

Solid Phases of Zn in Some Contaminated Soils in Sohag, Egypt.

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Received: 24th December 2022, Revised: 11th March 2023, Accepted: 13th March 2023.

Published online: 12th April 2023

Abstract: Almost all human activities have contaminated or polluted vast soil tracts. Measuring the total metal concentration needs to provide more information on the bioavailability or toxicity of metals. Therefore, it has been established that the free metal ion concentration (or activity) is crucial in determining metal bioavailability and toxicity in most circumstances. The present study aimed to: 1- evaluate the effects of prolonged use of three types of irrigated water (sewage effluent-, industrial effluent- and Nile- water) on some soil properties, 2- determine the active portion of Zn²⁺, and 3- identify the possible solid phases (minerals), which govern the solubility of Zn²⁺ in some soil in Sohag Governorate, using stability mineral diagrams. The results revealed that clay content increased by 3.38 %, 9.2 %, and 14.64% in industrial -, sewage -, and Nile- irrigated soil, respectively, over their corresponding values in the last layer of their profiles. Organic matter increased by 10 %, 30.9 %, and 8.69 % in industrial-, sewage- and Nile-irrigated soil, respectively. While CaCO₃ content decreased by 5.21%, 19.78 %, and 12.85% in industrial-, sewage- and Nile-irrigated soil, respectively. Soil acidity (pH) increased in industrial effluent irrigated soil by (9.65%), while it decreased by (6%) in both Nile- and sewage-effluent irrigated soil. Soil salinity increased in industrial and sewage effluent irrigated soil by 38.51% and 40.58%, respectively. However, the continual use of Nile water declined EC by 6.77% over their corresponding values in the last layer of their profiles. Moreover, the data also manifest that the continuous use of sewage effluent water in irrigation increased Zn content in soil by 877%, followed by industrial effluent irrigated water (525.3%), while in the Nile irrigated water soil, zinc content only increased by 1.42 %, over their corresponding values in the last layer of their profiles. The measured Zn²⁺ activities in the tested soils varied widely among the tested soil. It could be arranged to ascend as follows; in uncontaminated soil (Sohag) (5.24552 E-10 MI) followed by industrial effluent irrigated soil (Gerga) (2.05739E-09 MI) and sewage effluent irrigated soil (Kola) (4.20663E-09 MI). It is clear from these results that the continual use of industrial effluent water or sewage effluent water in irrigation has led to an increase in Zn activity by about (3.9 and 8) times, respectively, higher than its value in Nile irrigated soil. The established Zn-stability diagrams indicated that the estimated free Zn-ion (Zn²⁺) activities for all the tested soils were governed by the solubility line of franklinite mineral in equilibrium with soil-Fe, especially Nile irrigated soil (super saturated), and with increasing Zn activity and we found that the values of Zn activity shifted up near to Willemite (Zn₂SiO₄) mineral in equilibrium with quartz (undersaturated). The formation of highly soluble minerals, namely, willemite, indicates Zn's potential ecological risk in sewage – and industrial–effluent irrigated soils. As a result, needless to say, thing low water quality in irrigation requires more complex management practices and more stringent monitoring procedures than using good quality water.

Keywords: Soil Zn contamination – Zn activity – competitive chelation method – Zn stability minerals diagram.

1. Introduction

Rapid urbanization, industrialization, unwise and wrong agricultural practices, and prolonged use of sewage effluent water in irrigation have affected the release of heavy metal pollutants in agricultural land.

Although these toxic metals exist in low concentrations in soil, they have been considered soil contaminants due to their high toxicity abundance, and ease of accumulation by various organisms and usually persist in the soil for a longer duration due to their non-degradable nature [1, 2]. Measurement of the total metal concentration provides inadequate bioavailability or toxicity information. It provides little indication of metal's bioavailability, mobility, and reactivity in soils, particularly soils treated with wastewater, sludge, and other organic fertilizers [3, 4]. Therefore, it has been established that in most

circumstances, the concentration of free ions (or activity) is the key factor in determining metal bioavailability and toxicity [1, 5-8].

Several approaches have been widely used to determine the activity of metal Viz; electrochemical method (ion selective electrode (ISE)) and voltammetric electrochemical methods such as anodic stripping voltammetry (ASV); adsorptive cathodic stripping voltammetry (ACSV) and Donnan Membrane Technique (DMT) [9, 10]. Each method has its advantages and limitations [11-14]. The competitive chelation method proposed by [15] is widely used in this respect by scientists, has good sensitivity and reliability, and provides estimates of ion activities [8, 16].

Similarly, the identification of solid phases which govern the solubility of metal would be worthwhile in characterizing the intensity of these metal ions in soils. Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and metal concentration

(or activity). The diagrams also allow some prediction of which solid phase regulates metal activity in the soil solution [6, 7, 17].

Zinc (Zn) is one of the heavy metals which is considered an essential micronutrient for plants and also for soil if it exists at high concentrations, consequently, it may reduce the productivity of soil [18]. So, the main objectives of this work investigate the influence of different sources of pollution on the active portion of Zn^{2+} in some soils in Sohag Governorate and identify of possible solid phases of Zn which could govern its solubility in those soils using stability diagrams.

Geological setting and stratigraphy:

The studied area occupies the floodplain soils of Sohag Governorate stretching between longitudes 31° 15' and 32° 15'E and latitudes 26° 00' and 27° 00'N (Fig. 1). According to US Soil Taxonomy (19), these soils lie in the Entisols soil orders. They are usually sand, silt, and clay mixtures, different types of loams.

Based on the recent stratigraphic studies given by [20-22], the following stratigraphic units are recognized in the Sohag area (Fig. 2).

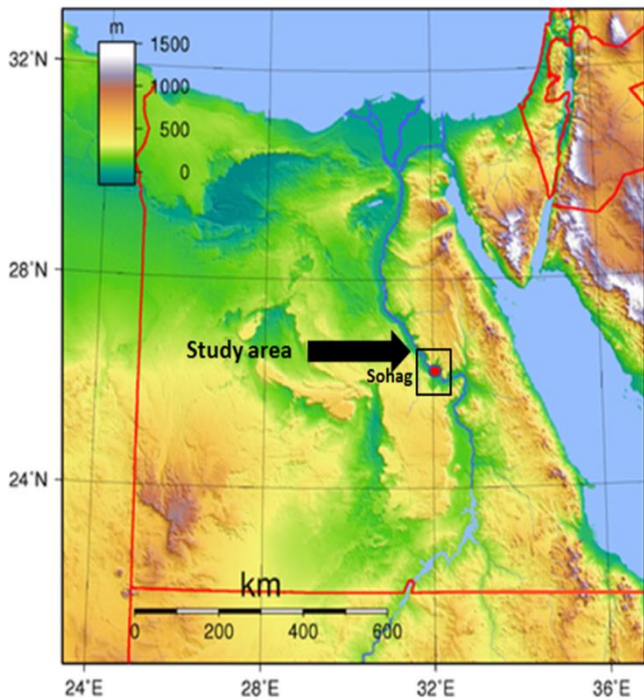


Fig. 1. Sohag Governorate map showing the sample locations in addition to the exposed stratigraphic units.

1. The Lower Eocene limestone sequence:

In Sohag Governorate, the Nile Valley region is bounded by the lower Eocene limestone sequence. Based on its variations in the lithology and faunal content, it was subdivided into two formations: the Thebes Formation (30 m of laminated limestone enriched with flint bands and concretions) representing the lower part of this sequence and graded upwards into the Drunka Formation (snow-white color and massive bedding).

2. The Late Oligocene- Miocene sequence:

This sequence includes the Katkut and Abu Retag formations. The Katkut Formation [23] comprises all the coarse clastic sediments that overlie the Eocene sequence.

Abu Retag Formation [24] consists of mottled reddish brown coarse clastic sediments, gravels, and gravelly sands enriched with basement pebbles [20, 24, 25].

3. The Pliocene-Quaternary sequence:

This sequence embraces Madmoud (chocolate brown claystone intercalated with siltstones and fine sandstones), Armant (mixed clastic-carbonate sequence), Issawia (well-cemented red breccias), Qena (cross-bedded sandstones and siltstones), Abbassia (yellowish white well-rounded sandy gravel sequence, Dandara (sand and silt intercalations) and El Gir (mixed conglomerate and sandstone changed to mixed siltstone, stromatolitic and biomicritic limestone and conglomerates) formations [26, 27].

The Holocene sediments in the study area are subdivided into three units: flood plain deposits sand dunes and wadi deposits.

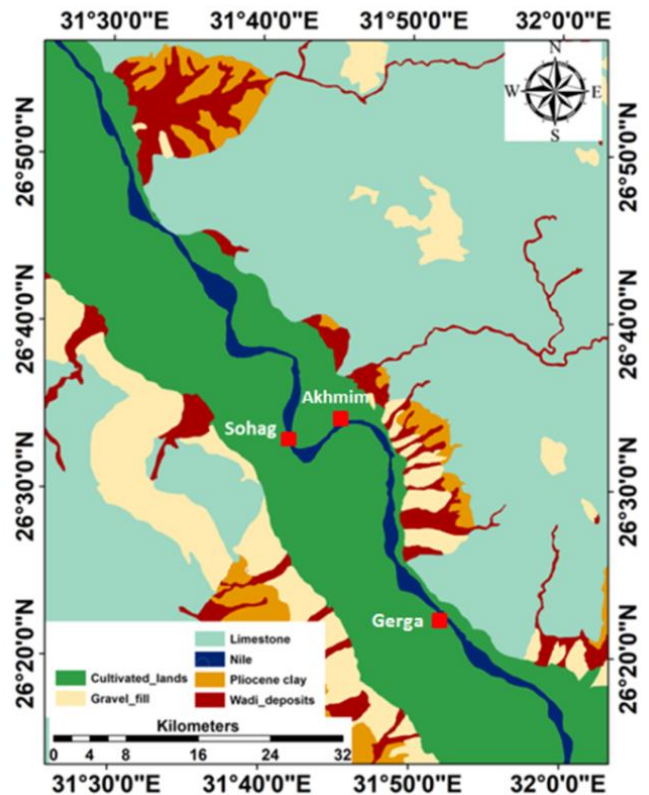


Fig. 2. A Sohag Governorate map showing the sample locations in addition to the exposed stratigraphic units.

2. Materials and method

2.1. Study area

The present study was conducted in Sohag Governorate, Upper Egypt (Fig.1). These provinces are characterized by the diversity of human activity, which may contribute to pollution with heavy metals. Therefore, three sites were selected (Fig.2); the first site is located at Eltal Al-awsat village (26°34'25" N, 31°42'34" E), Sohag District to represent Nile irrigated soil. The second site is

located at EL Kola village (26°31' 33" N, 31° 49' 14" E), Akhmim District to represents soils continuously irrigated with sewage effluent water, and the third site selected from west Gerga(industrial area) (26° 16' 40" N, 31° 46' 22" E), Gerga District, to represent industrial – effluent irrigated soils.

2.2 Soil Samples and chemical analysis

Three soil profiles were dug to 90 cm depth and sampled at 30 cm increments. At each depth, three disturbed sub-soil samples were collected to make a composite soil sample, stored in polyethylene bags and dried, followed by and sieved using a 2 mm sieve. Particle size distribution, soil reaction (pH), soil salinity (EC), organic matter content and total calcium carbonate were determined according the standard methods [28-30], and listed in Table (1).

2.3 Measurement of Zn²⁺ activity

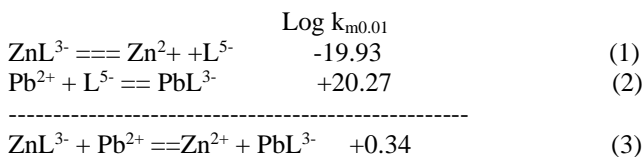
They measured using the competitive chelation method given in detail by [6]. This method depends on reacting soil with chelate solutions with different Zn and lead (Pb) mole fractions as competing metals. A series of the chelating solution, having different mole fractions of chelate ligand (L), that is, ZnL/(ZnL+PbL), were prepared using reagent grade diethylenetriaminepentaacetic acid (DTPA), Zn(NO₃)₂ and Pb(NO₃)₂. The initial ZnL/ (ZnL+PbL) mole fractions varied from 0.0 to 0.3.

Fifteen–gram subsamples of each soil were weighed in 125 ml Erlenmeyer flasks, and 30 ml of 0.01 M of CaCl₂ solution having a given ZnL/ (ZnL+PbL) mole fraction was added along with 10 mg of PbCO₃ to maintain a known Pb²⁺ activity in solution. A blank treatment without a chelating agent was prepared for each soil sample by shaking 15 g of soil with 30 ml of 0.01M CaCl₂ solution. The Erlenmeyer flasks were then covered with perforated parafilm to allow gas exchange with the atmosphere. The suspensions were shaken for 5 days, pH was measured, then centrifuged, filtered, and the clear solutions were analyzed for Zn and Pb using Plasma emission inductively coupled spectrometer plasma ICP (400).

2.4 Calculation:

The final mole fraction of Zn/ (ZnL +PbL) for each soil was calculated from the total soluble Zn and Pb after subtracting Zn and Pb in the CaCl₂ blank treatment. A graph relating initial and final Zn/ (ZnL +PbL) mole fractions were made for each soil, and the equilibrium Zn/ (ZnL +PbL) mole fractions were obtained (Fig.3), which was used to calculate Zn²⁺ activity in the soil.

Derivation of the equilibrium equation used to calculate Zn²⁺ activity is given as follows:



Where, k_m is the mixed equilibrium constant expressed in terms of concentration, except for H⁺, OH⁻, and e⁻ which, if

present, are expressed as activities [31], L⁵⁻ is the concentration of free DTPA, and [] indicates molar concentration.

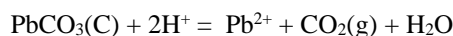
Rearranging Eq. (3); gives:

$$[\text{Zn}^{2+}] = [\text{ZnL}^{3-}] / [\text{PbL}^{3-}] * 10^{0.34} * [\text{Pb}^{2+}] \quad (4)$$

Since the activity coefficients of pb²⁺, Zn²⁺, PbL²⁺ and ZnL³⁻ are equal; Equation (4) can be written in terms of activities as follows:

$$(\text{Zn}^{2+}) = (\text{ZnL}^{3-}) / (\text{PbL}^{3-}) * 10^{0.34} * (\text{Pb}^{2+}) \quad (5)$$

Since PbCO₃ was added to the soil suspensions to control Pb²⁺ activity throughout the experiment and the solutions were open to atmospheric CO₂, Pb²⁺ activity was obtained according to [31]:



$$\text{Log } K^0 = 6.16 \quad (6)$$

$$(\text{Pb}^{2+}) = 10^{6.16} * (\text{H}^+)^2 / \text{CO}_2, \text{ at } 0.003 \text{ atm } .\text{CO}_2 \quad (7)$$

$$\text{Hence } (\text{Pb}^{2+}) = 10^{9.68} * (\text{H}^+)^2 \quad (8)$$

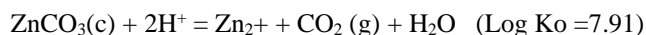
Substituting Eq. (8) into Eq. (5) gives:

$$(\text{Zn}^{2+}) = (\text{ZnL}) / (\text{PbL}) * 10^{(8.45-2\text{pH})} \quad (9)$$

The pH value used in Eq. (9) was the pH of the suspension closest to the equilibrium point in the initial and final mole fraction plot.

2.5 Stability diagrams:

Zinc minerals that may control the level of Zn²⁺ in soils were plotted on an equilibrium solubility diagram in terms of Zn²⁺ activity and pH (Fig 3a, b, and c) using the thermodynamic data in Table (2) taken from [31] to calculate the equilibrium relationships in the following manner:



$$\text{Log } (\text{Zn}^{2+}) = 7.91 - \text{Log } \text{CO}_2 - 2\text{pH}.$$

At CO₂ = 0.0003 atm, this equation becomes:

$$\text{Log } (\text{Zn}^{2+}) = 11.43 - 2\text{pH}.$$

At CO₂ = 0.003 atm, this equation becomes:

$$\text{Log } (\text{Zn}^{2+}) = 10.43 - 2\text{pH}.$$

The remaining minerals were plotted similarly; meanwhile, Zinc silicate minerals were depicted in equilibrium with SiO₂ (soil) and SiO₂ (quartz). Zinc phosphate minerals were depicted in equilibrium with various phosphate minerals, which depend on the level of CaCO₃, which is controlled by CO₂ partial pressure.

3. Results and discussion

The effect of different irrigation sources on some soil properties is shown in Table (1). Taking the last layer of the selected soil profile (60-90 cm) as a comparison layer, the data reveal that in soil irrigated continuously with Nile water (Sohag), pH, EC, CaCO₃, and Zinc content (in the top soil layer (0-30 cm) decreased by 6%, 6.77 %, 12.85%, and 1.42 %, respectively, compared with their corresponding values at the same profile's last layer (60 -90 cm). These observations are mainly due to freshwater's beneficial effects upon leaching

alkali metals and its effect on the dissociation of Zn minerals, consequentially more mobilization of Zn along the soil profile. Conversely, clay and organic matter content increased by 8.69 and 14.64%, respectively. These results are mainly attributed to the fine particles, debris, and dissolved organic acids that exist in water.

Moreover, in sewage effluent irrigated soil, as shown in Table (1), the continual use of the sewage effluent application has valuable effects in increasing clay content (9.2%), OM (30.9%), as well as decreasing undesirable soil characters as pH (5.62%) and CaCO₃ (19.78%), compared to their corresponding last layer. However, unfortunately, it also raises some of undesirable parameters like EC and Zinc content which increased by (40.58% and 877%, respectively) over their corresponding values in the last layer. Similarly, [32-35] studied the influence of using sewage water in irrigation for extended periods on some physical and chemical soil parameters. They reported that clay content, organic matter, soil pH, and EC progressively increased with increasing the period of application, while CaCO₃ content was reduced.

Table (1) Some of the soil properties of the selected soils

Type	Location - depth	pH	EC	Clay %	OM %	CaCO ₃ %	total Zn (mg/Kg)
Nile water irrigated soil	Sohag D1*	7.58	0.55	25	1.8	4	69.2
	D2	7.92	0.54	23.24	1.58	4.58	66.4
	D3	8.07	0.59	23	1.57	4.59	70.2
Sewage effluent treated soil	kola D1	7.22	3.95	28	2.58	6	238.5
	D2	7.74	2.87	29.07	2.49	7.05	22.2
	D3	7.65	2.81	25.64	1.97	7.48	24.4
Industrial effluent treated soil	Gerga D1	7.84	2.05	22	1.1	2	440.9
	D2	7.47	1.97	24.04	0.95	2.05	59.8
	D3	7.15	1.48	21.28	1	2.11	70.51

D1* represents a depth of 0-30 cm from the surface, D2 represents depth 30-60 cm from the surface, and D3 represents a depth of 60-90 cm from the surface

The data of industrial effluent irrigated soil (Table 1) revealed that due to the continuous use of industrial effluent in irrigation, some of the desirable soil parameters affected positively; OM increased by 10%, CaCO₃ decreased by 5.21%, and clay content increased by 3.38%. But regrettably, however, it also raises some undesirable like pH (9.65%), EC (38.51%), and Zinc soil content (525.3%), over their corresponding values in the last layer. pH values decrease to the depth due to the alkalinity nature of industrial effluent irrigated soil, and the first layer is more affected by pollution than layers to the depth. [36]

studied the effects of different land management on some soil properties in Egypt, the obtained results show that reclamation practices led to an increase in silt and clay contents in the reclaimed soils, especially in the surface layers, but only changed appreciably by the wastewater disposal practice.

3.1. Zn²⁺ ion activity in the soil

For the identification of the probable solid phases governing the solubility of the soils, the free ion activities of the metals were estimated following the competitive chelation method (4,6,16,17,37,38). The measured Zn²⁺ activities in the tested soils varied widely among the tested soil. It could be arranged to ascend as follows; In Uncontaminated soil (Sohag) (5.24552E-10 MI) followed by Industrial effluent Irrigated soil (Gerga) (2.05739E-09 MI) and Sewage effluent irrigated soil (Kola) (4.20663E-09 MI). It is clear from these results that Zn activity was higher by about 3.9 times in industrial effluent irrigated soil than its value in Nile irrigated soil samples, but it was higher by 8 times in sewage effluent irrigated soil than its value in Nile water irrigated soil.

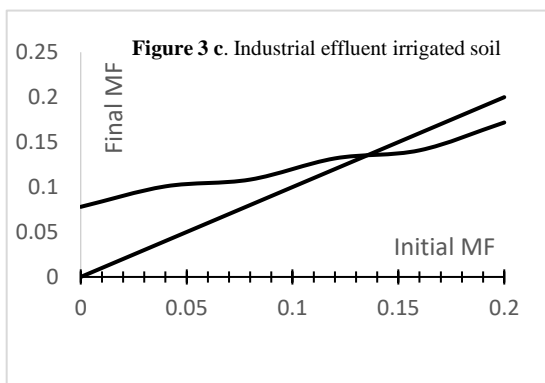
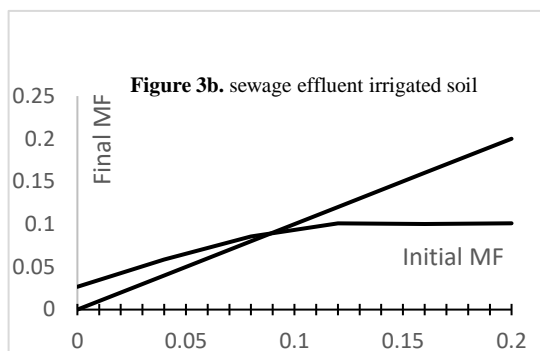
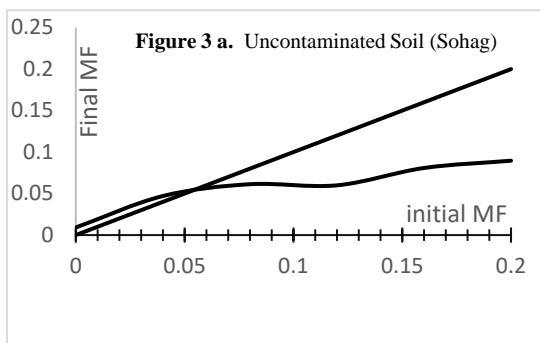
In the same context, [4] mentioned that the measured Zn²⁺ activities ranged from 10^{-9.97} to 10^{-6.9} M (mean= 6.29998E-08 MI) for the uncontaminated soils, and 10^{-8.11} to 10^{-2.26} M (mean = 0.002747708 MI) for the industrial contaminated soils Zn²⁺.

Meanwhile, the results of Zn²⁺ values determined according to Baker and Amacher methodology [39] by [40] were ranged between (8.47227E-12 and 3.22849E-07 MI) in zinc smelter effluent irrigated soils, and 1.39959E-10 MI, for noncontaminated soil sample. These data confirmed that human activities often contributed to the prevalence of high concentrations of heavy metals in some agricultural systems, especially industrial activities and waste disposal processes [16, 30]. A plot of the final Zn_L/(Zn_L+Pb_L) mole fraction of the filtrates against the initial mole fractions are presented from Figs. (3a, b, and c). The intersected between them pointed out to the equilibrium point, where the soil sample neither gain nor loss of Pb. This equilibrium value was used in the following equation to calculate Zn activities by using the following formula; and the results are listed in Table 3.

Table 2. Equilibrium pH, Zn mole fractions (MF) and Zn²⁺ activities in the tested soils

SOI	EQ. PH	Initial (MF)	Equilibrium		
			Eq. Zn (MF)	Log Zn ²⁺	PZn ^{2+*}
Nile water irrigated soil (Sohag)	8.22	0.0 – 0.3	0.041667	5.24552E-10	9.280211
Sewage effluent irrigated soil	7.96	0.0 – 0.3	0.10091	4.20663E-09	8.376066
Industrial effluent Irrigated soil	8.21	-0.3 0.0	0.156069	2.05739E-09	8.686682

pZn^{2+*}= (-log Zn²⁺).



A plot of the final $ZnL/(ZnL+PbL)$ mole fraction of the filtrates against the initial mole fractions is presented in Figs. (3a, b, and c). The intersection between them pointed to the equilibrium point, where the soil sample neither gains nor loses Pb. This equilibrium value was used in the following equation to calculate Zn activities using the following formula: the results are listed in Table 3.

3.2. Solid phases of zinc (Zn)

Solubility relationships of various Zn containing minerals (solid phases) namely, soil-Zn, franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4) and smithsonite ($ZnCO_3$) were developed with pH using the solubility equations (Table 3) and presented through solubility lines in the solubility diagram (Fig.5) ($Zn^{2+} = (ZnL)/(PbL) * 10^{(8.45-2pH)}$).

It's evident from Fig (4) that whether $ZnSO_4$ (Zinkosite) is controlled by SiO_4 (Concentration) at 10-4 or 10-2M, it is more soluble to persist in soil, in both cases. Also, Zn-hydroxide minerals, zincite (ZnO) and smithsonite ($ZnCO_3$) are too soluble in normal soils. For example, Zn- hydroxide is about 105 times more soluble than soil-Zn (Table 3).

Also, $Zn_3(PO_4)_2$ when equilibrium with calcite at CO_2 concentration (0.0003 or 0.003 atm.) were more soluble to exist in the tested soils. In the same manner, $ZnSiO_4$ (Willemite) when be in equilibrium by quartz was more soluble to governing Zn solubility in the tested soils. On the other side, the figure revealed that the measured Zn activities of the tested soils were supersaturated with Franklinitite ($ZnFe_2O_4$) in equilibrium by magnetite, soil-Zn, and Franklinitite ($ZnFe_2O_4$) in equilibrium by soil-Fe. Also, the figure indicate that for the sewage effluent irrigated soil, or for industrial-effluent irrigate soil, the measured Zn^{2+} activities were much higher than that of Nile water irrigated soil.

By examining the proximity of the values of Zn activities of the tested soils to the solubility lines of various Zn containing minerals, The results indicated that the estimated free (Zn^{2+}) activities for all the tested soils were governed by the solubility line of franklinite in equilibrium with soil-Fe especially Nile irrigated soil (it was very close), meanwhile, in the two contaminated soils, the values of Zn activity shifted near to Willemite (Zn_2SiO_4) in equilibrium with quartz.

Limited research has been performed to determine the solubility of zinc and the mechanism controlling zinc solubility in the soil. [38] reported that the measured Zn^{2+} activities in the uncontaminated soils were near that of franklinite ($ZnFe_2O_4$), while in the contaminated soils were close to those of Zn_2SiO_4 or $ZnCO_3$ depending on the contaminated soils. Also, in soil continuous irrigated with zinc smelter effluent, Zn^{2+} activity was limited by the solubility of willemite (Zn_2SiO_4) in equilibrium with quartz. However, in case of tube well water irrigated soil, franklinite ($ZnFe_2O_4$) in equilibrium with soil-Fe and was likely to govern the activity of Zn^{2+} in soil solution [40].

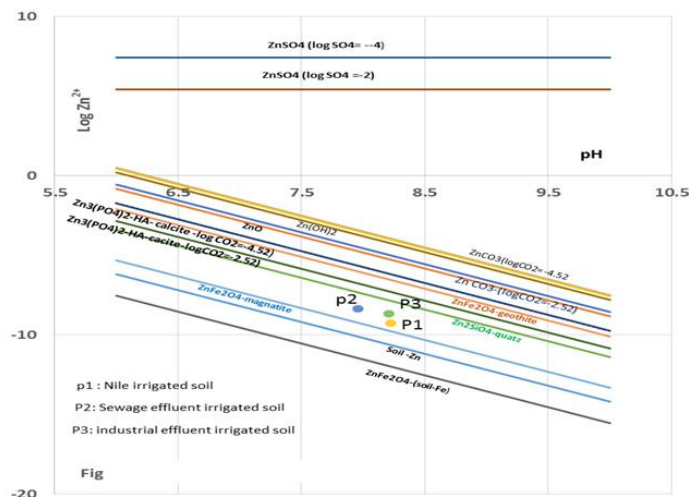


Fig. 4. Stability diagrams of Zn mineral.

4. Conclusion

Continual use of sewage effluent water or industrial effluent water could be an alternative way for scarcity of fresh water but it often fraught of soil Zn contamination and affects soil chemical and physical properties. Soil acidity (pH) increased in industrial effluent irrigated soil by (9.65%), while it decreased by (6%) in both Nile- and sewage effluent irrigated soil. Soil salinity increased in both sewage -, and industrial effluent

irrigated soil by 38.51 % and 40.58%, respectively. However, the continual using of Nile water declined EC by 6.77%. Organic matter increased by 10 %, 30.9% and 8.69% in industrial -, sewage- and Nile irrigated soil, respectively. Clay content increased by 3.38 %, 9.2 % and 14.64%) in industrial -, sewage –and Nile irrigated soil, respectively, over their corresponding values in the last layer of their profiles. While, CaCO₃ content decreased by 5.21%, 19.78 % and 12.85% in industrial -, sewage- and Nile irrigated soil, respectively. Zn activity values of industrial effluent irrigated soil were higher by about 3.9 times than its value of Nile irrigated soil, while it was high by 8 times of sewage effluent irrigated soil. These data confirmed that low water quality is considered a harbor of pollutants. Moreover , it can also be concluded that free ion activity of Zn²⁺ for all the tested soils were governed by the solubility line of franklinite in equilibrium with soil-Fe , particularly Nile irrigated soil (it was very close), meanwhile, in the two contaminated soils , the values of Zn activity shift higher near to Willemite (Zn₂SiO₄) in equilibrium with quartz. Such information may be useful in devising reclamation strategy to reduce Zn toxicity in zinc contaminated soils.

Table (3): The equilibrium activity constants (k⁰) of some of Zinc minerals

Element	Minerals	Eq. equations	Log k ⁰
Zn	Soil-Zn	Soil-Zn + 2H ⁺ ⇌ Zn ²⁺	5.8
	Franklinite (ZnFe ₂ O ₄)	ZnFe ₂ O ₄ + 8H ⁺ ⇌ Zn ²⁺ + 2Fe ³⁺ + 4H ₂ O	9.85
	Willemite (Zn ₂ SiO ₄)	Zn ₂ SiO ₄ + 4H ⁺ ⇌ 2Zn ²⁺ + H ₄ SiO ₄ ⁰	13.13
	Smithsonite (ZnCO ₃)	ZnCO ₃ + 2H ⁺ ⇌ Zn ²⁺ + CO ₂ (g) + H ₂ O	7.91
	Zincite (ZnO)	ZnO + 2H ⁺ ⇌ Zn ²⁺ + H ₂ O	11.16
	Zn(OH) ₂ (amorphous)	Zn(OH) ₂ + 2H ⁺ ⇌ Zn ²⁺ + 2H ₂ O	12.48
	ZnSO ₄ (zinkosite)	ZnSO ₄ ⇌ Zn ²⁺ + (SO ₄) ²⁻	3.41
Phosphorus (P)	Ca ₅ (PO ₄) ₃ OH (HA)	Ca ₅ (PO ₄) ₃ OH + 7H ⁺ ⇌ 5Ca ²⁺ + 3H ₂ PO ₄ ⁻ + H ₂ O	14.46
Calcium (Ca)	CaCO ₃ (calcite)	CaCO ₃ + 2H ⁺ ⇌ Ca ²⁺ + CO ₂ + H ₂ O	9.74
Iron (Fe)	Soil-Fe (Fe(OH) ₃)	Fe(OH) ₃ + 3H ⁺ ⇌ Fe ³⁺ + 3H ₂ O	2.70
	magnetite (γ-Fe ₂ O ₃)	1/2γ-Fe ₂ O ₃ + 3H ⁺ ⇌ Fe ³⁺ + 3/2 H ₂ O	1.59
	Goethite (α-FeOOH)	α-FeOOH + 3H ⁺ ⇌ Fe ³⁺ + 2H ₂ O	-0.02
Silicon (Si)	Quartz (α-SiO ₂)	α -SiO ₂ + 2H ₂ O ⇌ H ₄ SiO ₄ ⁰	-4.00
	SiO ₂ (amorphous)	SiO ₂ + 2H ₂ O ⇌ H ₄ SiO ₄ ⁰	-2.47

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