

Prediction of Zinc Precipitation Accompanying Sorption Process in Calcareous and Basaltic Soils

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□ ABSTRACT □

The aim of this study was to evaluate the distribution of zinc among solute, adsorbed and precipitated phases in calcareous and basaltic soils. For this purpose, the results of sorption batch experiment, conducted at $\text{pH} = 6 \pm 0.2$, have been investigated using Freundlich and Langmuir equations and combining a thermodynamic approach and X-ray diffraction (XRD) spectroscopy. It has been shown that both Freundlich and Langmuir models fit similarly well the data of zinc uptake, and corroborates the hypothesis that Baniyas soil expresses more affinity for zinc retention. The exponential evolution of distribution coefficient K_D with Zn_{TOT} indicates that higher affinity is expressed at low degrees of coverage. The partitioning among zinc species in solution indicated that the free ions of zinc Zn^{2+} were the most dominant in solution. The predictions based upon the thermodynamic calculation, and the evidences provided by XRD spectroscopy corroborate and show both the precipitation of zinc as franklinite ZnFe_2O_4 . This mineral hence may deeply affect the dynamic of zinc in natural environment in presence of iron minerals.

Key words: zinc, sorption, speciation, precipitation, affinity, calcareous soil, basaltic soil, distribution co-efficient.

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الاستقصاء عن ترسيب الزنك في أعقاب ادمصاصه في الترب الكربوناتية (الكلسية) والبازلتية

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□ الملخص □

هدفت هذه الدراسة إلى حصر ميزانية الزنك والتنبؤ بترسيبه في تربتين متباينتين بقوامهما وتركيبهما الفلزي: تربة كربوناتية (كلسية) وتربة بازلتية. وبحثاً عن هذه الميزانية درست إزاحة الزنك من قبل التريتين بصورتها الصوديومية (تربة - Na) عند قيمة $pH = 6 \pm 0.2$ وذلك كتابع للتركيز (0.00025 - 0.02 مول/لتر) في معلمات نسبها 1g : 25 ml. وتحليل النتائج تطبيقاً لعلاقتي فرنديش ولانغمير تبين أن العلاقتين تتبآن بإزاحة الزنك بكفاية عالية، وتدلان على أن تربة بانياس تزيح هذا العنصر باصطفائية أعلى، متفقتين بذلك مع مدلول معامل التوزع KD، الذي رسم مساراً أسياً متصاعداً بانخفاض التركيز الكلي للزنك. وأظهرت حسابات التوازن الترموديناميكي من ناحيتها السيادة شبه المطلقة لشاردة الزنك في المحلول. كما بيّنت هذه الحسابات أن الفرانكلينيت ($ZnFe_2O_4$) متبوعاً بـ "زنك- التربة" والولميت (Zn_2SiO_4) كانت الأطوار الفلزية القابلة للترسيب. فيما ظهرت أطوار أخرى كالسميثونيت ($ZnCO_3$) والهوبيت ($Zn_3(PO_4)_2 \cdot 4H_2O$) والهيدروكسيدات ($Zn(OH)_2$) غير مستقرة. وهذه النتيجة القائمة على حسابات ترموديناميكية خالصة أكدتها بطريقة ما نتائج التحليل بالأشعة السينية (XRD) التي كشفت عن تمايز الفرانكلينيت بصورتيه، المتبلورة النهائية ($ZnFe_2O_4$) أو الانتقالية ($Fe_{6.8} Zn_{3.2}$)، وكذلك الزنسييت. انطلاقاً مما تقدم يمكن التأكيد على أهمية الفرانكلينيت ودوره النوعي فيما يخص ديناميكية معدنه في الأوساط الطبيعية وبالأخص تلك التي تتميز بمحتواها العالي من أكاسيد الحديد.

الكلمات المفتاحية: زنك، إزاحة، ادمصاص، ترسيب، معامل توزع، اصطفائية، ترب كربوناتية، ترب بازلتية.

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Introduction:

Reactions at solid-water interfaces, such as sorption and precipitation, may dictate solute mobility and often control the fate, bioavailability, and transport of trace metals in aquatic and soil environments (Scheidegger et al, 1996; Stumm and Morgan, 1996). One metal that has been extensively studied is zinc. Although this metal doesn't relatively pose serious threat to biota and vegetation, it may however be detrimental to the environment at elevated levels resulting from the accumulation in soils as issue of smelting activities, or agricultural applications of sewage sludge and agrochemicals (Manceau et al, 2000; Roberts et al, 2002). At acidic pH values, Zn toxicity to plants enhances and may be the third most common after Al and Mn (Chaney, 1993).

Many researchers have shown the ability of zinc to interact specifically with Al, Si, Fe minerals, such as amorphous silica (Roberts et al, 2003), gibbsite (Roberts et al, 2002, 2003), α -Al₂O₃ (Trainor et al, 2000), pyrophyllite (Ford and sparks, 2000), and goethite - ferrihydrite (Nachtegaal and Sparks, 2004; Dyer et al, 2004; Trivedi et al, 2001; Schlegel et al, 1997; Waychumas et al, 2002; Roberts et al, 2002). In addition to the role of Al, Fe, Si minerals, calcite has been always an interest natural component known for its ability to incorporate trace elements in its lattice. This has been a major focus of investigations in a wide variety of fields. Traces elements abundance and their distributions in carbonates are used as tracers of petro-genetic and diagenetic histories, as proxies for changes in ocean chemistry, as sink in geochemical cycles, and for predicting the effectiveness of sequestration of contaminants (Elzinga and Reeder, 2002). Concerning zinc uptake by carbonate, evidences collected from X-ray absorption fine structure (EXAFS) spectroscopy have shown that zinc incorporated into calcite during crystal growth substituting Ca in octahedral coordination (Reeder et al, 1999). Similar findings have been also reported by other researches (Zachara et al, 1991; Cheng et al (1998). The ability of zinc to replace for calcium in octahedral coordination results in calcite isomorph ZnCO₃ formation, unlike some metals carbonate such as CuCO₃, which is not known to exist with calcite structure, probably as a consequence of the tendency of Cu²⁺ to undergo a Jahn-Teller distortion from octahedral coordination (Elzinga and Reeder, 2002).

For the identification of metals complexes, binding and metal precipitates on minerals surfaces a spectroscopic investigation of interface have been applied. In recent years, the researches in this field have given a variety of innovative studies (Eick and Fendorf, 1998; Yamaguchi et al, 2001; Scheckel and Sparks, 2001; Elzinga and Sparks, 2001; Trivedi et al, 2004; Peltier et al, 2004). The usefulness and advantageous employment of X-ray spectroscopy has acquired nowadays a new advancement. The progression gained here was the consequence of X-ray spectroscopy marriage with macroscopic investigations, initiated by relatively few contributions (Trivedi et al, 2003; Dyer et al, 2003a, b; Elzinga and Sparks, 2002; Roberts et al, 2002). The evidences evolved here show that metals, such as Zn, Ni and Co, can be incorporated into neo-formed precipitates, formed at the surface of phyllosilicate minerals (Ford and Sparks, 2000; Scheidegger et al, 1997; Eick and Fendorf, 1998) or at surface of Al oxide (hydroxide) minerals (Yamaguchi et al, 2001; Peltier et al, 2004). Depending on the Al-bearing clay minerals and metal oxides, the sorption of Ni, Zn, Co and other metal ions results initially in the formation of mixed metal-Al layered double hydroxide (Me-Al LDH). With increasing reaction time, the anionic species in the interlayer space of the LDH can be replaced by silica polymers transforming the LDH gradually into a more stable precursor Me-Al phyllosilicate. Similar process is also perceived for the interaction with Fe oxide

(hydroxide). It was proposed that, similar to the precipitation of Me-Al LDH, the formation of metal spinels ($\text{Me}^{2+}, \text{Fe}^{2+}$) $\text{Fe}_2^{3+}\text{O}_4$, at Fe oxides surface, such as goethite surface, may happened causing an enhancement of ions uptake (Coughlin and Stone, 1995), in addition to its penetration into the mineral lattice (Bruemmer et al, 1988). All these reports indicate the particular importance of iron oxides as reactive materials for zinc uptake from natural solution or within soils by precipitation with or on it (Lindsay, 1979; O'Day et al, 1998).

However, determining the adsorption mechanisms has not already been a simple task. Among difficulties encountered here, the interference with precipitation constitutes the chief problem, especially at high concentrations. The question that has been still evolved here, despite the great advance in EXAFS spectroscopic applications, is to determine correctly the boundary limits between the precipitation and the specific sorption, and to pass from the mechanistic aspect of process to its quantitative. In this respect, the thermodynamic of equilibriums may represent a valuable tool allowing, at least, to make predictions about precipitation, and to assess its quantitative aspect. The place of thermodynamic approach emerged in many textbooks (Lindsay, 1979; Stumm and Morgan, 1996). It was applied by Sadiq (1991) to evaluate zinc speciation and precipitation in calcareous soils. This study aimed at zinc speciation and precipitation basing upon the data collected from batch experiments, and using the thermodynamic of chemical equilibrium combined with XRD spectroscopy.

Materials and Methods:

1. Soil sampling and preparation

Two soils representing two different pedogenetic formations were retained for this study. An Inceptisol formed on calcareous parent material and Entisol formed on basaltic parent material. Four tailing samples were collected at each sampling site, from the top 25 cm soil, after removing the plant cover and residues. Samples were air dried in laboratory. Plant debris and stones were removed prior grinding and sieving at 2 mm. A bout 400 g (4×100) < 2 mm of each soil were suspended into 2 liters of 1N NaCl for 24 hour, the supernatant were discarded and the soil was suspended repeatedly twice into 2 liters for two hrs each time. The aliquot then leached with ethanol until the negative test with Ag^+ , and then dried at $\sim 75^\circ \text{C}$ for two days. The resulted Na-Soil was stored for the batch experiment, the X ray spectroscopy and specific surface measurements.

2. Batch experiment

1g of stored Na-soil was weighed into many flasks (borosilicate) and hydrated with a complementary precalculated volume (16-20 ml) of distilled water for 24 hrs. The necessary volume of stock solution of Zn metal ($\text{Zn}(\text{NO}_3 \cdot 4\text{H}_2\text{O})$) was added to give a total suspension volume 25 ml and an initial concentrations of zinc ranging from about 0.00025 to 0.021 mol/l. The pH adjustments were made either by HNO_3 or by NaOH to give a pH 6 ± 0.2 . All treatments were given in quadruplicate. The flasks were stopped with parafilm, stirred for two hrs, and left after then to equilibrate for 24 hrs. After the equilibration time the suspensions were centrifuged at $4500 \times g$ for fifteen minutes, filtered through Whatman No 41 and the final pH was measured. The contents of metals in the equilibration solutions were determined with a Buck Flame Atomic Absorption Spectrometer (FAAS). Analytical grade standard solutions were used to calibrate the instrument. For a kinetic aspect of zinc retention, an additional batch experiment has been conducted at fixed concentration (0.015 mol/l) and variable equilibration time ranging from 24 hrs to 20 days.

Results and discussion:

1. Soils analysis

Table 1 represents some characteristics of soils used in this study. It must be noted that the two soils are so different either by their physical and chemical properties. Bouqa soil is characterized by fine texture (Tu), dominated by the clay fraction, while Banias soil is distinguished by its coarse texture (Su) constituted of about 74% of sand and 26% of silt. The quasi absence of colloidal fraction in this soil reflects a very low transformation rate indicating that the volcanic parent material has not been highly weathered. Despite the coarse texture of Banias soil it must be mentioned that this soil possess much more extended specific surface S ($46.2 \text{ m}^2/\text{g}$) in comparison with Bouqa soil ($30.4 \text{ m}^2/\text{g}$). This difference in specific surface may be explained by the voided texture of volcanic materials of Banias soil.

The two soils are also contrasted by their mineralogy. This is expressed by the dominance of calcite in Bouqa soil and by the presence of low proportion of goethite associated with ferrihydrite, in opposition to Banias soil that is high in iron oxides formed of hematite combined with a certain quantity of magnetite. Concerning the elemental composition, the XRF indicate that calcium is the major element in Bouqa soil in comparison to iron in Banias soil. It is also shown that the two soils are high in titanium content, which is higher in Banias soil. Examination of results reveals as well that Banias soil is generally richer in miner and trace metals content except for strontium, which is more abundant in Bouqa soil as resultant of its association with calcium, and for zinc due probably to the much more use of agrochemicals in this soil.

Table 1. Some selected characteristics of Bouqa and Banias soils and their metals contents as analyzed by XRF.

soil	analysis							
	texture			%	CEC	BET	%	pH
	S	U	T					
	Sand	Silt	Clay	CaCO ₃	(meq/100g)	Specific Surface S (m ² /g)	OM	
Bouqa	9.5	36	54.5	46	12	30.4	1.4	7.9
Banias	74	26	--	2.5	10	46.2	0.5	7

soil	metals content							
	major elements (%)		Miner - Trace elements (ppm)					
	Ca	Fe	Ti	Mn	Zn	Sr	Zr	Y
Bouqa	18 ± 0.9	2.5 ± 0.1	2579±800	987±50	<30	483±24	102±7	19.2±3
Banias	2.2 ± 0.3	9.4 ± 0.4	7931±737	1546±180	77.4±12	235±12	116±7	16±3.4

2. X-ray diffraction

The x-ray diffraction, as used in this study, intended to characterize the mineralogical composition of soils and to show if zinc has precipitated as new mineral upon the adsorption process. For this purpose, the non treated soil sample, and the batch soil samples, only receiving zinc at 0.013 mol/l concentration, were examined by x-ray diffraction. As seen in table 2, Bouqa soil is mainly constituted of calcite, and contains a small quantity of iron oxides (less than 1% of calcite), dominated by goethite $\alpha\text{-FeOOH}$ (82 % of iron oxides) in association with ferrihydrie $\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ (18 % of iron oxides). It

is also shown that iron oxides are much higher in Banias soil and attain an elevated percent reaching 20%. However, it could be mentioned as well that the two principal iron oxides encountered in Bouqa soil are replaced in Banias soil by a dominant portion of hematite Fe_2O_3 (95 % of iron oxides) in association with a marginal quantity of magnetite (5 %), probably inherited from parent materials.

Table 2. X-ray diffraction analysis (XRD): Detection of zinc precipitates.

soil		XRD analysis										
		calcite	Iron oxides				zincite	Zn-Fe spinels	franklinite	hopeite	smithonite	willemote
			H	G	F	M						
Bouqa	BK	x		x	x		-	-	-	-	-	-
	BK-Zn	x		x	x		x	x	-	-	-	-
Banias	BA	-	x	-	-	x	-	-	-	-	-	-
	BA-Zn	-	x	-	-	x	-	-	x	-	-	-

BK = Bouqa soil, BK-Zn = Bouqa soil receiving zinc, BA = Banias soil, BA-Zn = Banias soil receiving zinc, x = detected by XRD without any signification quantitative, - = non detected. H = hematite, G = goethite, F = ferrihydrite, M = magnetite

For the two soils, the application of x-ray didn't reveal the presence of any zinc minerals in the non treated samples. However, the evidences provided by x-ray diffraction prove that zinc was neo-precipitated upon adsorption, as a mixed Zn-Fe oxide or simple zinc oxide ZnO. In the same time, the findings based on x-ray analysis indicate that the passway of zinc into the precipitate forms may be not the same in the two soils. This precipitate was represented by franklinite in Banias soil, whereas the precipitate rather took the form of Zn-Fe spinel ($Fe_{6.8} Zn_{3.2}$) in addition to zinc oxide ZnO in Bouqa soil. The Zn-Fe spinel formed in Bouqa soil, which is weakly higher in the atomic ratio Fe/Zn than the franklinite, may be the precursor of this later mineral. It can be concluded therefore, that the rate of formation of franklinite seems to be slower in Bouqa soil than Banias soil. This difference between the two soils may be, as a first glance, correlated with the nature and feature of iron oxides, organic matter content, and the association between these two constituents. In opposition to Bouqa soil, one observes that Banias soil is poor in OM, and characterized by free hematite present in high quantity. It would be likely that the low content of organic matter and the abundance of free iron oxides motivated franklinite crystallization in Banias soil.

3. Zn uptake

Figure 1 gives the retention isotherms of Zn by Bouqa and Banias soils. It can be seen that the amounts retained increase with the increase of equilibrium concentration, especially at low level of Zn loadings. Zinc uptake after then goes slowly and continues so, apparently tending toward a maximum, apparently equal for both soils (500 mmol/kg). It can be noted that the general drift of Zn retention is rather the same for the two soils. For both soils, this trend could be identified with a logarithmic function $q = a \ln C_e + b$ with approximately similar correlation coefficient R higher than 0.95. A power like function could also fit the sorption data. Perhaps, a slight difference between the two isotherms is already perceived. It must be noted as well that most zinc was uptaken within 24 hours, and the extending reaction time to 20 days, as seen in figure 2, did not change profoundly the equilibrium concentration.

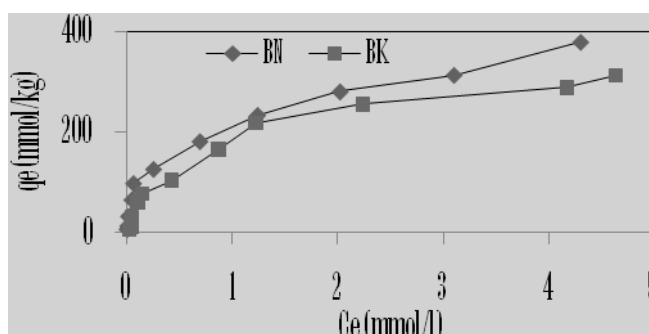


Fig.1. Isotherms of zinc uptake onto Bouqa and Banias soil suspensions (1g soil/25 ml, pH 6 ± 0.2, equilibration time = 24 hrs).

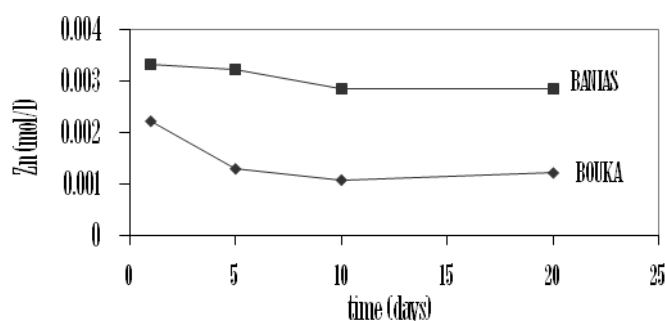


Fig.2. Evolution of equilibrium zinc concentration C_e (mol/l) as a function of time (days).

The experimental data of adsorption were examined using Langmuir and Freundlich equations. As seen in the summary table3, the high values of correlation coefficient R for both models and both soils, pretends that Freundlich and Langmuir equations apparently fit similarly well the data of zinc adsorption. It can be observed as well that the parameters of the two models (K_F , n, K_L) change in the same way for both soils. However, the interpretation on the parameters of both models corroborates the hypothesis that Banias soil expresses more affinity for zinc retention. This difference in behavior, as a first approximation, may be explained basing on the specific surfaces and the mineral compositions. However, referring to the data carried out for unit surface it'll be stated that things were not really changed. Hence, the difference in behavior between the two soils may effectively reflect a corresponding difference in affinity probably correlated with soils mineralogy. En fact, the x-ray diffraction study shows that the two soils are different both by their crystallographic features and by mineralogical composition. Banias soil is rich in iron oxides, while Bouqa soil is dominated by calcite. It might be as well expected that Banias soil has to be rich in Al – Si allophonic compounds. It is well established, as it is reported by many studies, that the minerals of these three major elements, in addition to Mn minerals, interact very specifically with metallic ions. (Schlegel et al, 1997; Roberts et al, 2003; Roberts et al, 2002, 2003; Trainor et al, 2000; Ford and sparks,2000; Nachtegaal and Sparks, 2004; Trivedi et al, 2001; Waychumas et al, 2002; Roberts et al, 2002).

Table 3. The linear Freundlich and Langmuir isotherms parameters for zinc retention onto Bouqa and Banias soils carried out for weight unit (light character) and surface unit (bold character).

Bouqa						Banias					
Freundlich			Langmuir			Freundlich			Langmuir		
K_F	n	R	q_{max} (mmol/kg)	K_L	R	K_F	n	R	q_{max} (mmol/kg)	K_L	R
162	1.57	0.99	500	0.91	0.98	221	1.93	0.96	500	2.35	0.99
0.0034	1.99	0.98	0.011	1.59	0.99	0.008	2.7	0.93	0.0071	3.75	0.99

Concerning the mechanisms of interaction, many evidences have shown that the specificity of interaction has been expressed first by the formation of inner, mono or bidentate sphere complex. These may develop later to give Zn - layered double hydroxide surface precipitate, or to incorporate within the oxides lattice, or to give free precipitate like $Zn(OH)_2$, Zn_2SiO_4 , $ZnFe_2O_4$. The thermodynamic findings collected in this study, as well as the x-ray diffraction spectroscopy results, confirm the importance of franklinite as a precipitate in the system. Hence, one can expect that the uptake of zinc will be effectively enhanced by the presence of high content of iron oxides, which are more abundant in Banias soil. However, one couldn't in the same time, overlook the specificity of zinc interaction with calcite, perhaps it may that the mechanism of zinc interaction with this mineral differs from its interaction with Fe, Al, and Si minerals. This difference may be essentially due to the ability of zinc to undergo a mixed metal-Zn layered double hydroxide (Zn-Me LDH) precipitation that couldn't with calcium. Basing on the results of many studies (Reeder, 1996, Reeder et al, 1999, Temmam et al, 2000; Elzinga and Reeder, 2002) it can be concluded that the specificity of zinc interaction with calcite is more expressed as a substitution process within calcite lattice that may take much longer time.

4. Speciation of Zn

Many inorganic and organic ligands are capable of forming complexes with Zn in soil solution. Water molecules and hydroxyl group are predominant in aqueous solutions, but their complexation effect may be reduced under the competitive effect of other ligands. Chloride, sulfate, phosphate, bicarbonate, carbonate and nitrate constitute the main competitive complexing agents. However, remembering that both soils were leached before batch experiment, one expects that no longer chloride, nor sulfate; neither organic ligands remained to give complexes with Zn. So, it will be possible to consider that Zn in solution is partitioned among the following species: $ZnHPO_4^0$, $ZnH_2PO_4^+$, $Zn(NO_3)_2^0$, $ZnNO_3^+$, $Zn(OH)_3^-$, $Zn(OH)_2^0$, $ZnOH^+$, Zn^{2+} . The application of mass conservation condition results in the following equality

$$[Zn_{tot}] = [Zn^{2+}] + [ZnOH^+] + [Zn(OH)_2^0] + [Zn(OH)_3^-] + [ZnNO_3^+] + [Zn(NO_3)_2^0] + [ZnH_2PO_4^+] + [ZnHPO_4^0]$$

Referring to the appropriate reactions given in appendix 1, it will be possible to express the activities of these species as a function of Zn^{2+} and H^+ . The calculation is then continued as exposed in the procedure plan (appendix 2), and ensured by substituting concentrations by activities, introducing the appropriate values of activity coefficients, then resolving for a given total concentration of Zn. The results as a function of pH are summarized in figure3 as percent. As it could be seen, findings show here that the free ions of zinc Zn^{2+} count for the predominant species for pH below 7, while hydroxyl complexes $ZnOH^+$, $Zn(OH)_2^0$ and $Zn(OH)_3^-$ only start to be quantitative at pH 7 and predominate at higher values. The other complexes play only a negligible role except for $ZnNO_3^+$, which

may constitutes 8-10% of total Zn below pH 7. One may consider Zn^{2+} species as the main species participating in adsorption, as it is most dominant species in solution for the experimental conditions of this study.

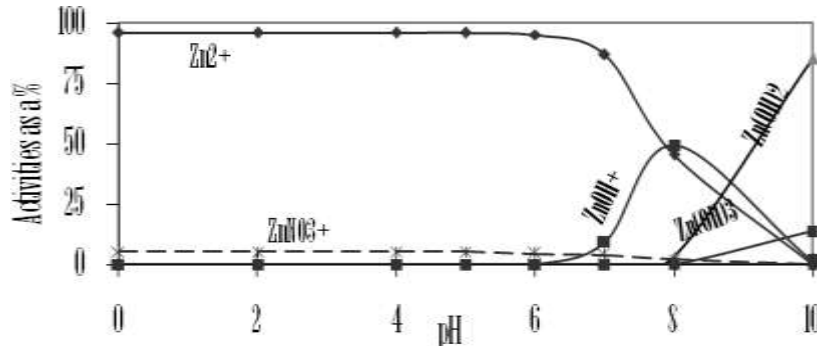


Fig.3. Variation of zinc species activities expressed in % as a function of pH. It is noticed that zinc ion Zn^{2+} is the most dominant species in the region of pH below 7. For this region It might therefore that zinc ion prevails in the sorption phase too. Hydroxyl complexes begin to be quantitative for $pH > 7$. The role of $ZnNO_3^+$ complex may not be negligible in the region of $pH < 7$. Other species are not seen because of their minor presence.

5. Heterogeneous Equilibrium: Precipitation Survey

The procedure of simulation was tested against zinc minerals reviewed by Lindsay (1979) in his book "Chemical Equilibria in Soils" including zinc hydroxides $Zn(OH)_2(c)$, zincite ZnO , willemite Zn_2SiO_4 , smithonite $ZnCO_3$, franklinite $ZnFe_2O_4$, hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ and Soil-Zn. The equilibrium reactions of these minerals are given in appendix 1. En effect; many of these minerals have been reported in literature as possible minerals for zinc scavenging, which may reduce zinc mobility and risk in natural systems.

The precipitation was predicted by confronting the Ionic Product (K_{sp}) represented by Zn_{th} and the Ion Activity Product (IAP) represented by Zn_{IAP} . By the mean of this comparison, it was possible as a first issue to predict the "critical" pH of precipitation for each mineral at each total zinc concentration (figure 4). Basing on the results conducted here, it can be concluded that, whatever is the total concentration of zinc, franklinite begins precipitation at very low pH values, succeeded by soil-Zn, and then willemite. Opposing to these three minerals, the precipitation of other minerals commonly needs higher pH even at high zinc concentrations.

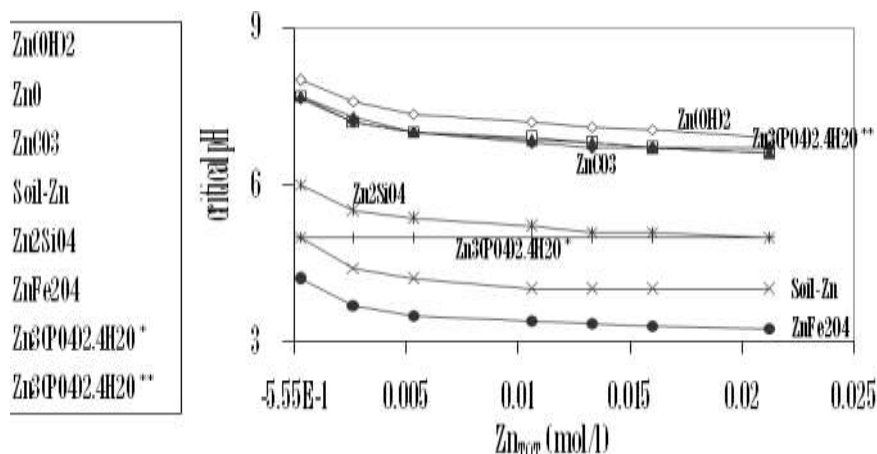


Fig. 4. The critical pH of zinc minerals precipitation as a function of total zinc concentration Zn_{TOT} . * = calculation for hopeite precipitation is given in equilibrium with strengite and soil- $Fe(OH)_3$, ** = calculation for hopeite precipitation is given in equilibrium with tricalcium phosphate, calcite and $pCO_2 = 10^{-3.5}$ atm. It is noticed that franklinite $ZnFe_2O_4$ may begin precipitation at low pH even at low Zn_{TOT} . Willemite Zn_2SiO_4 succeeds franklinite and may compete with it, whereas soil- Zn, which is an indefinite mineral phase, intermediates the two minerals. It might be concluded that franklinite is highly expected to precipitate for the batch experimental conditions of this study.

Since batch experiments were conducted at pH 6, the calculations were then reproduced at this value to evaluate precipitation as a function of total zinc loadings (Zn_{TOT}). Examination of results in figure 4 shows that zinc hydroxide and smithsonite are unlikely to precipitate. These findings, based upon pure thermodynamic calculation, and confirmed by negative test of X-ray diffraction (XRD), corroborate other results collected from literature, which indicate that the formation of such minerals necessitates in general higher pH conditions. Shuman (1977) have proposed that Zn may precipitate as $Zn(OH)_{2(s)}$ upon sorption to hydrous Al oxide at pH values above 8, joining Roberts et al (2003), who have given evidences concerning the formation of amorphous $Zn(OH)_2$ upon zinc retention by amorphous silica at pH 7.6. A comparable conclusions were as well done by Sadiq (1991) showing that the precipitation of $Zn(OH)_{2(s)}$, $Zn(CO_3)$ may control zinc solubility at alkaline pH values, and high initial Zn concentrations.

On the other hand, even though that the results indicate that hopeite is theoretically instable at pH 6, it is not impossible that this mineral precipitates in the present experimental conditions because this pH is at the boundary limit of phosphate control by strengite and tricalcium phosphate. Concerning zinc oxide ZnO , it must be mentioned that while the thermodynamic findings do not indicate its precipitation, the X-ray diffraction shows its formation in only Bouqa soil. Furthermore, it is also shown that the precipitation of franklinite $ZnFe_2O_4$ is highly expected, even at very low concentrations of zinc. This mineral appears the most stable, and it is probable that it affects deeply the dynamic of zinc. In fact, the role of franklinite and double oxide Zn-Fe in controlling Zn activity in natural systems has been mentioned in many studies. Sadiq (1991) stated that franklinite may control Zn solubility, while Lindsay (1979) has showed that this mineral is the most stable among zinc minerals in soils, whereas others (Gerth et al, 1992; Bruemmer et al, 1988) thought that the diffusion of Zn into the micropores of Fe oxides may immobilize Zn in soils. All these findings corroborates the repartitioning of zinc into Zn-Fe hydroxide phases, which may play a particular role upon oxidation and transformation of ZnS

prevailing in reduced environments (Hesterberg et al, 1997; Day et al, 1998; Webb et al, 2000).

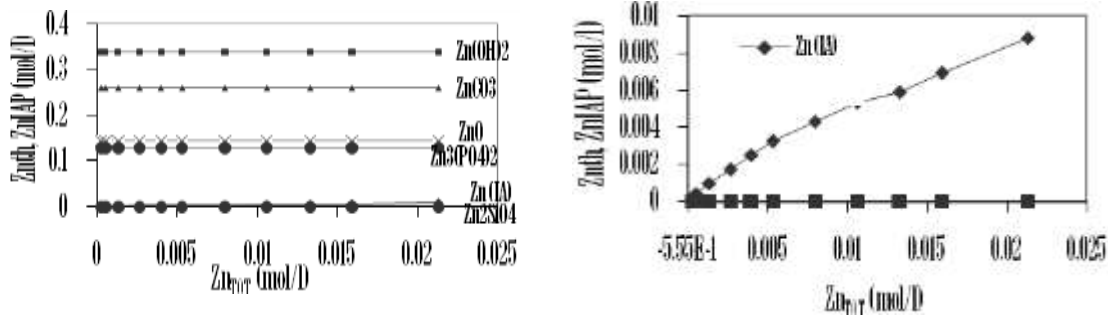


Fig. 5. Variation of Zn_{IAP} as a function of total zinc concentration Zn_{TOT} at pH = 6. The comparison among Zn_{IAP} and the equilibrium thermodynamic concentration Zn_{th} , which is independent of Zn_{TOT} , delineates, for each mineral, the range of Zn_{TOT} within which the precipitation is being possible. The thermodynamic condition for the precipitation is $Zn_{IAP} \geq Zn_{th}$. It is seen that the minerals capable of precipitation are limited to franklinite, soil- Zn and willemite ranged in the order of importance.

Nevertheless, the results show on the other hand, that the activity of Zn^{2+} is rather close to the thermodynamic concentration of willemite Zn_2SiO_4 (Fig.5). This may indicate the effectiveness of this mineral and other Zn-Si combinations too in controlling Zn^{2+} activity. The incorporation of Zn with Si into phyllosilicate structures is communally encountered. Huang and Rhoads (1989) speculated that $ZnSiO_3(s)$ was formed on aluminosilicate surfaces, whereas Manceau et al (2000) demonstrated that Zn was released from smelter metal-bearing minerals and precipitated as a Zn phyllosilicate phase. These authors also showed that upon weathering of Zn minerals Zn was removed from solution by the formation of Zn containing phyllosilicates and to a lesser extent by adsorption to Fe and Mn oxides or hydroxides.

Referring to the above results, one finds that zinc ion activity fluctuates between the thermodynamic concentration of willemite and that of franklinite. On the other hand, the fact that the stability of soil-Zn is located between the two thermodynamic concentrations of willemite and of franklinite suggests that soil-Zn may be the resultant of kinetic transformation among willemite and franklinite.

6. Zn partitioning: Distribution coefficient K_D and affinity

The indications collected from the thermodynamic approach, and the evidences sustained by the x-ray diffraction, suggest that zinc is precipitated giving at least more than one mineral. It will be convenient therefore to survey zinc repartition among its soluble, adsorbed and precipitated forms. The precipitated amount was calculated considering that the equilibrium was established with respect to soil-Zn, and assuming that the quantity precipitated of this mineral (A) is the difference between ion activity product (Zn_{IAP}) and equilibrium thermodynamic concentration (Zn_{th}): $A = Zn_{IAP} - Zn_{th}$. In the same time, the adsorbed quantity (E) was, in consequence, assigned to be the difference between the residual quantity (B) and the equilibrium concentration (C) such as $E = B - C$, where $B = Zn_{TOT} - A$. The results represented in figure 6 show a linear-like development of A, E and C as a function of Zn_{TOT} .

From an affinity standpoint, examination of data basing on the distribution coefficient K_D ($K_D = E/C$) may be interesting. In effect, the importance of this coefficient is expressed not only as a sign of partitioning and specificity, but also as a parameter of

retard affecting solutes transport in natural systems. The results, as seen in figure 7a, reveal that the distribution coefficient K_D follows an exponent model, slightly more pronounced for Baniyas than for Bouqa soil. The interpretation on K_D profiles suggests that Baniyas soil apparently expresses more affinity for zinc adsorption than Bouqa soil dose. The difference between the two soils deepens at low concentration. Perhaps, recalculation of K_D basing on the adsorbed quantity per unit surface instead of unit weight attenuates, as seen in figure 7b, the difference between the two soils except for the adsorption at low concentration for which Baniyas soil stills more efficient. These findings demonstrate that the values of the distribution coefficient K_D could be dependent of units used to express the concentration in solution and in sorption phase. Therefore, a special care must be taken when an interpretation is given to the distribution coefficient. Furthermore, the evolution on K_D coefficient shows that this parameter changes as a function of Zn_{TOT} , and takes higher values at lower total zinc loadings. This behavior hence, states for an equivalent progress of affinity, which is being higher at low concentrations. Perhaps, admitting this development of affinity implies that zinc adsorption becomes more difficult at high degree of coverage, and entails therefore more energy requirements.

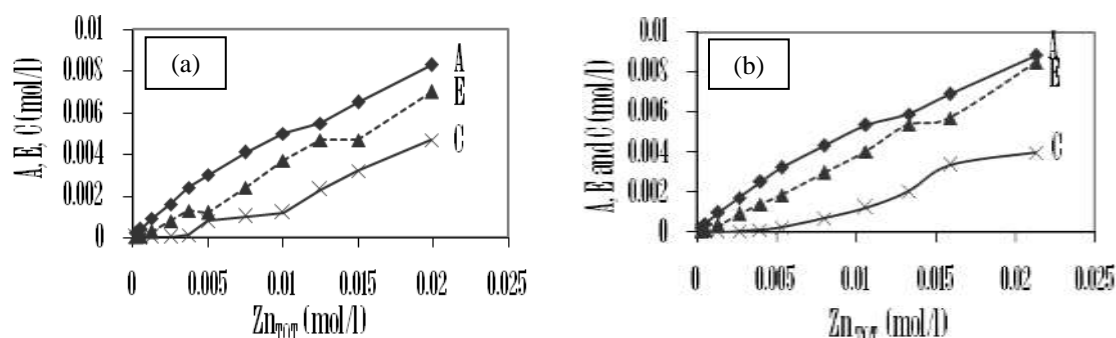


Fig. 6. Development of A, E and C quantities for Bouqa (a) and Baniyas (b) soils as a function of total zinc concentration Zn_{TOT} . It is seen that the three quantities almost show a linear development with Zn_{TOT} .

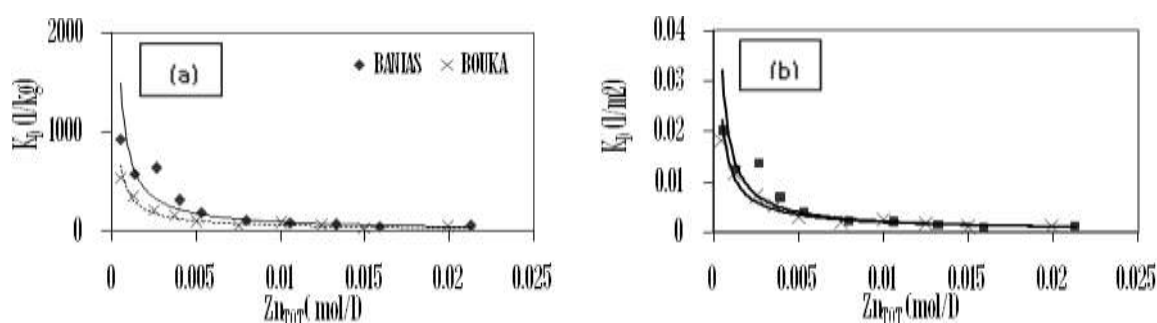


Fig. 7. Development of zinc distribution coefficient K_D for: Bouqa and Baniyas soils as a function of total zinc concentration Zn_{TOT} . Calculation of K_D has been conducted for unit weight (a) and for unit surface (b). It seems that the coefficient expresses an exponent function for both soils. It could be noted as well that the two soils rather have the same behavior, closer at higher zinc supply. The difference between the two soils at low zinc concentrations is reduced when K_D is defined as a function of unit surface.

Summary:

Zinc has been widely studied for the bioavailability and contamination concerns. As for many metallic ions, the investigations showed the ability of zinc to precipitate upon sorption onto the surfaces of many minerals. The partitioning of zinc to the aqueous, adsorbed and precipitate forms is therefore of prime importance for the fate, availability and mobility of this element in natural systems. Hence, the destiny and partitioning of zinc upon its retention unto calcareous and volcanic soils were performed by this study combining the macroscopic experimental data - sorption isotherms -, thermodynamic equilibrium theory and XRD spectroscopy. It appeared that the general trend of Zn uptake isotherms, identified with a logarithmic function $q = a \ln C_e + b$, was rather the same for the two soils. It was shown as well, that zinc uptake upon time achieved within 24 hours, and the extending reaction time to 20 days, did not change the equilibrium concentration. The application of Langmuir and Freundlich equations revealed that these two models apparently fitted similarly well the data of zinc retention, and corroborated the hypothesis that Baniyas soil expresses more affinity for zinc retention. The affinity of this soil vis-à-vis to the adsorption of zinc was also explicit in the evolution of distribution coefficient K_D , which changed as a function of Zn_{TOT} , and took higher values at lower total zinc loadings. This behavior of distribution coefficient K_D , hence, stated for an equivalent progress of affinity, which seemed higher at low concentrations. Perhaps, admitting this development of affinity implied that zinc adsorption became more difficult at high degree of coverage and therefore entailed more energy requirements.

The partitioning among zinc species in solution indicated that the free ions of zinc Zn^{2+} was the most dominant in solution for the experimental conditions of this study, and hence represented the main species constituting the adsorption phase. However, the complex $ZnNO_3^+$, which may constitute 10% of total Zn might be not negligible. On the other hand, the findings based upon the thermodynamic arguments, indicated that franklinite, succeeded by soil-Zn and willemite were capable of precipitation upon zinc retention, whereas the other zinc minerals such as smithonite, hopeite, zinc hydroxide and zincite were not. The conclusions relevant from the thermodynamic concept were almost corroborated by the results of XRD spectroscopy analysis. The data acquired here demonstrated the formation of franklinite in Baniyas soil, and Zn-Fe spinel like - franklinite and zincite in Bouqa soil, indicating probably the presence of two different passways of zinc into neoprecipitate perhaps depending on the abundance and the types of iron oxides. All indications evolved via the thermodynamic and the XRD spectroscopy highly supported the formation of franklinite $ZnFe_2O_4$, which means that this mineral will deeply affect the dynamic of zinc in natural mediums containing iron minerals even if these minerals constitute only a minor portion of soil mineralogy.

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Appendix 1. Chemical reactions considered for zinc speciation reproduced according to Lindsay (1979).

Log K⁰	Reaction
-7.69	$Zn^{2+} + H_2O = ZnOH^+ + H^+$
-16.80	$Zn^{2+} + 2H_2O = Zn(OH)_2^0 + 2H^+$
-27.68	$Zn^{2+} + 3H_2O = Zn(OH)_3 + 3H^+$
0.40	$Zn^{2+} + NO_3^- = ZnNO_3^+$
-0.30	$Zn^{2+} + 2NO_3^- = Zn(NO_3)_2^0$
1.60	$Zn^{2+} + H_2PO_4^- = ZnH_2PO_4^+$
-3.90	$Zn^{2+} + H_3PO_4^- = ZnHPO_4^0 + H^+$
2.7	Soil - $Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$
-6.85	$FePO_4 \cdot 2H_2O + 2H^+ = Fe^{3+} + H_2PO_4^- + 3H_2O$
10.18	$\beta - Ca_3(PO_4)_2 + 4H^+ = 3Ca^{2+} + 2H_2PO_4^-$
9.74	$CaCO_3 + 2H^+ = Ca^{2+} + CO_2^{\uparrow} + H_2O$
11.53	$\epsilon - Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O$
11.16	$ZnO + 2H^+ = Zn^{2+} + H_2O$
7.91	$ZnCO_3 + 2H^+ = Zn^{2+} + CO_2^{\uparrow} + H_2O$
5.8	Soil-Zn + $2H^+ = Zn^{2+}$
3.8	$Zn_3(PO_4)_2 \cdot 4H_2O + 4H^+ = 3Zn^{2+} + 2H_2PO_4^- + 4H_2O$

Appendix2. The plan of equilibrium calculation procedure.

