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Speciation of Trace Metals in Certain Groundwater in Egypt

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ABSTRACT

Several groundwater samples were analyzed in terms of drinking water quality, the groundwater samples were collected and tested for particle quality. The major elements and heavy metals in six groundwater samples were analyzed. A metal may be found in a number of different forms, such as soluble and/or complex forms. The free metal activity has been shown to be the key factor in determining metal toxicity. MinteqA2 code version 3.0 is a geochemical code was used to compute distribution of the dissolved metals in a certain groundwater samples in Egypt. Speciation of the metal; Ca, Mg, Na, K, Fe, Al, Sr, Co, Cd and Pb were calculated. Sr, Co, Cd and Pb are the most toxic metals. Concentrations of these metal are found exceed the standard limit values. The free of the metals Sr, Ca, Co, Cd. specie constitute the major part of the dissolved metal ions. Meanwhile most of Pb species were found as Pb-carbonate. The electrostatic adsorption of these metal ions was calculated at low ionic strength. The surface ionic charge and the electrical potential of binding the metal with the soil surface sites has been calculated.

Key words: MinteqA2 code, Groundwater, Speciation, Surface electrical charge.

INTRODUCTION

Groundwater is an essential drinking water resource in developing countries, especially where no public water supply exists due to an inadequate infrastructure and poor economic situation [1]. Various toxic heavy metals may be discharged into groundwater resources through different industrial activities; this constitutes one of the major causes of water pollution [2, 3]. The chemical composition of groundwater is regulated by various factors including weathering, mineral dissolution and rock-water interaction. Calcite, kaolinite and quartz are the most important minerals controlling groundwater chemistry because of its abundance in the earth crust [4]. Knowledge about metal speciation i. e, the different physical or chemical forms in which a metal occurs, is widely regarded as crucial to the understanding and prediction of metal behavior and impact in any environmental system [5-7]. The aim of this paper is to report about the different forms of heavy metals are present in some groundwater in Egypt. The groundwater samples were analyzed in terms of drinking water quality, different soil samples were collected

from the same locations of the groundwater at the selected sites. The surface charge density and the electrical potential of binding the metal with the solid were determined.

MATERIALS AND METHODS

Chemicals and Equipments

All chemical reagents used are of an analytical grade. Inductive couple plasma, atomic emission spectrometry (ICP-AES) was used for the heavy metals measurements. A UV/VIS. Spectrophotometer, Jasco model 7800 coupled with Microsoft computer was used for photometric measurements. A flame photometer model-400 was used for Na and K measurements and liquid ion chromatography, Dionex was used for the determination of anions, An Orion pH meter was used for the measurement hydrogen ion concentrations.

Groundwater and soil samples

Six groundwater samples were obtained from different aquifer regions, and six soil samples were obtained from the same sites of the groundwater locations at 10-30 cm depths down the ground surfaces. Ceramics, alum, and fertilizers industrial companies are located at about 1- 3 km distance from the groundwater location sites.

Chemical Analyses

About 0.5 g of the soil sample was added to 5 ml hydrofluoric and 0.5 ml perchloric acids in a platinum crucible, the soil sample was heated several hours on a sand bath until all contents were digested, and the residue was completed to one liter by distilled water [8]. This aqueous solution was analyzed for the desired metals.

The groundwater samples were filtered and chemically analyzed for the major cations, Na^+ , K^+ , Ca^{2+} and Mg^{2+} , major anions Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , and HCO_3^- and heavy metals (Co^{2+} , Cd^{2+} , Pb^{2+} , and Fe^{3+}). Na^+ , and K^+ concentrations. Ca^{2+} and Mg^{2+} concentrations were estimated by the titration using ethylenediamine-tetraacetic acid as a titrant [9]. Alkalinity was determined by the titration method with 0.02 N H_2SO_4 acid solution. The major anions F^- , Cl^- , SO_4^{2-} , NO_2^- , NO_3^- and PO_4^{3-} were also determined using liquid ion chromatography. Heavy metals such as, Sr, Cd, Co, and Pb, concentrations were analyzed using ICP-AES. Fe^{3+} , and Al^{3+} ion concentrations (mg/l) were colorimetrically estimated in both water and the digested soil samples using Ferron indicator method [10, 11].

An equilibrium study

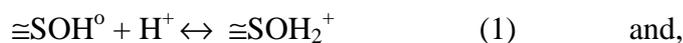
Two types of batch experiments were conducted in duplicate, the first consists of an equilibrating the powder soil sample with groundwater sample at a series of different solid to liquid ratios (1: 20, 1: 30, 1: 50, 1: 100). The second experiments were performed to study the time effect. Ten grams of the air-dried soil sample were added to 200 ml of filtrated groundwater sample in 500 ml volumetric flask at a constant stirred 300 rpm. Several flasks were prepared, after 1, 7, 14, 28, 42, 56, and 72 days, the mixtures were filtered through 0.45 μm membrane, and the filterates were immediately analyzed for the metals, Na, K, Ca and Mg.

Modeling

The MinteqA2 version 3.0 geochemical equilibrium model, Allison, 1991, [12] with thermodynamic database Parkhurst, [13] was used to perform speciation of the metals in solution, and to determine the degree of supersaturating of the solution with respect to the mineral phases. The water chemistry, mineral type, and the pH value are the input parameters were used in the MinteqA2 code calculations.

Surface complex model

The solid surface site $\equiv\text{SOH}^0$ of the soil was assumed to be neutral, this solid surface site will be hydrolyzed in water into positive and negative active sites as follows [14]:



Where, $\equiv\text{SOH}^0$, $\equiv\text{SOH}_2^+$ and $\equiv\text{SO}^-$ are the active part of the surfaces sites [14]. The surface solid site density was extremely depending on the pH values, surface charge density and the specific surface area of the solid

$$\sigma_p = F/s \langle(\Gamma_{\text{OH}} - \Gamma_{\text{H}})\rangle \quad (3)$$

Where, F is the Faraday constant (96,940 C/mol), s is the specific surface area of the solid (m^2/g). Γ is the amount of hydrogen and/or hydroxyl ions that are consumed from the system, and $\langle(\Gamma_{\text{OH}} - \Gamma_{\text{H}})\rangle$ is the amount of the adsorbed ions (mol/g).

At equilibrium, the remaining charge (σ_p) was balanced by the charge of the diffused particles (σ_d) in solution.

$$\sigma_p = -\sigma_d \quad (4)$$

According to Gouy and Champan theory, the surface particle charge density is related to the electrical potential, ψ (V) at the surface and the concentration of a solute in diffused aqueous phase, C (mol/l), the surface particle charge is given as follows [14-16]:

$$\sigma_d = 0.1174 C^{1/2} \text{Sinh}(Z\psi \times 19.46) \quad (5)$$

Where, Z is the electrolyte valences.

RESULTS AND DISCUSSION

Mineralogical investigations indicated that the soil samples contain 60-70% coarse and silt fractions mixed with the minor clay fractions. The sample having the grain size distribution 170 μm was used in all our experimental studies. The soil samples were found to have a similar of chemical and mineralogical analyses (Table 1). X-ray diffraction (Fig. 1) and chemical analyses of the soil samples showed the soil samples contain quartz, kaolinite, gypsum and carbonate minerals. The groundwater samples were found to be similar in their chemical analyses especially, concentrations of heavy metals and the pH. Table 2 gives the physical and chemical analyses of the groundwater samples. The quality of the water was determined from the charge balance error (%) factor, this factor was calculated from the major cations and anions analyses as follows [15]:

The charge balance error (%) =

$$\frac{\sum(\text{equivalent of cations}) - \sum(\text{equivalent of anions})}{\sum(\text{equivalent of cations}) + \sum(\text{equivalent of anions})} \times 100 \quad (7)$$

Table 1. The mean value of the physical and chemical parameters of the studied soil sample

Parameter	Value
Initial pH (solid: distilled water ratio 1: 20)	6.6 ± 0.02
Carbonate (% CaCO ₃)	18 ± 0.2
Cation exchange capacity (meq/100g)	22 ± 0.2
Specific surface area (m ² /g)	26 ± 1.0
Grain size fraction	(60 – 70 %) coarse and silt fractions
Clay fractions	(40 – 30 %)
X-ray diffraction	quartz, kaolinite, gypsum and carbonate minerals
Total Organic Carbon (TOC) %	0.7 %
Density (g/cm ³)	1.4 ± 0.02

Table 2: The physical and chemical parameters of the groundwater samples

Parameter	GW-1	GW-2	GW-3	GW-4	GW-5	GW-6
Conductivity (µS/cm)	380	740	670	530	1441.0	1160.0
TDS (mg/l)	220	420	300	390	830.0	670.0
pH	7.60	7.60	7.60	7.60	7.60	7.55
Chloride (mg/l)	35.2	70	29.0	40	135.0	157
Flourdie (mg/l)	0.32	0.32	0.40	0.35	0.50	0.15
Nitrate (mg/l)	0.2	0.03	0.6	0.12	0.65	0.12
Phosphate (mg/l)	0.01	0.01	0.02	0.06	0.13	0.05
Sulphate (mg/l)	31.7	32	8.5	64	220.0	85.0
Bicarbonates (mg/l)	134.0	270.0	250.0	380	450	360
Calcium (mg/l)	22.2	60.0	35.2	50.1	57.0	76.0
Magnesium (mg/l)	11.2	20.1	17.1	15.0	30.0	25.0
Sodium (mg/l)	21.0	22.0	23.0	21.0	122	65.0
Potassium (mg/l)	3.5.0	3.5	2.50	5.20	7.00	5.50
Strontium (mg/l)	0.10	0.20	0.10	0.30	0.20	0.30
Aluminum (mg/l)	0.39	0.10	0.09	0.08	0.10	0.13
Cadmium (mg/l)	0.01	0.02	0.01	0.01	0.02	0.03
Cobalt (mg/l)	0.01	0.02	0.02	0.03	0.02	0.01
Lead (mg/l)	0.03	0.02	0.01	0.01	0.01	0.02
Iron (mg/l)	0.07	0.05	0.03	0.30	0.40	0.30
Silicon (mg/l)	1.60	2.20	2.20	3.30	4.00	1.20

Table 3: The Standard Guideline of the WHO of Drinking Water

Parameter	Standard guideline (mg/l)
F	2.0
Cl ⁻	300
HCO ₃ ⁻	250
SO ₄ ²⁻	300
Sr	Nil
Cd	0.01
Co	Nil
Cr	0.10
Pb	Nil
Fe	0.3
N	< 10

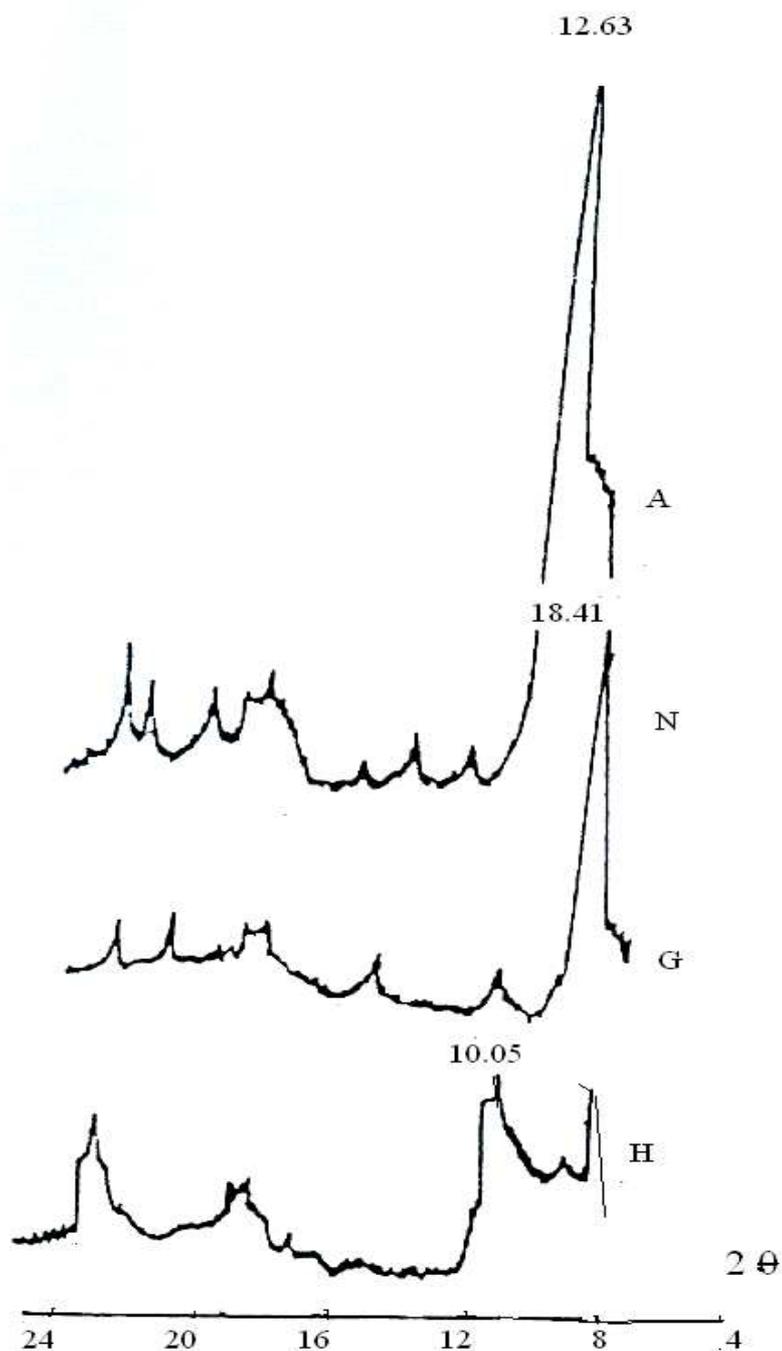


Fig. 1 : X-ray diffraction of the soil sample

The charge balance error factor of the groundwater samples were found to be between -1.48 and -4.34 %, which are within of the acceptable range ($< \pm 5.0$). Concentrations of the heavy metals, Sr, Cd, Co, Fe, Mn, and Pb in the groundwater samples were compared with those given by the standard guideline values of the world health organization, WHO, [17], as shown in Table 3.

The groundwater samples were found to have a higher Sr, Cd, Co, Pb, and Fe concentrations values than the guideline limit values are given in Table (3).

Equilibrium studies

Chemical analyses of the aqueous layers for each of the four S: L ratios were expressed in terms of solution concentrations (mol/l). Average values of the duplicated samples for each time interval were estimated. The results indicated that compositions of the aqueous extracts have little change or nearby nothing to do with the actual pore water composition. Similar findings were reported by other investigators [18].

Speciation calculations

Chemical analyses and the pH values of the groundwater samples were computed using MinteqA2 code version 3.0, with Parkhust thermodynamic database [13]. It was found that the most relevant cations have nearly a similar distribution, therefore, the groundwater samples (GW-1) was taken as an example of our investigations. Table 4 gives speciation of the major elements, Ca, Mg, Na, K, Fe, and Al. Table 5 gives the distribution of the heavy metals ions, Sr, Co, Cd, and Pb in a certain groundwater sample (GW-1). The percentage and the concentrations (mol/l) of those elements were calculated. from the program are given in Table (4 & 5). All metals were found to exist as free and complex species. The concentration of a free metals decreases from 99.81 to 93.96 in the following order; Na > Ca > Mg > K. According to these computations, aluminum and iron were mainly present as hydroxo-complexes. These results are similar to those given by other investigators [18]. Most of the heavy metals Sr, Co, and Cd exist as free metal ions which decrease from 94.23, 82.94, and 81.57 in the groundwater samples according to the following order Sr > Co > Cd respectively. Majority of the lead species (73.64 %) was found as carbonates. Similar investigations showed that the speciation of fresh and saline water samples are reported in the literature using MinteqA2 codes and other models [19].

Table 4: the main percentage species of Ca, Mg, Na, K, Fe and Al as calculated by Minteqa2 version 3.0

Calcium (Ca ²⁺) species			Magnesium (Mg ²⁺) species		
Species	(%)	Conc. (mol/l)	Species	(%)	Conc. (mol/l)
Ca+2	93.96	0.00052	Mg+2	95.03	0.000438
CaF+	0.02	8.75E-08	MgOH+	0.012	5.36E-08
CaCl+	0.17	9.66E-07	MgF+	0.092	4.24E-07
CaSO4 (aq)	3.55	1.96E-05	MgCl+	0.28	1.29E-06
CaHCO3+	1.87	1.04E-05	MgSO4 (aq)	2.85	1.31E-05
CaCO3 (aq)	0.42	2.34E-06	MgCO3 (aq)	0.21	9.88E-07
Sodium (Na ⁺) species			Potassium (K ⁺) species		
Species	(%)	Conc. (mol/l)	Species	(%)	Conc. (mol/l)
Na+1	99.74	0.000911	K+1	99.8	8.93E-05
NaCl (aq)	0.043	3.9E-07	KCl (aq)	0.043	3.83E-08
NaSO4-	0.121	1.11E-06	KSO4-	0.156	1.4E-07
NaHCO3 (aq)	0.09	8.26E-07			
Ferric (Fe ²⁺) species			Aluminum (Al ³⁺) species		
Species	(%)	Conc. (mol/l)	Species	(%)	Conc. (mol/l)
FeOH+2	0.016	2.03E-10	Al(OH)2+	0.31	4.41E-08
Fe(OH)2+	96.27	1.21E-06	Al(OH)3 (aq)	4.52	6.54E-07
Fe(OH)3 (aq)	2.001	2.51E-08	Al(OH)4-	95.17	1.38E-05
Fe(OH)4-	1.71	2.15E-08			

Table 5: the main percentage species of Sr, Co, Cd and Pb as calculated by Minteqa2 version 3.0

Strontium (Sr ²⁺) species			Cobalt (Co ²⁺) species		
Species	(%)	Conc.(mol/l)	Species	(%)	Conc.(mol/l)
Sr ²⁺	94.23	3.23E-07	Co+2	82.94	1.4E-07
SrCl+	0.11	3.69E-10	CoOH+	0.53	8.98E-10
SrSO4 (aq)	3.10	1.06E-08	Co(OH)2 (aq)	0.03	2.66E-11
SrCO3 (aq)	0.17	5.65E-10	CoF+	0.03	4.28E-11
SrHCO3+	2.39	8.19E-09	CoCl+	0.03	4.62E-11
Cadmium (Cd ²⁺) species			CoSO4 (aq)	2.71	4.6E-09
Species	(%)	Conc. (mol/l)	CoCO3 (aq)	4.26	7.23E-09
Cd+2	81.57	7.26E-08	CoHCO3+	10.03	1.7E-08
CdOH+	0.21	3.34E-09	Lead (Pb ²⁺) species		
CdF+	0.02	1.4E-11	species	(%)	Conc. (mol/l)
CdCl+	5.76	5.12E-09	Pb+2	8.013	1.16E-08
CdCl2 (aq)	0.02	1.83E-11	PbOH+	6.48	9.38E-09
CdSO4 (aq)	3.15	2.8E-09	Pb(OH)2 (aq)	0.08	1.1E-10
Cd(SO4)2-2	0.01	1.12E-11	PbF+	0.01	2E-11
CdHPO4 (aq)	0.02	1.32E-11	PbCl+	0.22	3.11E-10
CdHCO3+	4.05	3.6E-09	PbSO4 (aq)	0.65	9.36E-10
CdCO3 (aq)	5.19	4.61E-09	Pb(CO3)2-2	0.92	1.34E-09
Cd(CO3)2-2	0.02	1.63E-11	PbCO3 (aq)	73.64	1.07E-07
			PbHCO3+	9.99	1.45E-08

Saturation Index (SI)

Saturation indices (SI) were calculated for calcite, goethite, dolomite, and gypsum using the following expression:

$$SI = \log (IAP/Ks) \quad (8)$$

Where, IAP is the ion activity product, and Ks is the solubility product, the groundwater samples were computed at the pH 7.6. Table 6 shows that the groundwater is slightly oversaturated with respect to calcite, and dolomite, highly oversaturated with respect to goethite, and undersaturated with respect to gypsite. Similar investigations were reported [18].

The physical characteristics of binding of the free metal with the soil surface sites was calculated. The surface electrical charge density and the electrical potential of binding Sr, Co, Cd and Pb metal with the soil surface was calculated.

Table 6: Physical state of the water with respect to the solid phase

Log (IAP)	Log (IAP)	SI = log (IAP) – log Ks
Mineral		
Calcite	-6.769	1.711
CoFe ₂ O ₄	24.303	27.831
Dolomite	-13.518	3.022
Gypsum	-7.375	-2.765

Note: SI < 0 indicates undersaturated, and SI > 0 indicates oversaturated

The surface charge density and the electrical potential

Concentrations of the free metals, Sr, Co, Cd, Pb, and PbCO₃ species (mol/l) are given in Table 7. The ionic strength of the groundwater samples was computed using MinteqA2 code version 3.0. The surface charge density and the electrical potential of binding the metals with soils were calculated using the specific parameters of soils such as, the specific surface area (m²/kg) and the pH of the soils in water using soil to water ratio 1 : 10, and the CEC. Table 7

summarizes the electrical characterizations of binding the metals with the soil, such as, the surface electrical charge (σ) and the surface electrical potentials (ψ). These parameters are found to decrease for the heavy metals in the following order: Sr > Co > Cd > and PbCO₃.

Table 7: The surface electrical charge density (σ) and the surface electrical potential (ψ) of binding of Sr, Co, Cd, Pb and PbCO₃ species on soils

species	Conc. (mol/l)	pH	Ionic strength (mol/l)	SSA (m ² /kg)	Surface electrical charge σ (m ² /C)	Surface electrical potential ψ (V)
Sr	3.23E-07	6.6	0.00043	26000	0.0012	0.937
Co	1.4E-07	6.6	0.00043	26000	0.0005	0.406
Cd	7.26E-08	6.6	0.00043	26000	0.0025	0.209
Pb	1.16E-08	6.6	0.00043	26000	0.000041	0.035
PbCO ₃	1.07E-07	6.6	0.00043	26000	0.00041	0.319

CONCLUSION

Groundwater samples were chemically analyzed in terms of drinking water quality, MinteqA2 code version 3.0 was used to predict concentrations of the metal species existing in the aqueous phase. The free heavy metal ions of Sr, Cd, Pb, Co represent the major toxic species, Al and Fe were found as hydroxyl-compounds. The degree of saturating was determined with respect to the solid phase. The electrical characterizations of binding metals such as Sr, Cd, Pb, Co with the soil was calculated, these represented, the surface electrical chemical charge (σ) and the surface electrical potentials (ψ).

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