Volume 6 Issue 3



Environmental Science An Indian Journal Current Research Papers

Trade Science Inc.

ESAIJ, 6(3), 2011 [123-131]

Selenium status in some Egyptian soils

H.H.A.Sabrynal¹, N.S.M.Yahiya¹, E.A.M.Abdel-Rahman¹, S.A.Radwan^{2*} ¹Chemistry Department, Faculty of Science, Menoufia Univ., (EGYPT) ²Soil Chemistry and Physics Department, Desert Research Center, Cairo, (EGYPT) Received: 23rd March, 2011; Accepted: 23rd April, 2011

ABSTRACT

Fifteen surface soil samples (0 - 30 cm) representative of some the Egyptian soils types were collected from areas along Elsalam Canal, Sinai, Sewa Oasis and El- Nubaria. The samples were five samples from both Sewa Oasis and along EL Salam canal at west desert and the north coastal, respectively. Four samples from Sinai and one sample from Nubaria. The study areas are irrigating with different irrigation water qualities and have morphological variations. The collected soil samples were chemically analyzed for some chemical and physical properties, total Se, Se fractions and Se species. To assess the behavior of various geological Se, the collected Soil samples were partitioning to investigate the significance of different Se fractions in assessing solid - phase speciation and geochemical transformation. The Se fractions extracted by the partitioning technique were aqueous (0.25 M KCl) exchangeable (1 M KH2PO4), acid extractable (4 M HCl), sulfide and humic bound (KClO3 + 12M HCl) and siliceous (HNO₂+H₂SO₄+HCLO₄). Selenite and Selenate in each sample were measured by hydride generation atomic adsorption spectrometer. The chemical fractionation of soil Se, ranged between, 0.011 to 0.293, 0.02 to 0.280, 0.03 to 0.360, 0.033 to 1.211 and 0.061 to 0.710 ppm, for aqueous, exchangeable, acid extractable, sulfide and humic bound and siliceous, respectively. The amount of fraction-Se in soils did not correlated significantly with most of the studied soil properties with exception of the siliceous fraction that related significantly with pH (0.638*). Total Se was found to vary from 0.17 to 1.95 ppm. These levels are positively correlated significantly with exchangeable, acid extractable and sulfide extractable and siliceous fractions. The coefficient correlations were, 0.507*, 0.582*, 0.882** and 0.512*, respectively. Also, the species (Se+4) of aqueous and exchangeable fractions are positively correlated significantly with the total Se. The coefficient correlations were, 0.811** and 0.527*, © 2011 Trade Science Inc. - INDIA respectively.

INTRODUCTION

Trace elements play an important role in the func-

KEYWORDS

Egyptian soils; Total selenium; Fractionation; Speciation.

tioning of life on our planet. Some elements can be highly toxic to various life forms; others are considered essential, but can become toxic at higher doses. Many of

these effects depend strongly on the particular form in which the element is present in the system. Se is an essential trace element in animal nutrition that is toxic at elevated concentration^[11]. Elevated solution Se concentrations can occur as a result of mining operations and drainage of seleniferous soils^[24]. The range between Se deficiency and toxicity is narrow (Gupta and Watkinson, 1985). Sources of selenium contamination associated with anthropogenic activities arise from application of agricultural pesticides, disposal of industrial wastes, and combustion of fuels. Selenium is naturally enriched in fossil fuels well above the level of abundance in the earth's curst of $< 0.05 \text{ mg/kg}^{[7]}$. Selenium is further concentrated in coal combustion by-products such as fly ash (e.g., 6.9 to 760 mg Se/kg ash)^[26]. Se exists in the atmospheric, marine and terrestrial environments, where it may be transported and transformed via different chemical and physical pathways. The distribution of Se is greatly inhomogeneous, resulting in the relative Se enrichment and depletion in the different environments. In particular, elevated levels of Se in the aquatic environment and in terrestrial plants such as lichens and mosses remote from anthropogenic emission sources have been documented, indicating that atmospheric deposition may be an important source of contamination^[2-4,9]. Selenium exists in four oxidation states in natural systems: selenate (Se(VI)), selenite [Se(IV)], elemental Se [Se(0)], and selenide [Se(-II)]. Under the prevailing pH-pE range in soils, selenium is most mobile in the Se(IV) and Se(VI) forms, while elemental Se(0) and Se(-II) are present as stable metal forms^[16]. Se(VI) is present as SeO42- over the entire pH range of soils, while the major Se(IV) species is HSeO3- (pKa=2.68) at pH < 8.4 and SeO32-(pKa=8.4) at $pH > 8.4^{[22]}$. The major inorganic Se species found in soil solution are selenite, Se(IV), and selenate, Se (VI)^[1]. Selenium toxicity is dependent on its oxidation state (Harr, 1978). Selenite is generally considered to be more toxic than selenate. The transformation rates of selenite to selenate and selenate to selenite are slow so that both redox states can coexist in soil solution. Adsorption reactions with soil mineral surfaces attenuate solution Se concentrations. Selenite adsorbs strongly on soil surfaces while selenate generally adsorbs weakly or not at all and is readily leached^[17]. Because of the differences in toxicity and

Environmental Science An Indian Journal adsorption behavior, speciation of inorganic Se is important. The present investigation aims to study the Se fractions and species present and their relation with some Egyptian soil characteristics.

MATERIAL AND METHODS

Fifteen surface soil samples (0 -30 cm) representative of some the Egyptian soils types were collected from areas along Elsalam Canal, Sinai, Sewa Oasis and El- Nubaria. The samples were five samples from both Swia Oasis and along EL Salam canal at west desert and the north coastal, respectively. Four samples from Sinai and one sample from Nubaria. The study areas are irrigating with different irrigation water qualities and have morphological variations. The collected soil samples were air dried crushed by agate mortar, passed through a 2mm sieve and stored for chemical and physical analyses. -Determination of some physical and chemical properties of the collected soil samples was preformed according to the following:-

Mechanical analysis was using the international Pipette method with sodium hexametaphosphate as a dispersing agent Piper^[18]. Organic matter content was determined by the method of Weakley and black Jackson^[13]. Soil reaction (pH) was determined electrometrically in the soil paste using bench type Beckman glass electrode pH - meter. Total carbonate was determined volumetrically using Collin's calci-meter according to Jackson (1958) and calculated as CaCO3. Total soluble salts were estimated conduct metrically as Ec in the soil paste extract according to the described by Jackson^[13]. Cationic and anionic compositions of the soil saturation extract were determined as described by Richard^[20]. Cation exchange capacity and exchangeable cations were determined according to the methods described by Jackson^[13]. Anion exchange capacity was determined according to the methods described by Marc Pans and Jacques Gautheyrou^[14]. Se was determined by hydride generation atomic adsorption spectrometer after digestion of the samples with a ternary acids mixtures of HNO₂, H₂SO₄ and HCLO4. Extraction of Silica by successive washings of 5% Na₂CO₂ solution Follet et al^[10] the contents of Si and Al in each washing were measured spectro photo metrically using the ammonium molybdate method

124

for Si and Aluminum method for Al Snell and Snell^[25]. Free iron oxides were extracted by CBD method according to Mitchell and Mackenzie^[15] and determined spectra photo metrically using O - phenanrthroline speciation and geochemical transformation of soil method Snell and Snell^[25]. Fractional partitioning for assessing solid- phase Selenium was determined according to Chao and Sanzolone^[8]. The procedure extracts soils Se into five fractions. Soluble (0.25M KCL), legend exchangeable (0.1M KH₂PO₄) acid extractable (4MHCL) oxidative acid decomposable (KCLO₃ +conc HCL) and strong mixed – acid digestible (HNO₃+H₂SO₄+HCL). Selenite and Selenate in each sample were measured by hydride generation atomic adsorption spectrometer.

RESULT AND DISCUSSION

Before discussing the selenium status in the studied areas, it is important to throw light on the relevant physical and chemical properties of the investigated soils. The physical and chemical properties of the studied soils are shown in TABLES 1. An account on these soil properties is given hereafter.

Current Research Paper Characterization of the studied soils

TABLE 1 showed that soil texture varies from sandy to clay. At Elsalam region the texture is clay except sample No (II) is sandy –loam, Al Irish, Wadi- firan, Kantra East and El- Nubaria regions are coarse sand in texture but Ras Sudr is sandy clay loam. In Swia oasis the texture varies from fine sand in samples (I and III), coarse sand in sample No (II) and sandy – loam in samples (IV and V). TABLE 1 showed that almost all of the studied soils are mildly alkaline (pH 7.6-8.3) except Swia Osis regions already recognized as alkaline (pH>8.3). In El Salam canal region pH values range from 7.6 to 8.3 indicating neutral to alkaline In Swia Osis regions the pH values are mildly alkaline > 8.0 except sample (IV). The highest value is 8.9 in sample (III) and the lowest value is 7.8 in sample (IV).

Data in TABLE 1 showed that the soils under study are slightly saline to extremely saline, as indicated by EC_e values which range widely from 1.36 to 54.6 dS/m. The highest EC_e value characterizes Ras Sudr soil sample whereas the lowest value is associated with Wadi firan soil sample. Distribution of soil salinity shows that EC_e values tend to decrease with soils in El Salam region

Index (meq/100g) (meq/100g) %									
Elsalan CanalI 48.69 9.53 0.23 2.9 18.6 1447.9 51.81 28.07 20.12 ClII 10.60 12.71 0.12 0.1 13.8 307.87 6.58 18.68 74.74 LSIII 59.13 10.65 6.01 9.3 25.1 699.06 64.39 23.19 12.47 ClIV 49.56 12.09 6.04 2.2 25.5 1232.51 57.78 24.5 18.46 ClV 34.78 0.49 5.32 2.1 16.5 1849.39 48.81 32.73 18.4 ClSinaiRase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SLAlarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 SWadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 SEI-NubariaEI-NubariaIII.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$									
II 10.60 12.71 0.12 0.1 13.8 307.87 6.58 18.68 74.74 LS III 59.13 10.65 6.01 9.3 25.1 699.06 64.39 23.19 12.47 Cl IV 49.56 12.09 6.04 2.2 25.5 1232.51 57.78 24.5 18.46 Cl V 34.78 0.49 5.32 2.1 16.5 1849.39 48.81 32.73 18.4 Cl Rase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23									
III 59.13 10.65 6.01 9.3 25.1 699.06 64.39 23.19 12.47 Cl IV 49.56 12.09 6.04 2.2 25.5 1232.51 57.78 24.5 18.46 Cl V 34.78 0.49 5.32 2.1 16.5 1849.39 48.81 32.73 18.4 Cl Sinai Rase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El Kantara east 0.96 1.22 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
IV 49.56 12.09 6.04 2.2 25.5 1232.51 57.78 24.5 18.46 Cl V 34.78 0.49 5.32 2.1 16.5 1849.39 48.81 32.73 18.46 Cl Einai Sinai Sinai State 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
V 34.78 0.49 5.32 2.1 16.5 1849.39 48.81 32.73 18.4 Cl Sinai Rase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
Sinai Rase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
Rase sadre 9.57 21.82 1.48 26.2 12.0 1310.39 13.1 28.8 58.1 SL Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
Alarish 8.69 15.59 1.38 27.3 22.3 1310.39 5.9 6.6 87.4 S Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
Wadi firan 1.48 14.48 0.98 8.24 8.4 786.8 0.1 4.8 98.1 S El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
El Kantara east 0.96 1.22 0.57 1.18 16.5 280.85 0.3 2.4 97.3 S El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
El-Nubaria 11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
11.30 12.28 0.23 36.6 18.5 887.4 24.5 17.2 58.3 SCL									
Siwa Oasis									
I 0.52 4.15 0.17 14.4 11.4 228.89 2.5 3.5 94.0 S									
II 0.43 16.73 0.17 13.1 12.4 139.61 4.1 4.9 91.0 S									
III 0.69 4.06 0.29 14.7 14.8 226.61 2.4 2.08 95.52 S									
IV 6.95 22.86 0.75 32.4 27.7 96.8 5.86 31.11 63.03 SL									
V 1.82 23.49 0.35 8.8 16.4 515.29 6.67 17.23 76.1 SL									

 TABLE 1 : Some physical and chemical properties of the studied soils.

Environmental Science An Indian Journal

Loodian	PH -	Ec	S	oluble cat	ions (me/L)	Soluble anions (me/L)				
Location		(ds/m)	Ca ⁺²	Mg ⁺²	Na	K	$CO_3^{=}$	HCO ₃	Cl	SO ₄ ⁼
Along Elsalam canal										
Ι	8.1	12.79	28.34	7.77	64.24	1.45	3.24	2.43	61.13	33.70
II	7.8	18.61	28.00	12.45	98.09	1.47	-	1.56	128.37	10.09
III	7.6	7.42	21.97	5.53	60.89	1.15	2.20	3.29	56.03	7.12
IV	8.3	2.44	7.76	2.07	15.79	0.50	4.14	3.10	15.52	2.33
V	8.0	3.39	4.65	3.57	11.97	0.20	1.55	2.33	14.5	3.09
Sinai										
Rase sadre	7.08	54.6	76.05	28.68	289.7	1.11	-	2.17	334.9	4.01
Alarish	7.6	39.1	7.75	7.07	103.36	1.22	-	1.19	1118.8	43.95
Wadi firan	8.27	1.36	10.55	7.91	4.81	0.39	-	2.64	16.49	4.55
Kantar east	7.8	43.7	53.35	49.24	299.7	4.20	-	2.05	348.8	54.02
El-Nubaria										
	8.1	4.16	11.94	4.78	19.93	1.30	-	6.68	23.88	7.38
Sewa Oais										
Ι	8.4	18.1	34.02	17.39	74.28	2.90	1.51	1.51	77.11	25.02
II	8.63	14.29	32.70	22.7	87.16	3.95	-	2.27	103.5	22.45
III	8.9	2.20	4.84	2.42	6.14	0.95	-	2.02	12.52	2.25
IV	7.8	35.3	77.9	58.62	142.5	2.56	-	1.54	146.5	133.5
V	8.1	41.3	32.36	14.74	104.7	8.68	-	1.59	106.9	78.35

Current Research Paper

from sample (I) to (V). Under the condition of the alluvial soils of El Salam canal region, the distribution of soluble cations follows the order: Na⁺>Ca⁺²>Mg⁺²> K⁺ which characterizes all the soils. The anionic composition of soil saturation extract is dominated by Clfollowed by SO_4^{-2} in all samples. In all soils CO_3^{-2} and HCO_3^{-1} are the least abundant anions in all samples of the studied soil.Data in TABLE 2 showed that the soils organic matter content ranges from 0.17 to 6.24%. The highest content is recorded in sample (IV) of El Salam region while the lowest content is found in the sample (I and II) in the Siwa Oasis. The higher contents of organic matter rendered to manuring of cultivated soils, mostly the alluvial ones. In short, organic matter content is generally low due to the high rate of its decomposition under the prevailed semi-arid climatic condition.

Data in TABLE 1 showed that $CaCO_3$ content in the studied soils ranges widely from 0.1 to 36.6%. The highest content is found in the sample representing the calcareous soils of El Nubaria region while the lowest content is found in the sample (II) representing the alluvial soils of El Salam region. As expected, the calcareous soils are enriched with CaCO₃ which ranges from 14.4% up to 36.6% whereas fluvio marine and alluvial

Environmental Science An Indian Journal

soils are impoverished in this component since its content does not exceed 9.3%.

TABLE 2 : Fractional partitoning of soil selenium, (ppm)

Location	Aqueous	Exchange	Acid	Sulfide	Silinieous	Total			
Along Elsalam Canal									
Ι	0.044	0.101	0.131	0.103	0.271	0.650			
II	0.033	0.021	0.041	0.033	0.061	0.189			
III	0.080	0.121	0.321	0.122	0.112	0.756			
IV	0.121	0.090	0.172	0.161	0.271	0.815			
V	0.020	0.020	0.121	0.111	0.350	0.622			
Sinai									
Rase Sudre	0.042	0.054	0.172	0.084	0.095	0.447			
El –Arish	0.293	0.040	0.132	1.02	0.131	1.616			
Wadi –Firan	0.011	0.280	0.190	1.211	0.250	1.942			
Kantar- east	0.112	0.063	0.050	0.080	0.081	0.388			
		Al- Nu	baria						
	0.013	0.110	0.030	0.081	0.12	0.354			
Siwa Oasis									
Ι	0.022	0.042	0.021	0.053	0.083	0.221			
II	0.073	0.123	0.260	0.041	0.330	0.827			
III	0.071	0.052	0.360	0.440	0.710	1.633			
IV	0.042	0.021	0.173	0.134	0.380	0.750			
V	0.051	0.050	0.150	0.121	0.370	0.742			

127

Data in TABLE 3 showed that CEC of the soils under study varies widely from 0.43 to 59.13 mg/100g soil. The lowest value is recorded in the sample (II) in Swia osis while the highest value is associated with the sample (III) in El Salam canal region. The great variation in CEC of the studied soils is mainly rendered to their clay content and mineralogy.. So El Salam canal region recorded the highest values of CEC (10.6-59.13 mg/100g soil) because of its contents of clay Positive charge is originated either from rupture of planes of the structural units and the resulting edge charge or of iron and aluminum oxides that cover some crystalline clay or occupy an interlayer position in lattice layers. These charges induce adsorption of anions^[27].

TABLE 3 : Speciation of the available selenium fractions and total selenium in the studied soils (ppm).

	Location	Aqu	eous	Exch	ange	Sum of	T.
	Location	Se ⁺⁴	Se ⁺⁶	Se ⁺⁴	Se ⁺⁶	available	Se
El-Salam Canal	Ι	0.012	0.032	0.07	0.03	0.144	0.63
	II	0.011	0.021	0.011	0.011	0.054	0.17
	III	0.011	0.070	0.070	0.060	0.211	0.73
	IV	0.050	0.070	0.010	0.080	0.210	0.80
	V	0.002	0.018	0.010	0.010	0.040	0.59
Sinai	Rase sadre	0.020	0.022	0.031	0.015	0.088	0.42
	El arish	0.110	0.180	0.031	0.010	0.331	1.59
	Wadi firan	0.10	0.011	0.200	0.090	0.310	1.95
	Kantar east	0.011	0.102	0.041	0.022	0.176	0.38
El-Nubaria		0.011	0.012	0.060	0.050	0.131	0.34
Siwa Oasis	Ι	0.011	0.011	0.034	0.011	0.067	0.23
	II	0.031	0.040	0.062	0.053	0.184	0.84
	III	0.031	0.040	0.030	0.021	0.122	1.63
	IV	0.020	0.021	0.010	0.010	0.061	0.73
	V	0.010	0.041	0.020	0.030	0.11	0.77

The AEC was long considered to be a less important measurement than the CEC because the different anions involved in these exchanges are seldom retained be simple electrostatic bonds, but only by more complex strengths. Without selective fixation, only the exchange of Cl^- , NO_3^- and ClO_4^- anions is possible. The exchange of one anion with another anion of similar ionic force does not modify the electrophoresis mobility of the particles. There is no change in specificity related to the size of the anion and probably not to the phenomena of steric impossibility^[21]. Other anions can be more strongly retained on the oxide surface by coordination

Current Research Paper

bonds or chemisorption (e.g., different silicates, molybdates, arsenates, and organic anions), Bowder et al.^[6]. In case of the polyanions, whose economic repercussions in agronomy are considerable (e.g., PO³⁻ , SO $_{4}^{2}$ -), the AEC cannot account for exchangeable forms. Indeed, in addition to the exchange phenomena, other phenomena like precipitation of insoluble salts with iron, aluminum or alkaline -earth elements also have to be considered. Methods for the measurement of the AEC are based on the same principle as the CEC and subjected to the same constraints. Only the valence signs have to be reversed. If the surface is positively charged, any excess anions maintained by the electrostatic links in the double layer are exchangeable. In brief, the AEC is the maximum quantity of anions likely to be linked per unit of soil weight and generally accounts for 1-5 % of the CEC^[5].

Data in TABLE 1 show that AEC values vary from one soil to another, being at its lowest values in sample No (V) in El Salam canal region while reach its higher values in sample No (V) in Swia Osis. For convenience, the lowest AEC values range from 0.49 –1.22me/100g in El Salam canal region sample No (V) and Kantra – east whereas the highest values range from22.86– 23.49me/100g in samples (IV) and (V) in Swia Osis and the medium values range of 4.06 -16.73 me/100g in other samples. These variations in AEC values are mainly rendered to the differences in positive charges from one soil to another.

Selenium status in the studied soils

Generally, data in TABLE 3 recorded that the values of total Se ranged between 0.17 to 1.95. soil sample (II) along Elsalam canal have the lowest but soil sample from Widi Furan have the highest value. In detail data in TABLE 3 showed that the total Se content in the studied soils varies from 0.17 to 0.8 ppm, 0.23 to 1.63 ppm and 0.42 to 1.95 ppm for the collected soil samples from the areas, along Elaslam canal, Sinai and Siwa Oasis, respectively. There is a significant correlation between total Se and the studied Se fractions. There is also significant correlation between total Se and the studied Se and the studied Se speciation, (Se⁺⁴ and Se⁺⁶) for aqueous and exchangeable fractions. Total Se was found to vary from 0.17 to 1.95 ppm. These levels are positively correlated significantly with exchangeable, acid extractable



and sulfide extractable fractions. The coefficient correlations were, 0.507^* , 0.582^* , 0.882^{**} and 0.512^* , respectively. Also, the species (Se⁺⁴) of aqueous and exchangeable fractions are positively correlated significantly with the total Se. The coefficient correlations were, 0.811^{**} and 0.527^* , respectively.

Fractionation is defined as Process of classification of analyzes or a group of analyses from a certain sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties. So Fractionation techniques have been applied widely to assess the behavior of various geological trace elements However; relatively few studies have been conducted on solid phase speciation and geochemical assessment of selenium (Se) through fractional partitioning.

According to Chao and Sanzolon^[8] and Sharmasarkar and Vance^[23], selenium (Se) was partially fractionated and speciated to understand its mobility and contamination behavior in soils of contrasting properties. Five Se fractions (aqueous, exchangeable, acid-extractable, sulfide and humic bound and siliceous) were obtained by sequentially extracting the soils with 0.25 M KCl, 1 M KH₂PO₄, 4 N HCl, $(\text{KClO}_3 + 12 \text{ N HCl})$ and concentrated $(\text{HNO}_3 +$ $HClO_4 + H_2SO_4$), respectively. Each fraction was analyzed for total Se by atomic absorption spectrophotometry with hydride generation (AAS-HG). After a digestion with (30% $H_2O_2 + 12 \text{ N HCl}$). Solution of the selenite was analyzed before this pre treatment the selenate was calculated from the difference of these two results. However, the selenite or both Se species may be mobilized depending on soil conditions and sources of Se. Aqueous and exchangeable fractions will be available for leaching and plant uptake whereas the acid extractable fraction may be conditionally available. The last two fractions are weatherable with time and ordinarily remain unavailable. In this respect, Cary et al. (1967), the K2SO4 soluble Se consists of selenate and selenite or organic Se compounds of relatively low molecular weight compounds. The exchangeable fraction represents selenite sorbed on hydrous oxides and the NH4OH fraction consists of adsorbed Se on organic compounds. The Se fraction extracted by 6N HCl represents selenite occluded in sesquoxide particles, whereas HNO3 soluble and residual Se represent elemental Se and heavy metal se-

Environmental Science An Indian Journal lenides. The results of fractional partitioning of Se are shown in TABLE 4 these fractions are here after:

Aqueous fraction

Data in TABLE 2 showed that Se aqueous fraction which extracted by 0.25 MKCL ranged between 0.011 and 0.293 ppm, the highest level was associated with El Irish soil (sand) while the lowest was that of Wadi-firan (sand). In order to find out the relation between aqua-fraction and soil properties, correlation coefficient were calculated with particle size distribution (sand, silt and clay), OM, total caco₂, PH, Ece, CEC, AEC, Fe₂o₃ and SiO2. Data in TABLE 4 showed that the results were below the levels required for statistical significance for all cases. In order to find out the relation between Se aqua-fraction and other fractions and total selenium, data in TABLE 4 show that the correlation coefficients were higher significance with aqueous selenate, (972**) while significance with aqueous selenite, (591*) but the relations with the other fractions were under significans.

Exchangeable fraction

The data in TABLE 2 revealed the magnitude of variation in exhangeable fraction of Se extracted by $1MKH_2PO4$, the results ranged between 0.021 and 0.123 ppm, the lowest level with recorded for sample (2) in El Salam canal region and sample (14) in Swia oasis, the highest value recorded for Wadi–firan soil. In order to find out any relation between Exchangeable -fraction and soil properties, the calculated correlations with texture (particle size distribution), OM, total caco₃, PH, Ece, CEC, AEC, Fe₂o₃ and Sio₂, were below the levels required for statistical significance for all cases.

Data in TABLE 4 show the relationship between exchangeable fraction and other fractions and total selenium, the results reveal that the correlation coefficients between exchangeable fraction and other fractions were significance in case of sulfide, aqueous selenite, total fractions and total Se, the correlations were, 0.531*,0.478*, 0.500* and 0.507*, respectively. But were higher significance with exchangeable selenium in the species selenite (0.952**) and selenate (0.854**). The relationship between exchangeable fraction and siliceous fraction showed that correlation coefficient were below significance.

128

TABLE 4 : The simple correlation between soil properties, Se fractions and species.

	Aq.	Ex.	Acid	Sulfide	Silic.	T.Fr.	Aqu. Se ⁺⁴	Aqu. Se ⁺⁶	Exch. Se ⁺⁴	Exch. Se ⁺⁶	T.Se
PH					0.638*	·					
ECe		-0.434								-0.541*	
CEC											
AEC											
Fe2O3											
SiO2	0.412	-0.304						0.419	-0.419		
Clay										0.314	
Silt	-0.272	-0.284		-0.415		-0.378	-0.397				-0.396
OM										0.338	
CaCO3											
Aq											
EX											
Acid			0.633*								
Sulfide	0.416	0.531*									
Silic											
T.Fr.		0.500*	0.584*	0.885**	0.506*						
ASe^{+4}	0.591*	0.478*		0.926**							
ASe ⁺⁶	0.972**						0.508*		0.615**		
ESe^{+4}		0.952**		0.615*			0.487*				
ESe ⁺⁶		0.854**									
TSe	0.372	0.507*	0.582	0.882**	0.512*		0.811**		0.527*		

Acid –extractable fraction

Would correspond to Se associated with amorphous materials^[19] carbonates^[12] Acid -extractable fraction as extracted by 4 N HCl ranged between 0.021 and 0.360 ppm, the lowest level with recorded for sample (I) in Swia oasis and the highest level characterized sample (III) in Swia oasis. To investigate the relationship between this fraction and soil properties, the correlation coefficient were calculated between this parameter and each of texture, OM, total caco₃, PH, Ece, CEC, AEC, Fe₂o₃ and Sio₂ the results were below significance in all cases. To investigate the relationship between this fraction and other fractions and total selenium, data show that the correlation coefficient were significance with siliceous, total se fractions and total Se, the correlation coefficients were, 0.633*, 0.584* and 0.582*, respectively. The other relations were below significance.

Sulfide and humic bound fraction

Selenium associated with sulfide, organic matter as extracted by the combination of $KCLO_3$ and 12MHCL ranged between 0.033 and 1.211 ppm, the lowest level

with recorded for sample (II) in El Salam canal region, the highest level characterized Wadi furan soil. To investigate the relationship between this fraction and soil properties correlation coefficient were calculated between this parameter and each of texture, OM, total caco₃, PH, Ece, CEC, AEC, Fe₂o₃ and Sio₂ The results were below significance in all cases. With respect to the relations between this fraction and species of Se, data in TABLE 4 reflect the magnitude of correlation between this fraction as measured against the other fraction and species of Se. The relations in TABLE 4 proved highly significant were those between total fractions, total Se and Aqueou selenite. The correlation coefficients were, 0.885**, 0.926** and 0.882*8, respectively. The exchangeable selenite correlated significantly (0.615^*) with the studied fraction.

Siliceous fraction

Corresponding to highly resistant siliceous selenium of the layer lattices of siliceous minerals this fraction was obtained by extraction with mixed acid solution (HNO3+H2SO4 +HCLO3). Data in TABLE 4 reveal that the values associated with this fraction ranged be-



tween 0.061 and 0.71 ppm, the lowest content characterized sample (II) in El Salam canal region, while the highest is that recorded for sample (III) in Swia oasis. To investigate the relationship between this fraction and soil properties, correlation coefficient were calculated between this parameter and each of texture, OM, total caco₃, PH, Ece, CEC, AEC, Fe₂o₃ and Sio₂ the results were below significance in all cases, with exception of the correlation with pH witch correlated significantly with this fraction (0.638*).

With respect the relation between this fraction and other fractions and species of Se and total selenium, data showed that the correlation coefficient were significance with total fraction (0.506^*) and total selenium (0.512^*) , while below significance with aqueous, exchangeable, and sulfide fractions.

Selenium species (Se⁺⁴ and Se⁺⁶)

Geochemists and environmental chemists have often applied the word speciation to describe the transformations taking place during cycling of the elements. An example is the changes that occur between the leaching of trace elements from soil or rock and their subsequent distribution in the aquatic environment. However, in order avoid confusion, species and measuring their distribution. Sometimes, it is used to indicate that a method gives more information on the form in which the element is present than other more commonly applied techniques finally, the term speciation is also used to indicate the distribution of species in a particular sample characterized or matrix. Solid –phase Selenite -Selenate speciation in available fractions is shown in TABLE 4, these species (Selenite - Selenate) are here after:

Se⁺⁴ and Se⁺⁶ species in aqueous fraction

Environmental Science

An Indian Journal

The ranges of Se⁺⁴ in aqueous fraction were ranged from <0.01 to 0.11 ppm, the lowest content characterized for Wadi firan region while the highest is that recorded for El–Irish. With respect to Se⁺⁶, the values ranged from <0.011 to 0.18 ppm, the lowest level with recorded for Wadi firan region, while the highest level characterized soil sample (V) along Alsalam canal. To investigate the relationship between this fraction and Se⁺⁴ and Se⁺⁶, data show that no significance correlations were found between Se⁺⁴ and this fraction while high significance with Se⁺⁶. This clearly suggests that Se⁺⁶ in aqueous solutions would be the potential species, the similar conclusion was reported by Sharmasarkar and Vance^[23]. Data in TABLE 4 showed significant correlations between this specie and aqueous selenate (0.508*) and exchangeable selenite (0.487*), respectively and highly significant with total selenium (0.811**).

Se would gradually be transformed into aqueous Se. They added that the mechanism of transformation of exchangeable Se to aqueous fraction could be either selenite- selinate oxidation or possibly mass flow of Se to the bluk solution phase from adsorption site. However, selenite – selinate transformation would be a slow process.

Se⁺⁴ and Se⁺⁶ species in exchangeable fraction

Data in TABLE 5 showed that the values of Se⁺⁴ in this fraction ranged from 0.01 to 0.2 ppm. The lowest content characterized sample No (4) in El salam canal region while the highest is that recorded for sample of Wadi firan. With respect of Se⁺⁶ the values were from 0.01 to 0.09 ppm. The lowest level with recorded for sample No (V) in El salam canal region while the highest level recorded for Wadi firan soil. To investigate the relationship between this fraction in phase Se⁺⁴ and Se⁺⁶, data show a significance correlations was found between Se^{+6} and Se^{+4} in this fraction (0.615*), while a high significance between Se⁺⁴ in the studied fraction and total Se (0.527^*) . So the exchange phase maybe affected by Selenate and total selenium and their transformation from selenium forms to another according to the soil conditions.

REFERENCES

- [1] D.C.Adriano; 'Trace Elements in the Terrestrial Environment, Springer-Veriag, New York (1986).
- [2] F.Beavington, P.A.Cawse, A.Wakenshaw; Science of the Total Environment, 332, 39-49 (2004).
- [3] J.P.Bennett; Environmental and Experimental Botany, **35**, 259-277 (**1995**).
- [4] G.A.Cutter, T.M.Church; Nature, **322**, 720-724 (**1986**).
- [5] G.H.Bolt, F.A.M.De Hann; Anion Exclusion in Soil. In Soil Chemistry, B-Physico Chemical Models, G.H.Bolt, (Ed); Elsevier, Amsterdam, The Netherlands, Development in Soil Science, 5B, 233-257 (1982).

- [6] J.W.Bowder, S.Nagarajah, N.J.Barrow, A.Posner, J.P.Quirk; Aust.J.Soil Res., 18, 49-60 (1980).
- [7] H.J.M.Bowen; Environmental Chemistry of the Elements. Academic Press, London (1979).
- [8] T.T.Chao, R.F.Sanzolone; Soil Sci.Soc.Am.J., 53, 385-392 (1989).
- [9] G.A.Cutter, L.S.Cutter; Estuarine, Coastal and Shelf Science, 61, 463-476 (2004).
- [10] E.A.C.Follet, W.T.Mc Hardy, B.D.Mitchell, B.F.L.Smith; Chemical Dissolution Techniques in the Study of Soil Clays. Part: I, LL, Clay Minerals, 6-23 (1965).
- [11] C.A.Girling; Selenium in Agriculture and the Environment: Agriculture, Ecosystems, and Environment, 11(1), 37-65 (1984).
- [12] S.Goldberg, R.A.Glaubig; Sci.Soc.Am.J., 57, 704-708 (1988).
- [13] M.L.Jackson; Soil Chemical Analysis, Prentice Hall, England, U.K. (1973).
- [14] Marc, Jacques; Methods, 755-760 (2003).
- [15] B.D.Mitchell, R.O.Makenzie; Soil Sci., 77, 173-184 (1954).
- [16] R.H.Neal, G.Sposito, K.M.Holtzclaw, S.J.Traina; Soil Sci.Soc.Am.J., 51, 1161-1165 (1987a).
- [17] R.H.Neal, G.Sposito; Soil Sci.Soc.Am.J., 53, 70-74 (1989).
- [18] C.S.Piper; Soil and Plant Analysis, Waite Agric.Res. Inst., S.A.Adelaide, (Ed); Australia (1950).

- [19] S.S.S.Rajan, J.H.Watkinson; Soil Sci.Soc.Am.J., 40, 51-54 (1976).
- [20] L.A.Richard; Diagnosis and Improvement of Saline and Alkali Soils. U. S. D. A. Handbook No. 60, Washington, D.C., U.S.A. (1954).
- [21] U.Schwertmann, R.M.Taylor; Iron Hydroxides. In: Minerals in Soil Environments, J.B.Dixon, S.B.Weed, (Eds); Soil Sci.Soc.Am.J., U.S.A., 8, 379-438 (1989).
- [22] F.Séby, M.Potin-Gauntier, E.Giffaut, O.F.X.Donard; Analusis, 26, 193-198 (1998).
- [23] S.Sharmasarkar, G.F.Vance; Soil Sci.Soc.Am.J., 43-65 (1994).
- [24] S.Sharma, R.Singh; Reviews in Environmental Control, 13(1), 23-50 (1983).
- [25] F.D.Snell, C.T.Snell; Colorimetric Methods of Analysis. Including Some Turbidimetric and Nephelometric Methods. van Nostrand Company, England, 11, (1969).
- [26] T.L.Theis, K.H.Gardner; Crit.Rev.Environ.Contr., 20, 21-42 (1990).
- [27] L.W.Zelazny, H.E.Liming, M.An Vanwormhoudt; Charge Analysis of Soils and Anion Exchange. In: Methods of Soil Analysis. Part 3, Chemical Methods, J.M.Bigham, J.M.Bartels, (Eds); SSSA-ASA, Madison, W. I.Sc. Etats-Unis, U.S.A., 1231-1253 (1996).

