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FORMS OF SELENIUM IN SOME SOUTHERN IRAQI CALCAREOUS SOILS

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ABSTRACT

Selenium is an essential microelement, necessary for normal functioning of human , animals and organisms. Eight extraction solutions were used to extract selenium forms (0.25M KCl, Soluble; 0.1M KH_2PO_4, ligand exchangeable; 1M NaOAC, Carbonate ; 4M HCl, crystalline oxides; 0.5M NaOH, Alkaline soluble; 0.1M NH_2OH- HCl, easily reducible oxides; 0.25M NH_2OH-HCl + 0.25M HCl, amorphous oxides; 16M HNO_3, total) from ten calcareous soils collected from southern parts of Iraq. Total selenium concentration in studied soils was ranged between 35.0 mg kg^{-1} for Zubair desert soil to 78.5 mg kg^{-1} for Adel marsh soil. Amount of selenium extracted with 1M NaOAC(carbonate form was the greatest 25.87% of to totals), and that extracted with 0.25 M KCl (soluble from) was the smallest. Selenium forms concentrations significantly correlated with soil properties (organic matter, CEC, $CaCO_3$, clay, and sand).

Keywords: Selenium forms, calcareous soils

1. INTRODUCTION

The biological importance of selenium that it is essential for humans and animal in one side (Rayman, 2000), and toxic when in high concentration on the other. The main function of selenium in animal and human health is related to the biochemical resistance to some diseases (Rotraer and Poue, 1993). Selenium was found to play a Key role in glutathione peroxidase, an enzyme that catalyze the decomposition of hydrogen peroxide thus protecting cells from oxidative damage (Curardic, 2003).

In environmental samples, selenium can exist in inorganic (as elemental selenium, selenide, selenite, and selenite ions) and as organic species (methylated compounds, seleno amino acids, seleno proteins and their derivatives) (Pyrzynska, 2002). Inorganic selenium species can be transformed into volatile compounds such as dimethylselenide $(CH_3)_2Se$ through microbial action of fungi and plants. Organic selenium species are more frequently found in biological systems as selenoaysteinyl (SeCys) or selenomethionyl (SeMet) residues (Fishbein, 1991).

Selenium is a constituent of 40 minerals and occurs as a minor component of 37 others, most being sulfides. The Se concentration in the earth's mantle is ~ 0.09 mg Se kg^{-1} (NRC, 1983) It is concentrations in rocks are generally comparable to those found in soils and sediments (1ow mg kg^{-1}). Selenium concentration in soils vary geographically depending on the parent rock (Pyrzynska, 2002). Soil Se varies from 0.01 mg\kg in deficient areas to 1200 mg kg^{-1} in organic rich soils in toxic areas (Keller, 2000). The concentrations and chemical forms of selenium in soils are governed by various physical and chemicals factors, including pH, chemical and mineralogical composition, adsorbing surface, and oxidation status (Dhilon and Dhillon, 1999. Selenium is normally present in soil at low contents ranging from 0.01 to2 mg kg^{-1} (Dungan and Frankenberger, 1999), Cao et. al., (2001) reported that selenium content both in total and bioavailable forms were very low (25-35 and 9.5 mg kg^{-1}) respectively. Dhillon et. al., (2005) found that total selenium concentration varied from 0.6 to 3.1 mg kg^{-1} while selenium extracted with hot water (17.72 to 68.62mg kg^{-1}),0.5M Na_2CO_3 (11.59 to 51.98 mg kg^{-1}), 1M NH_4HCO_3 +DTPA (15.64 to 60.63mg kg^{-1}),0.25M KCl (13.56 to 82.47 mg kg^{-1}) and 0.1 M KH_2PO_4 (32.41 to 16874 mg kg^{-1}).Martens and Suarez (1997) found the total concentration of eight soils (pH 7.28 to 8.06) was varied between (0.1 to 83.8 mg kg^{-1}). The aims of this study is to knowledge. The concentration of different forms of selenium in some calcareous soils from southern parts of Iraq and soils properties affecting theirs concentrations.

2. MATERIAL AND METHOD

Ten surface (0-0.3 m) samples of calcareous soils were collected from villages of Basra province (1 to 6 samples), Mesan province (7 to 10 samples). The soils samples were air-dried, ground to pass a 2-mm sieve, and stored for analysis. Physio-chemical characteristics of soils reported in table 1 were determined by procedures mention by Black (1965) and Sparks et. al., (1996). Eight chemical extracts were used to extracts of different forms of soil selenium concentration in sturdies soils. Five grams of each soil sample was shaken with 50 ml of 0.25M KCl (soluble form), 0.1M KH_2PO_4 (ligand exchangeable form), 1M NaOAC, pH= 5 (carbonates form), 4M HCl (boil) (crystalline oxides form), 0.5M NaOH (boil) (Alkaline soluble form), 0.1M NH_2OH – HCl, pH_2 (KOH following) (Easily reducible oxides form), 0.25M NH_4OH – HCl, 0.25 M HCl (KOH following) (Amorphous oxides form) for 1 h. Soil suspensions were then filtered through a whatman filter paper No.42 and Se in the filtrates were analyzed by atomic absorption spectrophotometry (Phoenix-986AA).Total soil selenium was extracted by digestion 0.25 g soils sample with nitric acid (16M) by using 30-ml Teflon beakers and 9 ml of concentrated HNO_3 and 0.25 ml of 1.2M HCl. Two ml of concentrated $HClO_4$, 2ml of conc. H_2SO_4, 10 ml of conc.

HF, and heated overnight at 125ºC. Samples were cooled and 25 ml of 6M HCl were added. Quantively transferal the samples to 50 ml volumetric flask and brought volume with deionized distilled water for AASP analysis. (Sparks et. al., 1997). Correlation coefficient (r) between soils properties and forms of selenium was calculated by using (SPPS program Ver. 16).

Table 1. Some Chemical and Physical Properties of some southern Iraqi soils.

Soil	pH (1:1)	EC (1:1) (dSm^{-1})	O.M (gkg^{-1})	$CaCO_3$ (gkg^{-1})	CEC	Clay	Silt	Sand
					($Cmol\ kg^{-1}$)	($gmKg^{-1}$)		
Medayna	7.60	7.50	14.00	285.0	28.9	553.3	292.6	154.1
Hartha	7.37	8.50	9.24	330.0	28.5	552.0	233.0	215.0
Bradia	7.18	16.33	12.40	326.0	28.0	533.4	434.6	32.0
Salhea	7.36	18.25	12.35	310.6	20.8	196.6	730.0	73.4
AbulKhaseb	7.28	26.25	11.50	335.5	18.8	395.0	513.5	91.5
Zubair	8.14	1.60	3.23	78.50	4.20	12.00	24.00	964.0
Mesan	8.25	7.50	16.60	266.2	25.4	593.8	383.7	22.5
Bterah	8.35	7.25	9.50	334.8	16.6	390.0	518.5	91.5
Adel	7.22	14.1	45.1	298.0	38.5	652.8	30.50	42.1
Njera	7.35	8.7	27.60	324.6	30.3	600.0	235.8	164.2

3. RESULTS AND DISCUSSION

3.1 Soluble form

The mean value of water soluble selenium concentration extracted with 0.25 M KCl of studied was 1.13 mg kg $^{-1}$. The lowest value was 0.80 mg kg^{-1} (Zubair soil) and the highest value was 1.40 mg kg^{-1} (Adel-marsh soil) (table 2). The soils developed under desert and humid tropic conditions, the higher water soluble selenium concentration was under temperad humid conditions (marsh soils) while the lowest levels of water soluble selenium concentration in desert condition (Zubair soil). These results were in agreement of results of Tan et al., (2002).

ISSN: 2455-6939

Volume:02, Issue:04

Table 2. Concentration (mg kg^{-1}) of Selenium forms of southern Iraqi soils.

Soil	0.25M KCl	0.1M KH_2PO_4	1 M NaOAC	4 M HCl	0.5M NaOH	0.25M Hydrooxy amine + 0.2 M HCl	0.1 M NH_2OH-HCl	Residual Se	Total Se
Medayna	1.25	12.75	13.75	1.30	16.25	1.60	1.2	9.90	58.0
Hartha	1.20	12.50	19.25	1.77	15.75	1.65	1.5	6.88	60.5
Bradia	1.10	12.25	18.50	1.32	15.0	1.72	1.1	19.11	70.1
Salhea	1.0	12.0	15.25	1.77	14.25	1.62	1.1	21.51	68.5
AbulKhaseb	1.0	12.0	19.5	1.61	14.0	1.65	1.2	9.45	60.5
Zubair	0.8	8.0	10.5	1.48	7.50	1.67	1.2	3.85	35.0
Mesan	1.25	13.0	13.0	1.60	16.75	1.80	1.3	5.4	54.1
Bterah	1.0	12.0	19.30	1.52	14.25	1.43	1.4	13.1	64.0
Adel	1.40	13.5	14.25	1.68	18.5	1.50	1.63 1.60	26.04	78.5
Njera	1.30	13.25	16.25	1.30	17.5	1.73	0.98	20.69	73.0
Mean	1.13	12.15	15.96	1.54	15.0	1.64	1.3	13.59	62.17

Statistical analysis results showed high significant effect between water soluble selenium concentration and soil organic matter (r= 0.791**), cation exchange capacity (r= 0.946**), and clay content (r= 0.921**) (table 3). Results indicated that there was exchange of selenium between solid and solution of soils. In soil, selenium is distributed among all its components. Thus, it is present in soil solution, is related to organic matter, adsorbed on clay surface.

3.2 Ligand exchangeable form

The concentration of selenium extracted with 0.1 M KH_2PO_4 was between 8.00 mg kg^{-1} (Zubair soil) to 13.50 mg kg^{-1} (Adel marsh soil) with the mean value of 12.15 mg kg^{-1} (table 2). It was represented 19.54% of total selenium concentration. The correlation coefficients between soil properties and ligand exchangeable form, showed highly significant effect with cation exchange capacity (r= 0.895**), calcium carbonate (r= 0.839**), and clay (r = 0.894**), and negatively with sand (r = - 0.912**) (table 3). That's mean soils with high content of calcium carbonate and clay has ability to adsorb selenium on their surfaces. These results are in agreement with the results of Martens and Suarez (1997), who found 0.1M KH_2PO_4 a good extraction of selenium associated with clay and amorphous and carbonaceous soils.

ISSN: 2455-6939

Volume:02, Issue:04

Table 3. Correlation coefficients (r) between soil properties and selenium forms

Soil properties	0.25 M KCl	0.1M KH_2PO_4	1 M NaOAC	4 M HCl	0.5 M NaOH	0.25 M hydroxyl amine +0.2 M HCl	0.1 M NH_2OH - HCl	Residual Se	Total Se
pH	-0.368	-0.414	-0.208	-0.055	-0.412	-0.091	0.116	-0.591	-0.630
EC	- 0.006	0.328	-0.120	0.279	0.235	-0.018	-0.128	0.399	0.492
Organic matter	0.791**	0.625	-0.206	0.040	0.716*	-0.188	0.343	0.711*	0.698*
CEC	0.946**	0.895**	0.176	-0.012	0.939**	-0.011	0.284	0.582	0.792**
$CaCO_3$	0.488	0.839**	0.228	0.106	0.755**	-0.185	0.068	0.465	0.808**
Clay	0.921**	0.894**	0.193	-0.159	0.922**	0.078	0.289	0.305	0.635*
Silt	-0.287	0.209	-0.137	0.184	0.060	-0.017	-0.378	0.118	0.234
Sand	0.604	-0.912**	0.006	-0.117	-0.845**	0.093	-0.112	-0.490	-.0794**

3.3 Carbonate form

Selenium concentration adsorbed by calcium carbonate and extracted with 1M NaOAC (at pH= 5) was between 10.50 mg kg^{-1} to 19.50 mg kg^{-1} with the mean value of 15.96 mg kg^{-1} (table 2), and represent 25.87 % of total selenium. All studied soils was calcareous at the same time high content of clay (table 1), indicated that selenium adsorbed on $CaCO_3$ particles. Andriano (1980) had reported that selenium tends to concentrate in carbonaceous derbs in sandstone. Handy and Gissel-Nielsen (1976) reported that addition of $CaCO_3$ increased selenium adsorbed by $CaCO_3$ in mineral soils-Statistical analysis showed there was no correlation coefficients between soil properties and carbonate form of selenium because all of studied soils were calcareous and differed in their properties (table 1).

3.4 Crystalline oxide form

The crystalline oxide form of selenium in studied soils ranges from 1.30 mg kg^{-1} to 1.77 mg kg^{-1} with the mean value of 1.54 mg kg^{-1}, and represent 2.48% of total selenium (table 2). The obtained results show selenium adsorbed with soil oxides were low because they are calcareous soils with low concentration of oxides. There were no correlation coefficients between soil

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Volume:02, Issue:04

properties and crystalline oxide form of selenium. Tan et al., (2002) mentioned that distribution of selenium in soils depends on content of clay, oxides , and organic matter.

3.5 Alkaline soluble form

Results in table 2 showed the concentration of selenium extracted with 0.5 M NaOH of studies soils which was ranged between 7.50 mg kg^{-1} to 18.50 mg kg^{-1} with the mean value of 24.13% of total selenium. Correlation coefficients value (table 3) showed high significant effect between soil organic matter ($r = 0.716^{*}$), cation exchange capacity ($r = 0.939^{**}$), clay ($r = 0.992^{**}$), and negatively with sand ($r = -0.845^{**}$). Soil organic matter is known to influence the retention of selenium in soils, it has increased sorption sites, which facilitates direct complexation with selenium (Aldea and Luca, 2010). Hamdy and Gissel – Nielsen (1976) remembered that organic matter possibly effects through chelating of selenite by proteins, fulvic acids, or other organic compounds that are continuously produced in soils through the activities of microorganism. From the results of the current study, we found high concentration of alkaline soluble form in soils with high content of organic matter and clay, unlike the sandy desert soils.

3.6 Easily reducible oxide form

Concentration of easily reducible form of selenium was ranged between 0.98 mg kg^{-1} to 1.63 mg kg^{-1} with the mean value of 1.3 mg kg^{-1}, and represent 2.09 % of total selenium (table 2). The highest value of this form (1.63 mg kg^{-1}) was found in marsh soil which controlled by redox condition. In addition, the soil is rich with organic matter as compared with other soils (table 1.Aldea and Luca (2010) remember that selenium can be easily reduced to hydrogen selenide (H_2Se) or selenides (HSe^-) in humid regions. The results showed no significant effects between soil properties and easily reducible oxide form of selenium (table 3).

3.7 Amorphous oxide form

Results in table 2 showed concentration of amorphous oxide form of selenium in studied soils which ranged between 1.43 mg kg^{-1} to 1.80 mg kg^{-1}. This form of selenium is unstable which may change to other forms of selenium depending on soil physical and chemical properties and it condition effect between soil properties and amorphous oxide form of selenium (table 3).

3.8 Total Selenium

Total selenium concentrations in studied soils was ranged from 35.0 mg kg^{-1} (Zubair desert soil) to 78.5 mg kg^{-1} (Adel marsh soil) with the mean value of 62.17 mg kg^{-1} (table 2). Generally, selenium in soils seems to be present in high concentration in marsh humid soils than arid desert soils. It's presented 28.87% of total selenium. The distribution of selenium forms depends on soil

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Volume:02, Issue:04

properties such as organic matter, calcium carbonate, clay and sand content, and cation exchange capacity. As soil is a complex system affected by many unstable factors. Agricultural activity and atmospheric fallout (Wang et al., 1995) and parent materials (Cao et al., 2001) may be the factors affecting total selenium contents of soils. These results in agreement with the results of Pyrzynska (2002). Results of statistical analysis of correlation coefficients between soil properties and total selenium concentration showed high positive significant effect of calcium carbonate (r= 0.808**), cation exchange capacity (r = 0.792**), organic matter (r = 0.698*), and clay (r = 0.635*), and negatively with sand content (r= - 0.794**). We concluded from these results, soil properties and their condition has effects on soil selenium and it's species

CONCLUSION

A recent investigation indicates . Amount of selenium extracted with 1M NaOAC(carbonate form was the greatest 25.87% of to totals), and that extracted with 0.25 M KCl (soluble from) was the smallest. Selenium forms concentrations significantly correlated with soil properties (organic matter, CEC, CaCO3, clay, and sand).

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