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Research Article

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Evaluation of selenium levels for the water surfaces in southern of Iraq

Zuhair A. Abdulnabi[*], Wesal F. Hassan, Dounia K. Kassaf Al-Khuzaie, Salah M. Saleh and Mahasin G. Hashim

Department of Marine Chemistry, Marine Science Center, University of Basra, Basra, Iraq

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ABSTRACT

Fifteen stations from water surfaces were selected in southern of Iraq at Basra city , it was distributed on Euphrates river , Shatt al-arab and Main outfall Drain River . All water samples were collected from surface water at 10-15 cm depth . Selenite and total Selenium were measured by Spectrophotometric method through complex formation with Selenium(IV) in acidic medium from Hydrochloric acid , some physical properties of water were recorded in these stations . The results of recording have shown the highest concentration of selenite(36.0069 µg/l) in station W_3 *and lowest concentration(12.224 µg/l) in station* W_5 *, while , the highest concentration of total Selenium(54.413 µg/l) was recorded in station* W_8 *and lowest concentration(17.381µg/l) was recorded in station* W_5*. Standard deviation of all stations (n=3) for Selenite and total Selenium were calculated, it shows at extent (0.013014-0.289165), (0.073961- 0.477617) respectively .*

Keywords: Spectrophotometric method, Selenite, Total Selenium

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INTRODUCTION

Selenium was isolated the first time in 1817 by the Swedish Chemist Jons Jacob Berzelius[1] . Selenium belongs to chalcogen group in periodic table and it's present in many chemical species and has the four natural oxidation state which are elemental selenium (0), selenide (II), selenite (IV) and selenate (VI). Inorganic selenite and selenate are dominant species in water[2], while principal species found in vegetables and grains are organo selenium compounds which include selenocysteine and selenomethionine[3,4]. Selenium is present naturally in the environment and is an essential nutrient that enter for food chain of animals and humans. However, the selenium level is of great interest because it is an essential nutrient in low concentrations and toxic at higher concentrations[3-6]. Selenium concentration can be increased through accumulation operation in the body tissues because this element cannot be created or destroyed in environmental , but selenium does have the ability to change form[7] . In 1973, Selenium was identified as an essential component of the enzyme glutathione peroxidase (GPx). This enzyme is present in most body tissues and catalyses the breakdown of the highly reactive metabolite hydrogen peroxide[8,9] . Five different type from family (GPx) enzyme have been identified to date and these exhibit protective activity against damage due to oxidation through their ability to reduce hydrogen peroxide and lipid hydroperoxides[1,10]. Selenium is essential element for humans . Deficiencies or excess of selenium concentration about allowable limit causes a lot of diseases such as cardiac and degenerative bone disease and liver carcinoma, cirrhosis, paralysis, loss of teeth, hair, nails and irritation of the eyes [6,9,11]. In this study, selenium(IV) and total Selenium were measured by Spectrophotometric method through complex formation between selenium(IV) and complex agent (4-methyl-o-phenylene diamine) in acidic medium [2,12] .

EXPERIMENTAL SECTION

• Site Selection

Fifteen stations from water surfaces were selected on the Shatt Al-Arab , Euphrates river and Main outfall drain river in southern of Iraq . The stations were distributed on the revers about two stations on Euphrates river before confluence with the Tigris river and Shatt Al-Arab formation , eight stations were distributed along Shatt Al-Arab from Qurna to Fao , this region is important because it contains many industrial and anthropogenic activities and five stations were distributed on part from Main outfall drain river, of the nearby region of oil fields . All the samples were collected at 10-15 cm depth in low tide ,from various regions in spring season in March, 2015 . Physical properties of water were measured in field such as pH ,electric conductivity EC ,temperature of water and total dissolved solid TDS, the results were compared with some the world limits such as World Health Organization (WHO2011) , European Communities (EC1998) , Canadain Drink Water Guidelines (CGL2014) and Iraqi Standard(IQS2001) [13-16] , the results as shown in table 1.

Table 1: Physical properties of selected water samples

Sampling locations	pH in field	Temperature of water ºC in field	Salinity ppt in field	TDS mg/l in field	EC µmhos cm^{-1} in field	EC µmhos cm^{-1} at 25 ºC
W_1	8.123	20.8	1.4	1806.492	2820	3065.951
W_2	8.286	20.7	1.4	1806.492	2820	3072.331
W_3	8.44	17	1.6	1979.454	3090	3647.309
W_4	8.44	17.1	1.6	1979.454	3090	3639.104
W_5	8.221	20.2	2.1	2504.746	3910	4304.65
W_6	7.725	21	2.4	2921.136	4560	4937.202
W_7	7.586	20.7	2.7	3205.254	5070	5523.658
W_8	8.220	17.8	2.7	3186.288	5040	5843.614
W_9	8.355	17.6	1.8	2267.724	3540	4122.703
W_{10}	8.364	16.9	3.5	4090.334	6470	7654.178
W_{11}	8.44	15.05	9.1	9749.7	15700	19383.79
W_{12}	8.14	13.6	8.5	9252.9	14900	19047.38
W_{13}	8.43	14.04	8.5	9190.8	14800	18718.44
W_{14}	8.36	12.66	8.1	8756.1	14100	18448.11
W_{15}	8.44	13.69	6.7	7389.9	11900	15178.98
WHO 2011	6.5-8.5	-	-	1000	-	-
CGL 2014	6.5-8.5	-	-	500	-	-
EC 1998	6.5-9.5	20	-	1500	2500	2763.95
IQS 2001	6.5-8.5	-	-	1000	-	-

After that , all these samples were collected in polyethylene containers[17] , kept in cooling and then transferred to laboratory for experience different operations. Fig.1 is shown below describes the selected sites in southern of Iraq.

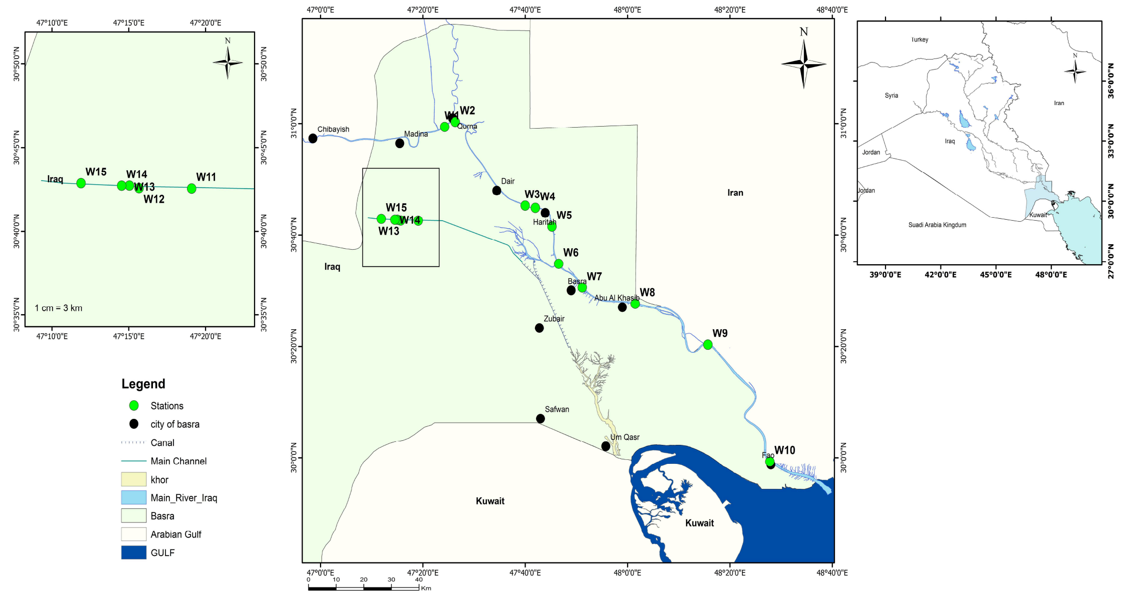

Figure 1 : Locations of the samples selected in southern of Iraq

- **Material and Chemicals**

Selenium dioxid (Purity99.8%) and KSCN were supplied by Sigma-Aldrich. Nitric acid (65%) and Hydrochloric acid (37%) were obtained from Scharlau . Haxan was purchased from J.T.Baker , 4-MOPDA was supplied by Merck , Hydrogen Peroxide(35%) was obtained from Riedel-de Haen(Germany) , $EDTANa_2$ was obtained from G.C.C and Sodium hydroxide was obtained from Himeda . Deionized water was used for preparation of all solutions.

- **Instrumentation**

UV-Vis spectrophotometer double- beam from type (Shimadzu 1800 PC , Japan) with 1.0 cm quartz cell was used for all spectral measurements at 332nm after complex formation between selenium(IV) and MOPDA as complexing agent. Magnetic stirrer was used to mix all samples. Instrument water sampler collection were used for collecting all samples from surface water at 10-15 cm depth. Physical properties were measured by WTW (Multi 3410 Set C ,Germany) .

- **Procedure**

Solution volume of samples about 25 ml and adjusting pH for this solution by using Hydrochloric acid . KSCN and EDTA disodium were used as complexing agents for eliminating interferences Fe^{+3},Cu^{+2} and Zn^{+2} ions with measurement of selenium (IV) . In this study the same procedure previously described is used for the analysis Selenium (IV) [12].

RESULTS AND DISCUSSION

The physical properties of the water samples were measured in field ,from the results of measurements as shown in table 1 and fig.2 , the pH data for different regions at extent is (7.586-8.44) , this refers to the behavior of alkali water because of many species are present in water from carbonate system such as carbon dioxide , carbonic acid , bicarbonate ions and carbonate ions.These parameters are responsible for changing the value of pH in water[18] . This explains the increase of pH value for some sites (W_1- W_5) because this region undergoes anthropogenic activities which are associated with industrial and domestic effluents and decrease of pH value for the stations W_6 , W_7 because the increase has released wastewater without treatment to water [12]. However , an increase in pH value of the sites (W_8 -W_{15}) was also noted , may be due to a high concentration from bicarbonate and carbonate salts in sea waters resulting from tides[19].The results of pH are within the acceptable limits of WHO 2011, EC1998 , CGL2014 and Iraqi standard(2001) for drink water.

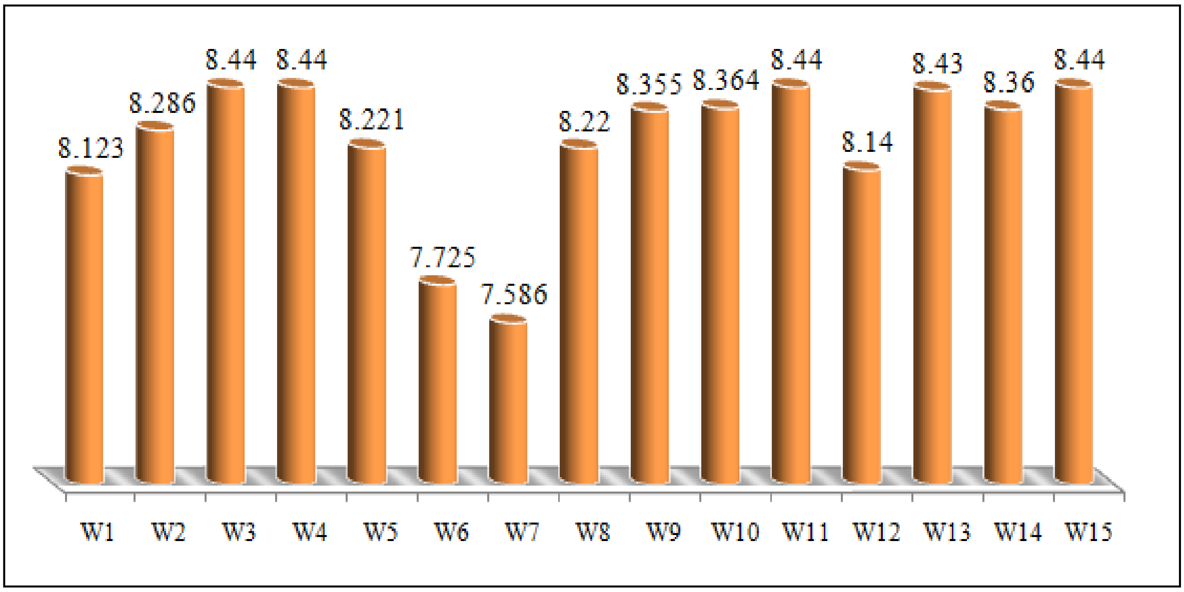

Figure 2 : pH level for selected sites in field

The electric conductivity (EC) was recorded in the fields directly and showed at extent (2.82-15.7 mmhos cm^{-1}) , the results are shown in table 1 and fig. 3. The electric conductivity (EC) was corrected at 25 °C[18] , as shown in fig. 4 . Recorded data has shown an increase of EC value from station W_1 towards station W_{10} except for station W_9 because this area undergoes for the effect by flow rate the karun river towards Shatt Al-Arab in nearby region from Seba zone (W_8) therefore we noted highest effect in station (W_9) . However, the decrease in EC value was noted from station W_{11} towards W_{15} because of the decrease of tide influence in this regions beginning from station W_{11} towards W_{15} .

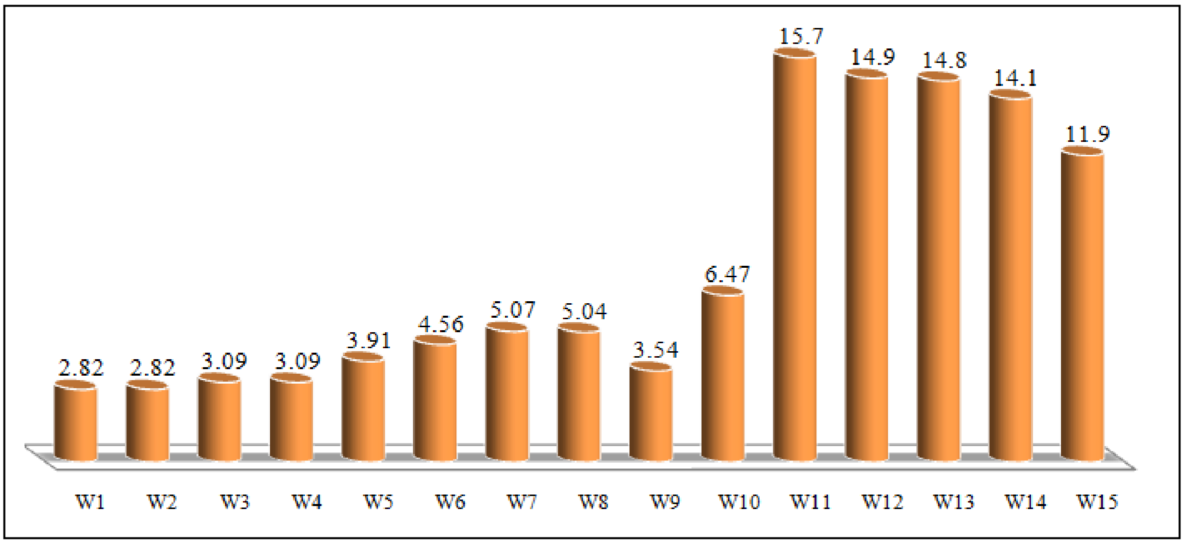

Figure 3 : Electric Conductivity (mmhos cm^{-1}) for selected sites in field

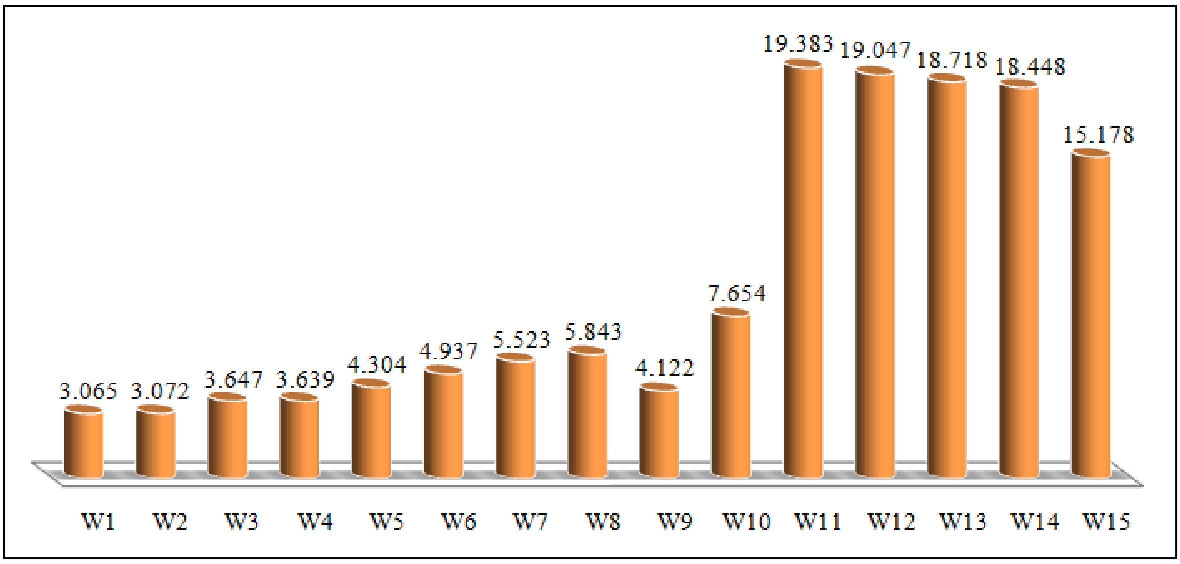

Figure 4 : Electric Conductivity (mmhos cm^{-1}) for selected sites at 25 ºC

The total dissolved Solid (TDS) was measured in the filed and showed at extent (1806 - 9749 mg/l).This results are higher than the allowed limits of drinking water (<1000) [13,16]. Uses of this water can be described[17] as shown in the table 2 and the of type water selected [20] for this study is shown in table 3.

Table 2. Classification uses of water samples

No.	TDS class	Number of samples within class	Water uses
1-	< 500	-	D
2-	501-1000	-	D + I
3-	1001-1500	-	I
4-	1501-2000	4	I
5-	>2000	11	I

D : Drink water *I: Irrigation water*

Table 3. Classification of Water samples depending on TDS

No.	TDS class mg/l	Number of samples within class	Water type
1-	< 1000	-	Fresh water
2-	1000 - 3000	7	Slightly brackish water
3-	3000-10000	8	Brackish water
4-	10000-35000	-	Saline water
5-	>35000	-	Brine Water

Selenium (IV) and total selenium were measured for all samples by spectral method in ultraviolet region from electromagnetic radiation [2,3,12] . All results are given in table 4 and fig.5 . Selenite was measured for all the samples and showed at extent (12.22 – 36.00 µg/l) . By comparing the results of the sites on Euphrates river an increase in the concentration of selenite in W_2 zone was noted as compared with W_1 zone because this area undergoes anthropogenic activities due to released wastewater to river without treatment [9] , while, W_1 zone undergoes agricultural activities [9,21]. The sites along Shatt Al-Arab from site W_3 to site W_{10} were measured . By comparing the results the highest value was noted in site W_3 because this area undergoes industrial activities [11,21] ,thereafter , it was noted a decrease in concentration of selenite to site W_5 because this area has no industrial and anthropogenic activities . Also an increase in selenite concentration was noted from site W_5 towards W_7 because the agricultural, industrial and anthropogenic activities in addition to river navigation are present in this region [21,12]. Also the concentration of selenite was recorded in site W_8 at 29.30 µg/l because this region undergoes river navigation continuously because of the presence of the commercial port of Abu Flus and the concentration increase of selenite may be due to river navigation and the loading and unloading operations of commercial loads inside the port [12] . Later a decrease in the concentration of selenite wes noted from site W_8 towards site W_{10} . Also the concentration value of selenite recorded a decrease from site W_{11} towards site W_{15} because of the decrease of tide phenomenon influence in this regions from station W_{11} towards W_{15} and there is another reason which is station W_{11} is nearby processes of natural gas burning which accompanies extraction operations of oil and gas[9,22] . This effect was decreased from station W_{11} towards station W_{15} . The most important sources of selenium pollution of surface water are weathering of rocks, combustion of coal and oil , movement of wind, irrigation and drainage operations, wastewater and industrial waste. All these processes cause the ecosystem pollution of selenium [9,11,12,21,22].

Table 4: Concentration of Selenite and total Selenium of stations selected from surface water samples

No. of samples	Mean(n=3) of Conc. of selenite µg/l	Standard Deviation (SD)	Mean(n=3) of Conc. of total selenium µg/l	Standard Deviation (SD)
W_1	28.62241	0.173119	51.74828	0.289165
W_2	31.64828	0.23918	49.66207	0.477617
W_3	36.0069	0.056668	42.29483	0.065894
W_4	30.01724	0.107682	49.52931	0.146665
W_5	12.22414	0.17	17.38103	0.194396
W_6	25.66724	0.281879	27.25517	0.330288
W_7	33.94655	0.123546	41.55862	0.172178
W_8	29.3069	0.054541	54.41379	0.125856
W_9	18.53793	0.085871	45.63621	0.143348
W_{10}	15.80172	0.042941	41.13793	0.304183
W_{11}	18.71379	0.241644	41.94483	0.14275
W_{12}	18.18793	0.013014	33.26207	0.110509
W_{13}	16.22241	0.0777	40.5931	0.093664
W_{14}	13.12759	0.126135	37.58621	0.300951
W_{15}	12.53966	0.289165	26.20345	0.073961
WHO 2011	-	-	40	-
CGL 2014	-	-	50	-
EC 1998	-	-	10	-
IQS 2001	-	-	10	-

Total selenium of all the samples was measured after a digestion process as described in the above procedure . The results are shown in table 4 and fig. 5 . Concentrations of total selenium were showed at range (17.38-54.41 µg/l). However , the highest value of concentration of total selenium was recorded in station W_8 . That may be due to river navigation in Abu Flus port. This reason is consistent with previous studies[12] . On the other hand , the lowest value of total selenium concentration was recorded in station W_5 because this region has no anthropogenic activities as the release of wastewater without treatment towards river or navigation of river . The highest value of concentration of total selenium may be attributed to agricultural activities such as in W_1 station because some selenium compounds are added to the phosphate fertilizers about 400 mg /ton after that , selenium is transmitted towards river through irrigation and drainage operations [9,12,21,23] , or may be attributed to anthropogenic and industrial activities and river navigation , therefore we have noticed difference in the concentration of total selenium between stations because of the effect of the contrast between these parameters . Also we noted gradual decreased in value of total selenium concentration from station W_{11} towards station W_{15} because of the decreased effect of tide from site W_{11} towards site W_{15} .The impact of processes to burning natural gas which accompanies extraction operations of oil and gas was decreased on surface water from station W_{11} towards station W_{15} [21-23] . The results of total selenium concentration for all samples the higher of acceptable limits of EC 1998 and IQS2001 . but these concentrations of all samples within acceptable limits for CGL 2014 except concentration for station $W_1$and W_8 , while some samples has been within acceptable limits for WHO 2011 and other samples were highest from acceptable limits of WHO 2011.

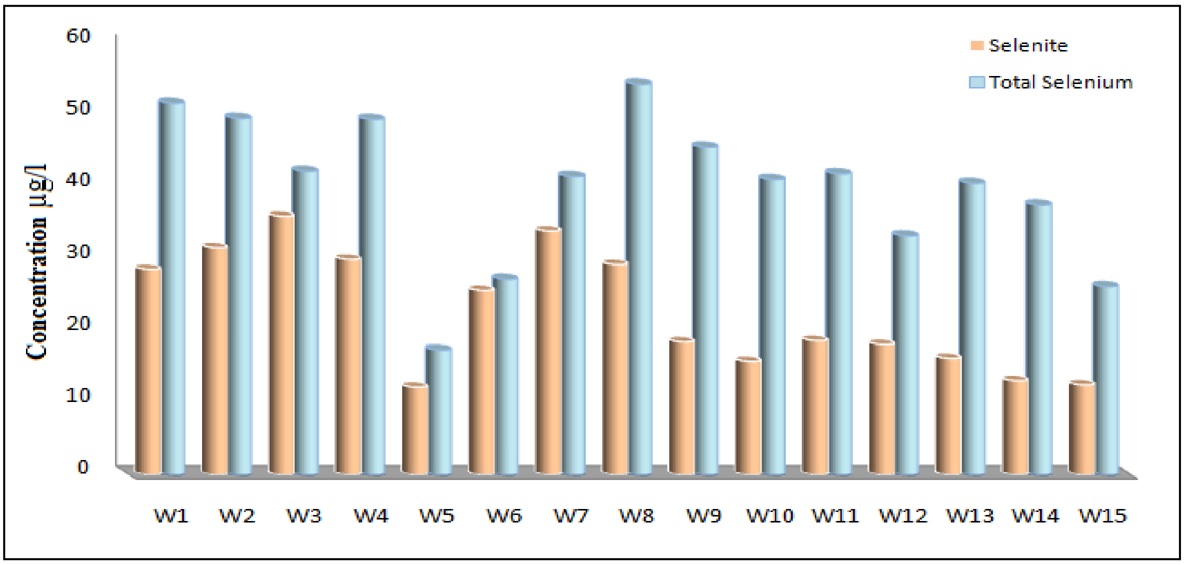

Figure 5 : The concentration of Selenite and total selenium µg/l

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