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RESEARCH ARTICLE

Evaluation of Selenium and Iron Levels in Shatt Al-Arab Sediment and the Iraqi Marine Environment

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ABSTRACT

Sixteen Samples of sediment were collected from Shatt Al-Arab river and the Iraqi marine environment in southern of Iraq.The samples were distributed one station on Euphrates river before its confluence with Tigris river, seven stations along Shatt Al-Arab river and eight stations selected from the Iraqi Marine environment.All samples were collected from surface sediment at different waters Column in low tide time. Selenium was measured by Spectrophotometric method through using 4-Methyl-o- phenylene diamine as complex agent in acidic medium (pH= 1.5). The Iron was measured by Spectrophotometric method also by using complex formation with Potassium thiocynat.The results of the total selenium measurement and total iron showed the values at extent (1.928-13.818 µg/g) , (2298.418 -4238.702 µg/g) respectively in Shatt Al-Arab sediment , while total Selenium and total iron in the marine sediment was recorded at range (1.044-11.449 µg/g) ,(1822.789-3996.228 µg/g) respectively . Standard deviation for all the stations (n=3) of Selenium and Iron was calculated and showed at extent (0.00160- 0.03032) , (0.25225-4.69526) respectively .

Keywords : Spectrophotometric method , Total Selenium , Total Iron.

INTRODUCTION

Selenium exists in trace amounts in most crustal materials of earth , the concentration of total selenium in most soil lies within the range of 0.01 - 2 µg Se /g [Mayland et al.,1989 , EPA, 1976] , but it´s concentration rarely exceeds

500µg/g[UNEP, 1988] .The selenium is found in nature in several states of oxidation and some of its chemical forms are volatile and has the four states from oxidation which are elemental selenium (0), selenide (II), selenite (IV) and selenate (VI) [Bao et al., 2012, Abdulnabi et al., 2015] . The chemical forms of Selenium present in soils and sediments are closely related to the oxidation-reduction potential and depend on pH in sediment and soil and the role of microorganisms[Gonzalez et al.,2006 , Oldfield ,1972] . Selenide (II) can be aerobically oxidised to selenium (0) and selenite (IV) at the pH of sea water can be oxidised to selenate (VI) , but in biological systems selenite can also be reduced by thiol groups to selenide to form a selenotrisulphide complex. Selenium-protein binding can occur, as in the synthesis of seleno-amino acids from inorganic selenium and their subsequent incorporation into peptide chains. This process is biologically mediated, involving carbon-selenium bonding[EPA, 1976]. Selenium in soil and sediment binds with Fe_2O_3 in clay minerals and organic material and the binding strength increases as the pH decreases [Oldfield ,1972]. The most of sources selenium in soil was divided to natural source such as volcanic eruptions , movement of wind , rain water and weathering of rocks and industrial sources such as stations of generation of electric power and combustion of coal and oil [Schneider et al.,2015, Staicu et al.,2015, Bauer ,1997] , these parameters released volatile selenium which is subsequently deposited over the surface of the earth[UNEP, 1988, Eisler, 1985] and thus it´s transformed to an aquatic system via several operations and reaches to sediment by deposition operation through biochemical cycles [EPA, 1976, Porcella et al., 1991]. Sedimentary rocks usually contain concentrations of selenium much higher than the earth's . The selenium content sometimes reaches 0.5 mg/g in limonite rocks, 2.6 mg/g in vanadium-uranium rocks[Deepa and Lingappa ,2014 , Bem ,1981] while the concentration of selenium in sandstones are shows at range 0.05-1.12 µg/g ,0.0-30 µg/g for carbonate rocks[UNEP, 1988] and contains at extent 1-100 µg/g in phosphorites rocks [Mayland et al.,1989] and the ratio between the selenium to sulfur in igneous rocks are 1:6000 [UNEP, 1988] . Iron metal is the fourth most abundant between the elements and second most abundant metal in the Earth’s crust after aluminium. It has the two states from oxidation in natural , ferrous ion (Fe^{+2}) and ferric ion (Fe^{+3}) . It is one of the seven metals known in antiquity along with gold, silver, copper, mercury, tin and lead . It has both properties lithophile and chalcophile. Iron exist in several common minerals such as pyrite FeS_2, magnetite Fe_3O_4, haematite Fe_2O_3 and siderite $FeCO_3$. It is also found in many rock-forming minerals such as mica , garnet , amphibole , pyroxene and olivine . The abundance of iron in sedimentary rocks is determined by various factors such as provenance and pH conditions[EPA ,1994 , James ,1966]. Iron rich sedimentary rocks contain 15% or more from iron. However, most sedimentary rocks contain iron in varying degrees such as sedimentary ironstone , where the dominant iron minerals are siderite, ankerite or oxides of the goethite-limonite type , may contain >30% Fe_2O_3. Typical levels of iron in sedimentary rocks are given as described: limestone 0.33% ; sandstone 0.98% , shale 4.7%, and banded iron formation 28% [James ,1966 , EPA ,2003]. This study focuses on two important elements in sediment which are selenium and iron because they are essential nutrients that enter in the food chain of animals and humans[Abdulnabi et al., 2015]. In addition to that selenium is related with iron in differental sediments it depends on pH value . Therefore by knowing the concentrations and distribution of metals in sediments the sources contaminants in aquatic system can be known . Furthermore , many studies worldwide used the sediment of rivers, estuaries and seas as indicators for pollution by trace metals[Al-Khuzaie ,2015 , Benzer et al.,2013].

Experimental Part

Site Selection

Sixteen stations of sediment samples were Selected from sediment rivers and marine sediment in southern of Iraq . The stations were distributed as one station(S_1) on Euphrates river before its confluence with Tigris river and Shatt Al-Arab river formation. Seven stations (S_2 - S_8) were selected along Shatt Al-Arab river from north of Basra city to south of it .These areas are important as they involve many activities such as population, agriculture, industry and commerce [Abdulnabi et al., 2015]. Eight stations (S_9 - S_{16}) were selected from the Iraqi marine environment , they are distributed in three sites(S_9 - S_{11}) in the iraqi marine region from southern Fao city towards Khor Abdullah and five stations (S_{12} – S_{16}) from nearby region of Um Qasr port towards Khor alZubair port in the nearby region from confluence with Basra canal . This area is important in marine navigation for large number and different loads of Ships pass through it to Arabian gulf. All samples were collected in winter season, December in 2014 and spring season,March in 2015 , in different regions from surface sediment in low tide and kept in plastic bags [Al-Saad et al. ,2007] undercooling and then transferred to laboratory for carry out different operations . Fig.(1) are shown below describing the selected sites .

MATERIAL AND CHEMICALS

Nitric acid (65%), Sulfuric acid(97%) and Hydrochloric acid (37%) were obtained from Scharlau .Selenium dioxid (Purity99.8%) and KSCN were supplied by Sigma-Aldrich . Perchloric acid(70%) and Hydrofluoric acid (40%) were supplied by Himedia . Haxan was purchased from J.T.Baker , Ferric Sulfate was obtained from BDH , 4-MOPDA was supplied by Merck and EDTANa$_2$ was obtained from G.C.C . Deionized water was used for the preparation of all solutions.

Instrumentation

Different complex agents were used for the determination of selenium and Iron through complex formation in optimal conditions ,selenium was measured in acidic medium at 332nm through using MOPDA,while the Iron was measured through using the potassium thiocyanate at 462 nm , all spectral measurements through using UV-Vis spectrophotometer double- beam from type (Shimadzu 1800 PC , Japan) with 1.0 cm quartz cell . Magnetic stirrer was used to mix all samples . Thermometer was used for adjust solution temperature. Grab sampler were used for collecting all samples from surface sediment.

Procedure

Digestion of sample

All the samples of sediment were collected from various regions of the river sites and marine sites in Basra city . These samples were preserved in cooling , after that , all samples left to dry at room temperature and then grinded and sieved through a 63 μm screen to obtain homogeneous particles [Al-Saad et al. ,2007] . Digestion operation carried out for all samples with various acids through weight less then 1g from sieved samples in beaker teflon and then 9ml of concentrated nitric acid was added with 1ml from hydrochloric acid (1N) and allow for the solution stand overnight at room temperature , after that all samples were digested as in the method described in methods of soil analysis [Sparks et al. ,1996] .

Determined of Selenium in the samples

Total selenium was measured through complex formation between 4-Methyl-o-phenylene diamine as complex agent with selenite (Se^{+4}) through taking 25 ml from digestion solution and then adding an amount of disodium ethylene diamine tetra acetic acid and Potassium thiocyanate , they are used as for eliminating interferences for different ions such as (Fe^{+3} , Cd^{+2} , Cu^{+2}) with measurement of Selenium . After that, the same procedure previously described was carried out for the analysis Selenium (IV) [Abdulnabi et al., 2015] . All the results for determining total selenium are shown in table 1 and figure 2 .

Determined of Iron in the samples

Spectrophotometric method for the determination of Iron as ferric ion in solution in acidic medium was used through complex formation , reddish brown color was obtained with potassium thiocyanate [Jeffery et al. ,1989 , Janardhan et al., 2014] . This procedure is rapid and easy and include preparation of standard solution of Iron (1000 ppm) , from this solution serial dilutions were made to obtain different concentration levels of (1 ,5 ,10 ,20 ,30 ,40, 50 ,60 , 70 ,80 ,90

,100 ppm) from ferric Ion , after that , 5ml from standard solution and adding 0.1ml potassium thiocyanate (0.05M) for this solution then the Iron was measured directly at 462nm and made standard curve according for Beer law . This step was repeated on samples through 5ml from digestion solution for sample and 0.1ml of potassium thiocyanate was added and measured at 462nm [Janardhan et al., 2014] . Furthermore , the blank solution was used in order to obtain high accuracy of results . All the results for the determination of total Iron are shown in table 1 and figure 1.

RESULTS AND DISCUSSION

Iron for all samples were measured by spectrophotometric method at 462nm[Janardhan et al., 2014] . The results are shown in figure (1) and table (1) for Iron measurement. Station (S_3) showed the highest value when compared with all the sites measurements while the highest value of marine sediment was recorded at station (S_{14}). The data of Iron measurement were compared in all the stations of Shatt Al-Arab river , the data recorded the highest value in station (S_3) and the lowest value in station (S_6) because the Hartha region (S_3) has not undergone dredging operations and also it contains the generating station for electrical energy , while the regions of stations (S_6) and (S_7) have undergone continuous dredging works because they are regions of commercial port and furthermore the Seba site (S_7) is an important region between Iraq and Iran as a navigation line. Also noted the high value was recorded in station (S_5) because this region contains different immersed iron bodies and has undergone drainage water and waste water release without treatment , while the highest value in the Qurna Station (S_1) was recorded compared with some other stations on Shatt Al-Arab river because the Iron concentration in sediment depends on the type and nature of sediment whether it's sand sediment or clay sediment or silt sediment [EPA , 2003] and also depends on different activities as the anthropogenic, agriculture and industry [Al-Khuzaie ,2015, Al-Saad et al. ,2007] . In order to compared the results of Iron concentration between the marine sediment stations under study , the high value of total Iron concentration was recorded in station (S_{14}) while the lowest value was recorded in station (S_{13}) . Also a gradual increase in the value of total Iron concentration was noted from station (S_9) towards (S_{11}) and then it decreased in stations (S_{12}) and (S_{13}) . Furthermore the concentration value of Iron was noted increasing from station (S_{15}) towards (S_{16}) because station (S_{15}) has undergone dredging operations because of its location as commercial port and an important oil port . Station (S_{16}) is the confluence region between the basra canal and Khor al-Zubair port , the Shatt al-Basra canal is a drainage channel, where to the wastewater and industrial waste are released into canal without treatment and this explains the increase of iron concentration at this station in comparison with (S_{15}) site . The results of Iron analyses in this study has recorded the lowest values when compared with the recorded data in previous studies[Mahmood ,2008 , Hassan ,2007] for some of the stations studied here , while it is consistent with the data recorded in other studies [Alshmery ,2013].The levels of Iron is exist the most abundant in earth's crust and exists more in sediment , especially in clay sediment [EPA ,2003]. On the other hand , the iron levels in sediment depend on multi operations occurring in aquatic system such as adsorption and ion exchange on outer surfaces for some particles of clay and organic material , they also depend on deposition of some elements in sediment through operations of weathering rocks , most of the heavy metals existed within the crystal lattice of the sediment particles [Mahmood ,2008] . Furthermore the increase of the concentration levels of Iron in the sediment, might be attributed to anthropogenic sources such as domestic wastes , industrial wastes and petroleum refinery operations . All these activities were released to the aquatic system without treatments [Al-Khuzaie , 2015 , Al-Saad et al. ,2007] .

Total selenium for all the samples was measured by spectrophotometric method at 332nm by using complex agent in acidic medium . The results are shown in table1 and figure2. This data records the highest value in station (S_2) when compared with the results of all the rest sites. Results of selenium was compared for all sites along Shatt Al-Arab river from Qurna (S_1) towards Fao station (S_8) ,the measurement showed high value in station (S_1) when compared with all the other stations except for (S_2) site because the qurna station undergoes different anthropogenic activities such as agriculture , domestic wastes and river navigation . This activities increase the selenium concentration in the aquatic system [Abdulnabi et al., 2015, Staicu et al., 2015] . After that selenium was converted to Selenium metal through biochemical pathways and deposited in sediment, these stages are called biogeochemical cycle for Selenium

[Porcella et al., 1991] . Similarly the concentration value of selenium increased from station (S_1) to station (S_2). After that the concentration of selenium decreased from station (S_2) towards station (S_6) because , in station (S_2) this region has not undergone dredging works but was subjected to various pollutants such as wastewater release and industrial waste to river without treatment [Abdulnabi et al., 2015] . Additionally , the region was affected by agricultural activities and burning natural gas processes which usually accompany extraction operations of oil and gas . All these processes cause the ecosystem pollution of selenium [Schneider et al., 2015, Staicu et al., 2015] . Moreover the concentration of selenium was increased in station (S_7) and (S_8) when compared with sites (S_4-S_6) . The results of the selenium concentration were compared for all the marine stations(S_9-S_{16}) . The data has shown gradual increase of selenium concentration from station (S_8) towards (S_{11}) site and recording the highest value at station (S_{11}) in marine stations that might be attributed to marine navigation [Abdulnabi et al., 2015] or its depend on the type and nature components of the sediment . After then the concentration of selenium was decreased from station (S_{11}) towards (S_{14}) and the station (S_{13}) recorded lowest value in the concentration of selenium in marine stations . The frequent Increase in the concentration of selenium was noted in station (S_{15}) because this area undergoes the loading and unloading operations of commercial loads and oil loads inside the Khor Al-Zubair port , while station (S_{16}) recorded low concentration of selenium when compared with station (S_{15}) and high value compared from station (S_{12}) to station (S_{14}) . The most important sources of selenium pollution of aquatic system 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 [Abdulnabi et al., 2015, Schneider et al., 2015, Staicu et al., 2015] .

REFERENCES

1. Mayland,H.F.,James,L.F.Panter,K.E. and Sonderegger,J.L. , Selenium in seleniferous Environments . Soil Science Society of America and American Society of Agronomy , SSSA Special Publication no. 23. , pp.15-50 , 1989 .
2. EPA (Environmental Protection Agency) . Selenium .Office of research and development . Health effects research laboratory . EPA-600/1-76-014 , 1976 .
3. UNEP (United Nations Environment Programme) . Arsenic, mercury and selenium in the marine environment**.** UNEP Regional Seas Reports and Studies No. 92 , 1988 .
4. Bao,P. , Huang,H. , Hu,Z.-Y. , Haggblom,M.M. and Zhu,Y.-G., Impact of temperature, CO_2 fixation and nitrate reducation on selenium reducation, by a paddy soil clostridium strain. Journal of Applied Microbiology . Vol.114 , pp.703-712, 2012 .
5. Abdulnabi,Z.A. , Hassan,W.F. , Al-Khuzaie,D.K.K., Saleh,S.M. and Hashim,M.G. , Evaluation of selenium levels for the water surfaces in southern of Iraq . Journal of Chemical and Pharmaceutical Research. Vol. 7, No.10, pp.495-501, 2015.
6. Gonzalez, R.C.- , Simunek, J. , Sauve,S. and Adriano, D. , Mechanisms and pathways of trace element mobility in soils . Advances in Agronomy.Elsevier .Vol. 91, pp.111-177 , 2006.
7. Oldfield,J. E. , Selenium Deficiency in Soils and Its Effect on Animal Health . Geological Society of America Bulletin . Vol. 83 , pp. 173-180 , 1972 .
8. Schneider, L. ,Maher, W.A. ,Potts, J.Taylor, A.M.,Batley, G.E. , Krikowa, F. ,Chariton, A.A. and Gruber, B., Modeling food web structure and Selenium biomagnification in lake Macquarie ,new south wales ,Australia , usingstable carbon andnitrogen isotopes Environmental Toxicology and Chemistry. Vol.34 , No.3 ,pp.608-617,2015.
9. Staicu,L.C. , Hullebusch,E.D.V. , Oturan,M.A. , Ackerson,C.J. and Lens,P.N.L. , Removal of colloidal biogenic Selenium from wastewater .Chemosphere.Vol. 125 , pp. 130-138 , 2015.
10. Bauer, F,Selenium and Soils in the Western United States.Electronic Green Journal .Vol.1, No. 7 , Article 3 , 1997
11. Eisler, R. , Selenium hazards to fish, wildlife and invertebrates: a synoptic review . U.S. Fish and Wildlife Service Biological Report 85 (1.5). 1985.
12. Porcella,D. B. , Bowie,G.L. , Sanders,J.G. and Cutter,G.A., Assesing Se Cycling and toxicity in aquatic ecosystems .Water, Air and Soil Pollution.Vol.57-58, No.1, pp. 3-11, 1991.

13. Deepa,K. and Lingappa,Y. , Spectrophotometric determination of selenium in industrial and environmental samples using vanillin-2-aminonicotinic acid (VANA) . Der Pharma Chemica . Vol.6 , No.1, pp.52-60 , 2014 .
14. Bem,E. M. , Determination of Selenium in the Environment and in Biological Material . Environmental Health Perspectives .Vol. 37, pp. 183-200, 1981.
15. EPA (Environmental Protection Agency) . Technical resource document , extraction and beneficiation of ores and minerals , Volume 3, Iron . Office of Solid Waste Special Waste Branch . EPA 530-R-94-030 , 1994 .
16. James,H.L. , Data of Geochemistry . Chemistry of the Iron-rich Sedimentary Rocks , Chapter W. , 6th ed , United States Government Printing Office, Washington , 1966 .
17. EPA (Environmental Protection Agency) . Ecological Soil Screening Level for Iron . Office of Solid Waste and Emergency Response , November 2003 .
18. Al-Khuzaie,D.K.K. , Assessment of sediment quality collected from shatt al-arab river, Basra, southern Iraq . Journal of international academic research for multidisciplinary . Vol.3, No. 6 , 2015 .
19. Benzer,S. , Arslan,H. , Uzel,N. , Gül,A. and Yılmaz,M. , Concentrations of metals in water, sediment and tissues of Cyprinus carpio L., 1758 from Mogan Lake (Turkey) . Iranian Journal of Fisheries Sciences . Vol.12, No.1, pp. 45-55 , 2013 .
20. Al-Saad,H.T., Al-Imarah,F.J. M., Saeed,M.A. R. , Distribution and levels of trace metals in the red sea coasts and comparison with their levels in the Arabian Gulf . MARINA MESOPOTAMICA . Vol.22 , No.1, pp.1-16 , 2007 .
21. Sparks,D.L. , Page,A. I. , Helmke,D.A. , Loeppert,R.H. , Soltanpour,P.N., Tabatabai,M.A. , Johnston,C.T. and Sumuer, M. E. , Method of soil analysis Part. 3. Chemical methods. Madison Wisconsin, U.S.A. 1996 .
22. Jeffery,G.H. , Bassett,J. , Mendham,J. and Denney,R.C. , Vogels , Text Book of Quantitative Chemical analysis . 5th ed , John wiley &Sons , Inc., New York , 1989 .
23. Janardhan,P. , Dhanalakshmi,R. and Ruby,J.J. , Study of invitro anti-oxidant activity of ipomea pes-caprae . Intercontinental Journal of Pharmaceutical Investigation and Research , Vol.1 , No.1 , pp. 25-31 , 2014 .
24. Mahmood,A. A. , Concentrations of pollutants in water , sediments and aquatic plants in some wetlands in south of Iraq. Ph.D.Thesis . University of Basrah . Iraq . 2008.
25. Hassan,W. F. **,** Geochemical and hydrochemical Study at Shatt Al-Arab Canal Sediments and Overlying Water . Ph.D.Thesis . University of Basrah . Iraq . 2007.
26. Alshmery,A.Y. H. , Estimation of some heavy metals in clams, sediments and water from Shatt Al-Arab and treatment rocks porcellanite .M.Sc.Thesis .University of Basrah. Iraq.2013.

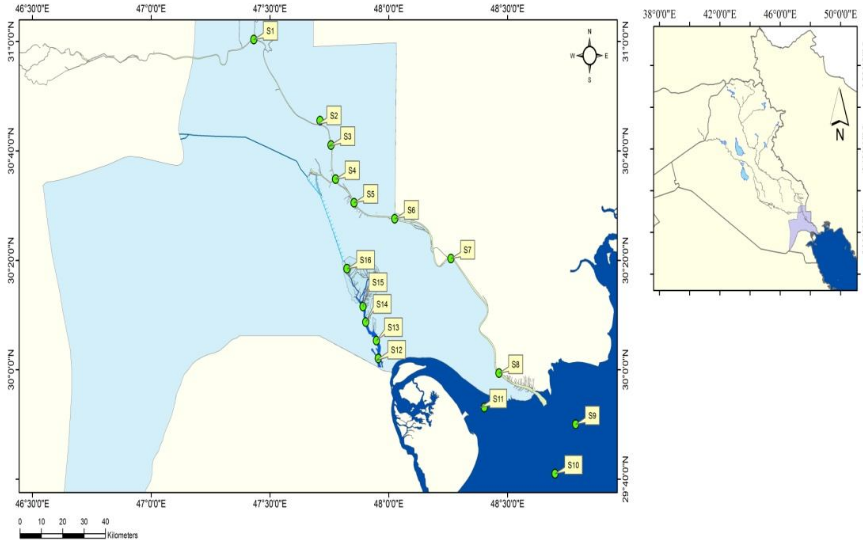

Fig 1 : Locations the sample selected in Southern of Iraq

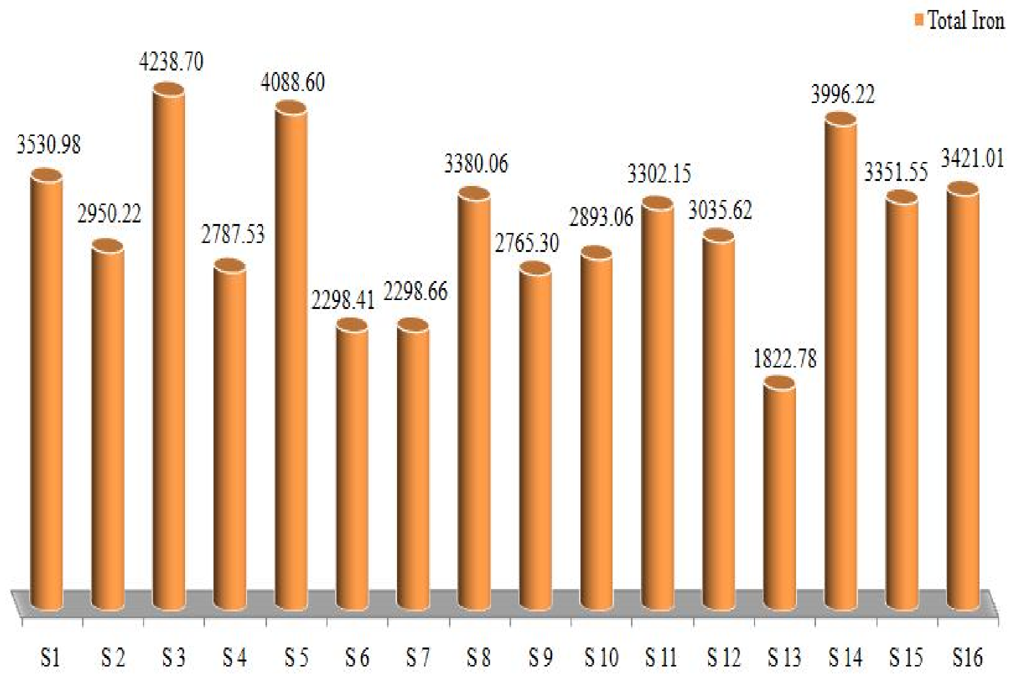

Fig. 2: Concentration of total Iron µg/g

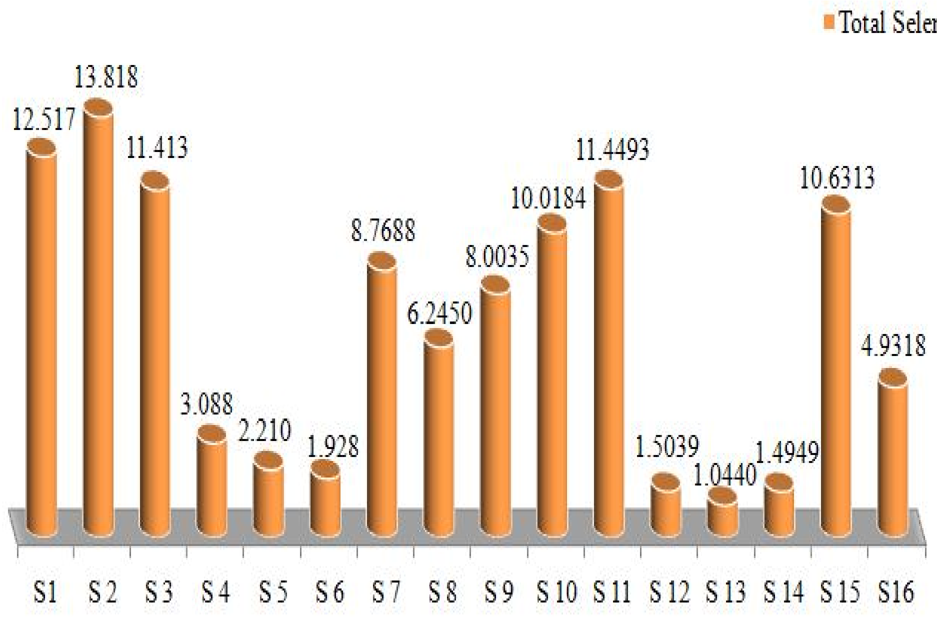

Fig. 3 : Concentration of total Selenium µg/g

Table 1: Concentration of total Selenium and total Iron of stations selected from surface sediment samples

No. of samples	Mean(n=3) of Conc. of Selenium µg/g	Standard Deviation (SD)	Mean(n=3) of Conc. of Iron µg/g	Standard Deviation (SD)
S_1	12.5171	0.01769	3530.9826	1.80851
S_2	13.8181	0.01508	2950.2284	0.25225
S_3	11.4135	0.03032	4238.7022	0.92949
S_4	3.08873	0.01763	2787.5308	4.36139
S_5	2.21071	0.01565	4088.6053	2.75607
S_6	1.92871	0.00368	2298.4189	0.68903
S_7	8.76880	0.01031	2298.6669	1.27416
S_8	6.24506	0.00771	3380.0613	2.34808
S_9	8.00352	0.01580	2765.3078	1.98205
S_{10}	10.0184	0.01669	2893.0633	2.07168
S_{11}	11.4493	0.02742	3302.1541	2.51323
S_{12}	1.50397	0.00675	3035.6283	4.69526
S_{13}	1.04407	0.00645	1822.7891	3.23124
S_{14}	1.49494	0.01923	3996.2288	2.73351
S_{15}	10.6313	0.00160	3351.5558	4.22377
S_{16}	4.93188	0.00697	3421.0106	4.18162