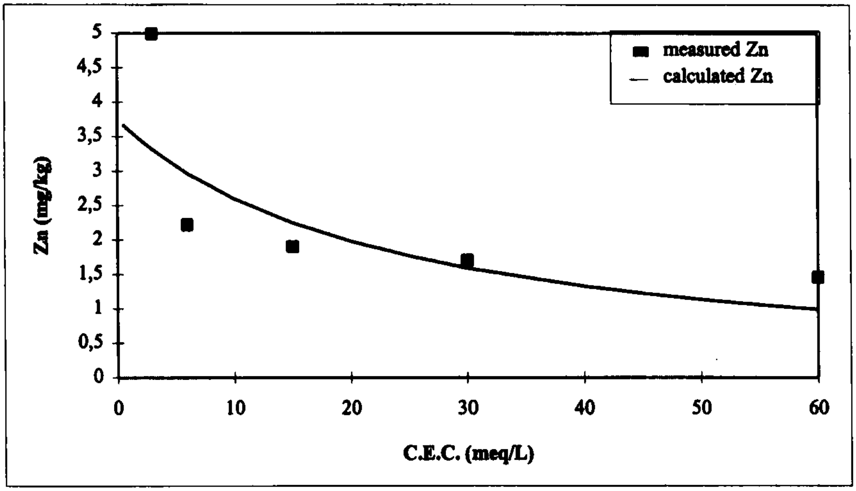

FIGURE 6 Comparison between measured and calculated Zn obtained by Equations 11 and 12 with $K=2.28 \times 10^{-2}$, CEC=30 meq/100g and $(Zn_T)=3.75$ mg/kg

This increase in the quantity of extracted metal with the volume of the extractant may be due to a better soil dispersion in the solution, for instance by a decrease in the interactions between particles[49]. Moreover, since the concentration of $Mg(NO_3)_2$ is kept constant, the increase in the volume leads to an increase in the number of moles of magnesium in solution. This involves the displacement of the exchange reaction (5) towards the release of zinc in solution[52].

Varying the soil/solution ratio between 1/5 to 1/50 has little effect on the quantities of extracted zinc. The same result is found in the case of cadmium in the range 1/5 to 1/20. For a soil/solution ratio of 1/100, maximum extracted quantities are observed but the high dilution rate leads to very small metal concentrations in solution, near the detection limit of the FAAS. For these reasons, the ratio 1/20 has been chosen for the procedure.

Selectivity of the procedure

Thanks to all previous experiments the procedure has been optimised. The reagent, the magnesium nitrate solution is used at 0.5 mol/L with an initial pH adjusted at 7 with KOH. A soil/solution ratio of 1/20 is retained and the extraction time is fixed at 2 hours, with an end-over-end continuous agitation, at room temperature.

Table V presents the extracted quantities of different elements obtained for the exchangeable fraction with the magnesium nitrate solution. The insignificant quantities of Al and Si indicate that compounds including Si and Al, like Al oxides or clays, are not degraded. The selectivity is good for iron and manganese oxides too. Low quantities of organic matter measured in the leachate (2.6% of the total organic matter) are certainly due to soluble organic matter.

TABLE V Extracted quantities of different elements obtained in the exchangeable fraction

Elements	*mg/kg of soil*	*% of the total element*
Zn	2.25	0.23
Cd	0.46	2.6
Cu	<0.8	insignificant
Pb	<4	insignificant
Ca	7699	30
Mn	1.24	0.3
Fe	<2	insignificant
Si	<40	insignificant
Al	<20	insignificant
Organic matter	1100	2.6

The most released element is Ca, with 7.7 g/kg or 0.19 mol/kg of soil. In previous conclusions, we have seen that Ca in solution may come from both exchangeable cations and carbonates dissolution. If the totality of the soil CEC (30 meq/100 g) is saturated by exchangeable Ca, this exchangeable calcium will be valued at 0.15 mol/kg, therefore accounting for 78 % of the extracted Ca. The remaining 22 % of Ca may come from carbonates dissolution as pHeq is above pHi. If these 22 % of Ca really come from carbonates, it represents 11 % of the Ca contained in the calcite.

CONCLUSION

Generally, the first fraction of a speciation scheme values the exchangeable metal. In our scheme, a magnesium nitrate solution was chosen, for its divalent cation and non-complexing anion. For instance, complexing anions like Cl^- may induce an 11 times over-estimated result for the Cd extraction. The influence of four parameters were studied. The extraction time was fixed at 2 hours, since the desorption and rebinding reactions are at this time equilibrated. The pH was fixed at 7 with a KOH solution in order to avoid excessive carbonate dissolution in acidic conditions or metal coprecipitation in alkaline ones. The re-sorption rate can be estimated by a simple calculation, from the results of 2 or 3 successive extractions. These results were also used to determine the value of the exchange coefficient K. From this value, the theoretical influence of the extractant concentration and the soil/solution ratio can be modelled. Although the efficiency of the extraction is better in high salinity conditions, the $Mg(NO_3)_2$ concentration was limited to 0.5 mol/L in order to avoid analytical problems due to too strong a salinity of the solution. For similar reasons the soil/solution ratio was fixed at 1/20 in order to avoid the analytical problems due to an excessive dilution of the metal concentration. The analysis of the leachate shows a good selectivity of the nitrate magnesium extraction towards soil constituents.

Finally, now that the procedure has been optimised, it would be interesting to do more comparison with other reagents used for the exchangeable fraction.

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