DETERMINATION OF HEAVY METALS CONTAMINATION IN HUMIC ACID EXTRACTED FROM RIVER SEDIMENTS OF VARYING DEPTH

Dhrubajit Borah*, Kaushik Sarmah, Biva Rani Saikia, Bondita Hazarika
* N. N. S. college. Titabor, 785630

DOI: 10.5281/zenodo.162152

KEYWORDS: Heavy metals, Humic acid, E4/ E6 ratio, Kakodonga river, Atomic absorption spectroscopy.

ABSTRACT

In this work humic acids were extracted from surface, below 15 cm and 30 cm depth of Kakodonga river sediments. The acids were investigated by UV-Vis spectroscopy and the heavy metal contents are determined by atomic absorption spectroscopy (AAS).Moreover, E4/ E6 ratio is determined. Our studies reveal that E4/ E6 ratio decreases from 30cm depth soil to surface which indicates that humic acid, at surface contains more aromatic groups compared to other two samples. In addition to that we found that copper (Cu) presents in the soil of river sediment is higher than other metals which can be attributed to association of Cu in process of formation of Humic acid.

INTRODUCTION

A typical humic substance is a mixture of many molecules, some of which are based on a motif of aromatic nuclei with phenolic and carboxylic substituents, linked together. The functional groups that contribute most to surface charge and reactivity of humic substances are phenolic and carboxylic groups.[1] Humic acids behave as mixtures of dibasic acids, with a Pk_1 value around 4 for protonation of carboxyl groups and around 8 for protonation of phenolate groups. There is considerable overall similarity among individual humic acids.[5] For this reason, measured pK values for a given sample are average values relating to the constituent species. The other important characteristic is charge density. The molecules may form a supramolecular structure held together by non-covalent forces, such as van der waal forces, π-π, and CH-π bonds.[6]

The presence of carboxylate and phenolate groups gives the humic acids the ability to form complexes with ions such as Mg^{2+}, Ca^{2+}, Fe^{2+} and Fe^{3+}. Many humic acids have two or more of these groups arranged so as to enable the formation of chelate complexes.[7] The formation of (chelate) complexes is an important aspect of the biological role of humic acids in regulating bioavailability of metal ions.[5]

Humic acids contain many functional groups which can effectively bind other substances and participate in ion – exchange reaction. There are many advantages of using HA as adsorbents such as development of soil structure, plant and microorganism growth simulation, increasing of water retention and soil fertility. Their application in soil remediation is actual and effective. (GIL –SOTRES et ai.1995). However, due to rapid increase of industrialisation , lead to production of huge industrial waste products containing poisonous heavy metals such as Pb, Cd, Hg and in general, these waste products are thrown to river which in turn create deleterious effect in the composition of river soil and water body. Therefore, research on heavy metal deposition and accumulation in the environment is the current attention of most environmental scientist throughout the world. These heavy metals can enter the food chain and produce a range of metabolical and physiological disorder. Metals like Hg, Cd and Pb are toxic even at minute concentration. Though metals like Fe, Zn and Mn are needed for the normal development of living beings, they can be detrimental above their threshold field. Metal released into aquatic environments bound to the particulate matter which in due course settle down and become part of the sediment. (Suthar et.al 2009). Thus, understanding of heavy metal accumulation in soil is an important requirement in environmental science.

Keeping it mind, in this work, We aim to determine the concentration of Pb, Cd, Hg , Cu and Cr present in humic acid of river sediment of different depth and characterise the humic acid with the help of U.V. –Vis spectroscopy . Moreover, we have also determined the ratio of E_4 and E_6 in order to evaluate the extent of humification of soil.

MATERIAL AND METHODS

Study Area

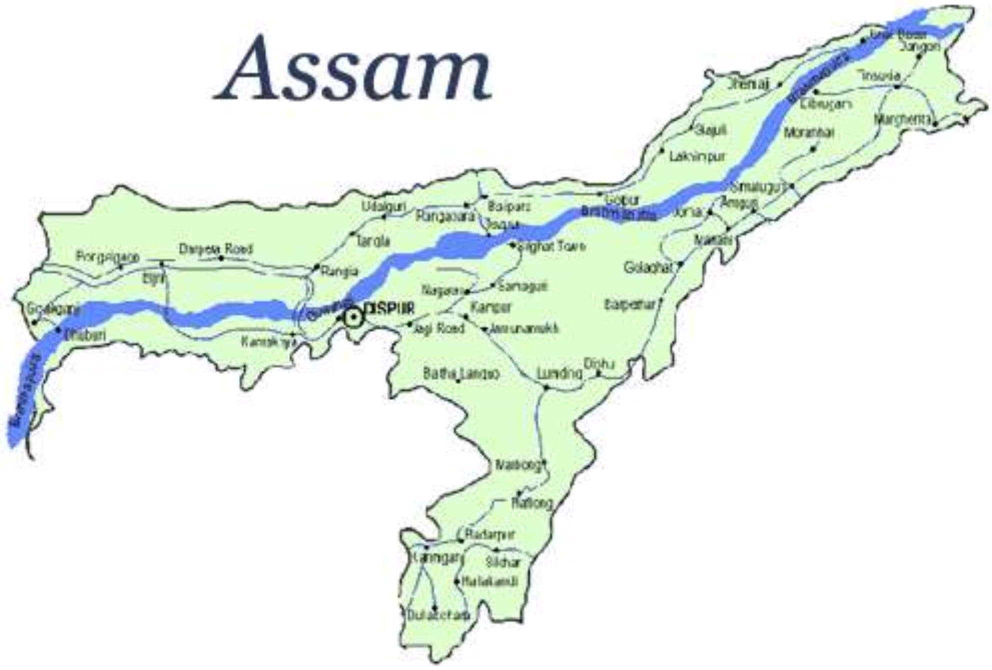


Fig-2

Soil samples were collected from the surface, below 15 cm and below 30 cm depth of the river Kakodonga situated in Titabar sub-division (Latitude:26º35'10''N; Longtitude: 94º9'35''E), Jorhat district, Assam (Fig. 2). The samples were dried in air. These were ground, sieved and then Stored in polythene bags.

Sampling procedure and preservation

Three soil samples are collected at a depth of 0, 15 and 30 cm from river Kakodunga. The collected samples were stored in polythene bags and transported to the laboratory. The samples were air dried for 5 days at room temperature, crushed in a porcelain motor and then sieved through a 2mm mesh prior to chemical analysis

Extraction of humic material from river sediment

100 g of each air dried soil sample was taken in 1000 ml beaker and to it 0.1 M 300 ml NaOH solution was added slowly with occasional stirring. The materials in the beaker were kept overnight at room temperature (28ºC). The supernatant liquid was siphoned out and collected in 1000 ml beaker. The alkaline extraction was repeated additionally two times and in those cases, the soluble humic material was also collected as before. The brown colour soluble humic material was then centrifuged to remove any clay material present. The process was repeated twice. The clear soluble humic material was stored in a plastic bag.

Precipitation of humic acid

The clear soluble brown humic material was transferred to a 1000 ml beaker. The solution was acidified by slowly adding 6M HCl until stable P^H 1.0 was attained. The whole materials were stirred well. After a brief period, precipitation occurred and it was kept overnight for complete precipitation. The precipitate almost settled down in the beaker and the supernatant clear was siphoned out. The precipitate was washed several times with distilled water till chloride ion gave negative test. The wet material was collected and then kept in a freeze. This wet brown material was humic acid.

For the precipitation of dry humic acid, wet organic matter was taken in a petre disk and it was kept in an electric oven. The temperature of the oven was maintained at 60^0 C and the organic matter was heated for two hours. The dry humic acid was ground in a morter and finally kept in a plastic bottle.

Analysis of Humic acid

Some important analysis was carried out to understand the nature and type of humic acids extracted from surface, below 5cm depth and 15 cm depth river soil samples. We have carried out moisture content of humic acid and for determination of ratio of E_4 and E_6, UV-Vis spectra was taken in our collage laboratory. Atomic absorption spectra were recorded for determination of metal concentration in Humic acid in Parkin Elmer Model "AAnalyst-300" Atomic absorption spectrophotometer using Graphite/Flame and FIAS techinique.

Absorption in the UV –Visible region

A humic acid sample 0 .1 mg was dissolved in 10 ml of 0.05 M $NaHCO_3$ solution adjusted to P^H 8.5 with 0.1 M NaOH to enhance solubility. The light brown colour Humic acid was transferred into quartz cell (200- 340 nm) and glass cell (350-800 nm) and the spectrum of absorbance vs wavelength is plotted.

Atomic absorption of spectra

Weigh out 0.75g of dry humic acid from each of the three samples. Add 9 ml of concentrated HNO_3 and 2 ml of $HClO_4$ to the content and heating the content in a hot plate till the solution becomes equal to the volume of 2ml. This solution is analysed in Tokolai Research Centre with the help of Parkin Elmer Model "AAnalyst-300" Atomic absorption spectrophotometer using Graphite/Flame and FIAS techniques.

RESULT AND DISCUSSION

In the spectra obtained in the U.V-VIS region for humic acids from surface soil, 15 cm and 30 c.m depth soil of river decrease in the absorption intensity with the increase of the wavelength have been observed. In the spectra, a minor shoulder is observed around 260 nm. The presence of this band can be attributed for the aromatic structure in the organic substrate.

Chen et al demonstrated that E4/E6 ratio is related to the molecular weight and the oxygen content of the humic substance; usually the E4/E6 ratio is expected to decrease with increasing molecular weight and content of condensed aromatic ring. Here, we have observed that E4/E6 ratio decreases from 30 c.m depth soil to surface. From it, we can conclude that humic acid at surface contains more aromatic groups than other two samples.

Moreover, E4/E6 ratio can also be used as humification index. In our study, the value of E4/E6 ratio is for humic acid extracted from surface soil, 15c.m depth soil are in the range of 3.53-4.38 while the ratio is much higher at 30 c.m depth. Typically, E4/E6 ratio is large for non humified material by the presence of proteins and carbohydrate, which increases absorptivity at the U.V region of the spectrum.[16]

TABLE- 1

	E4	E6	E4/E6
Surface	0.452	0.128	3.53
15 c.m	0.368	0.084	4.38
30 c.m	0.114	0.008	14.25

Atomic absorption of spectra

The metal concentrations obtained at the different sampling points are presented in Table 2. Analysis showed that the concentration of metal Copper(Cu) was found high in surface while other metals- lead(Pb), chromium(Cr), mercury(Hg) and cadmium(Cd) were it high concentration at 15 c.m depth. From the data depicted in table, it is clear that the concentration of the metals is relatively low at the surface as expected. The highest concentration in sediment sample was recorded for copper and the lowest for cadmium (Cd). The origin of the elements could be attributed to the geological environment surrounding the river and surrounding industrial facilities near the river. The metal concentrations in humic acid extracted from samples were sequenced as Cu>Cr>Pb>Hg>Cd.

The data shows that there is high concentration of Cu in the humic acid extracted from the river soil and this is due to association of Cu in the process of formation of humic acid. Copper shows high affinity to carboxylic groups that occur in the humic substances (Kinniburgh etal 1999 powell d tenton, 1996, wei etal, 2004. The relative stabilities of humic acid metal complexes [17] have been reported as Cu>Pb>Cd or Pb>Cu>Cd.
So, high concentration of Pb compared to Cd in the river sample can be attributed to better complexing abilities of Pb with humic acids compared to Cd.

The lower concentration of mercury in humic acid samples is probably due to formation of soluble complex in presence of humic acid which has relatively lower interaction at the sediment/ water interface and is more prone to spread through the aquatic environment.[18]

Cr and Cu from Kakodunga River presented concentrations greater than background values prescribed by the national oceanic and atmospheric administration. (In mg/kg Cd: 0.1-0.3, Cr: Pb: 7-13, Cu: 10-25) Other metals remained at levels compatible with NOAA. TEL/PEL criteria were used to access the health risk for aquatic life. Table shows total concentration of Cr in river sediments from Kakodunga river with values above TEL(52.3 mg/kg), while Cu is above both TEL and PEL(i.e. 18.7 and 108 mg/kg respectively as shown in Table- 3) as prescribed to aquatic environments. Within this range, occasionally adverse effects for aquatic life can be observed.

TABLE-2 Heavy metals (mg/Kg) in Humic acid samples

Element	Cd(mg/kg)	Cr(mg/kg)	Cu(mg/kg)	Pb(mg/kg)	Hg(mg/kg)
Surface	0.08	43.67	246.80	2.46	0.73
15 c.m	0.07	66.60	171.13	2.40	2.14
30 c.m	0.05	62.07	217.47	2.38	1.63

TABLE 3 TEL and PEL Value (mg/Kg) of Metals

METALS	Cd	Cr	Cu	Pb
TEL	0.68	52.3	18.7	30.2
PEL	4.21	160	108	112

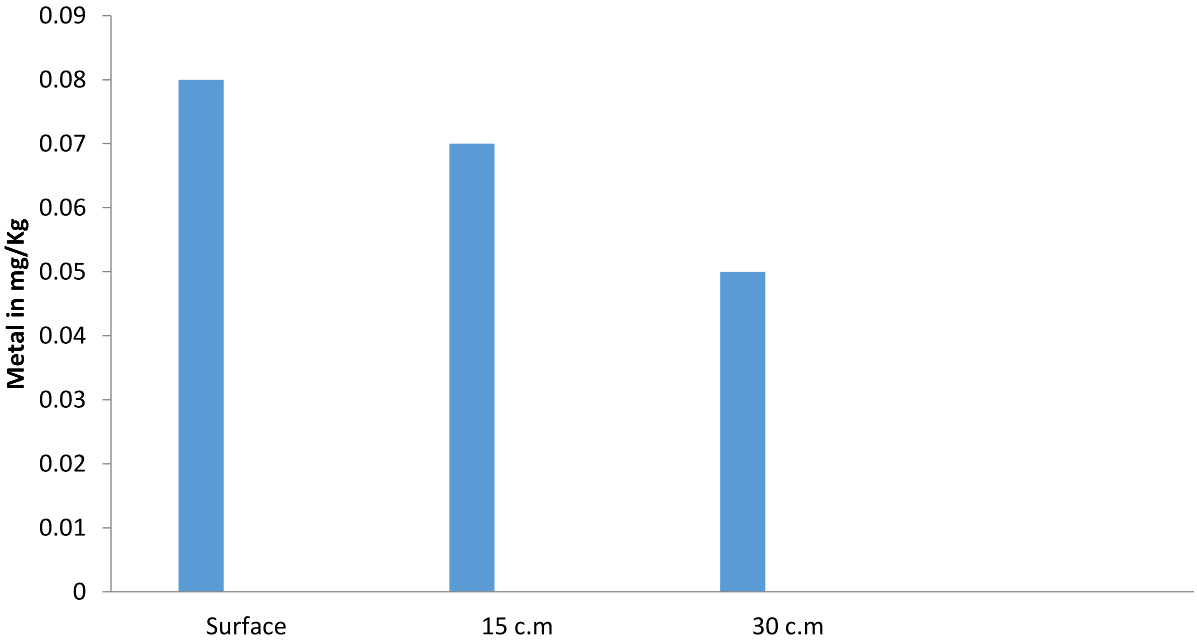


Fig:3 Cadmium(Cd)

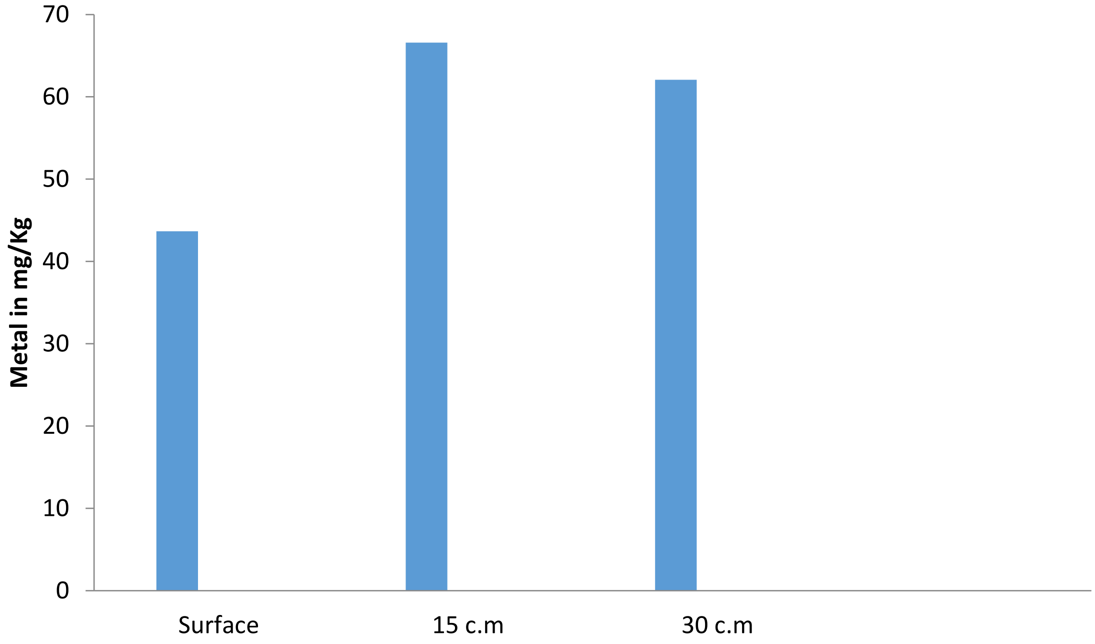
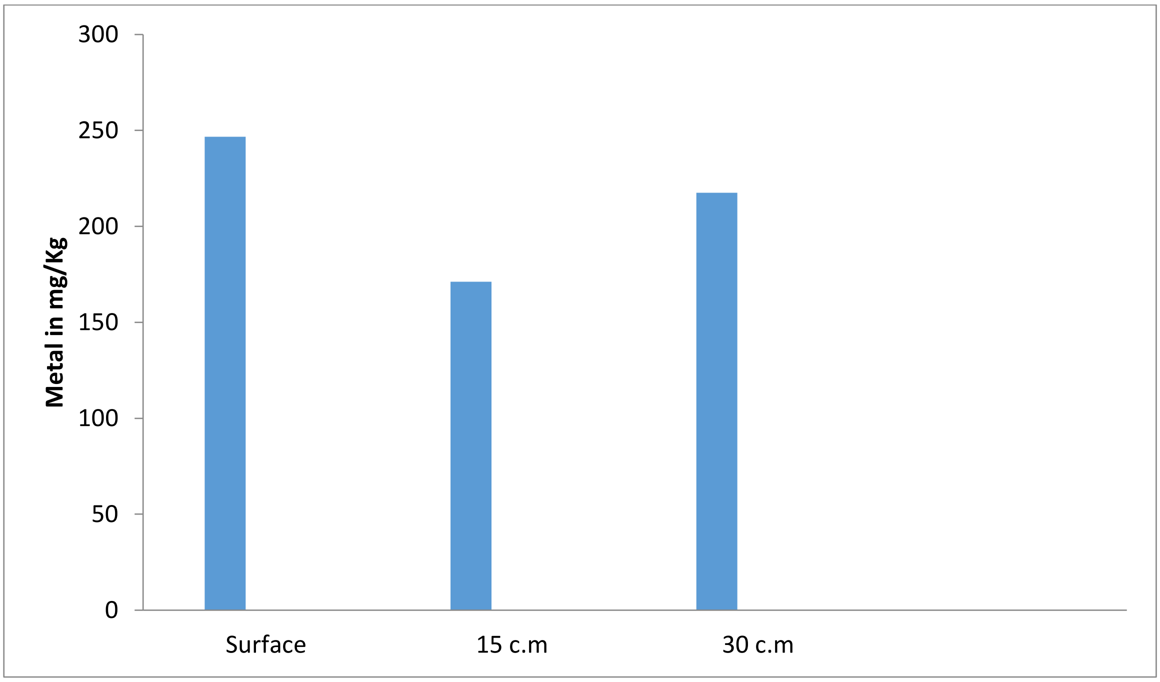


Fig:4 Chromium(Cr)



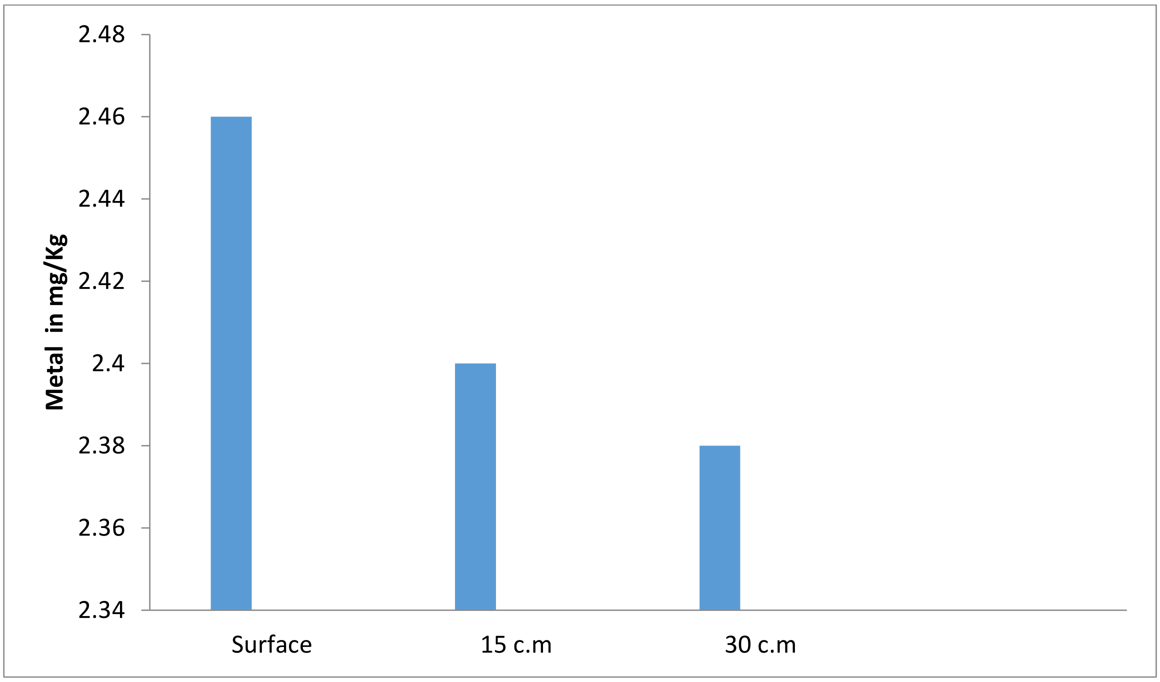


Fig6-Lead(Pb)

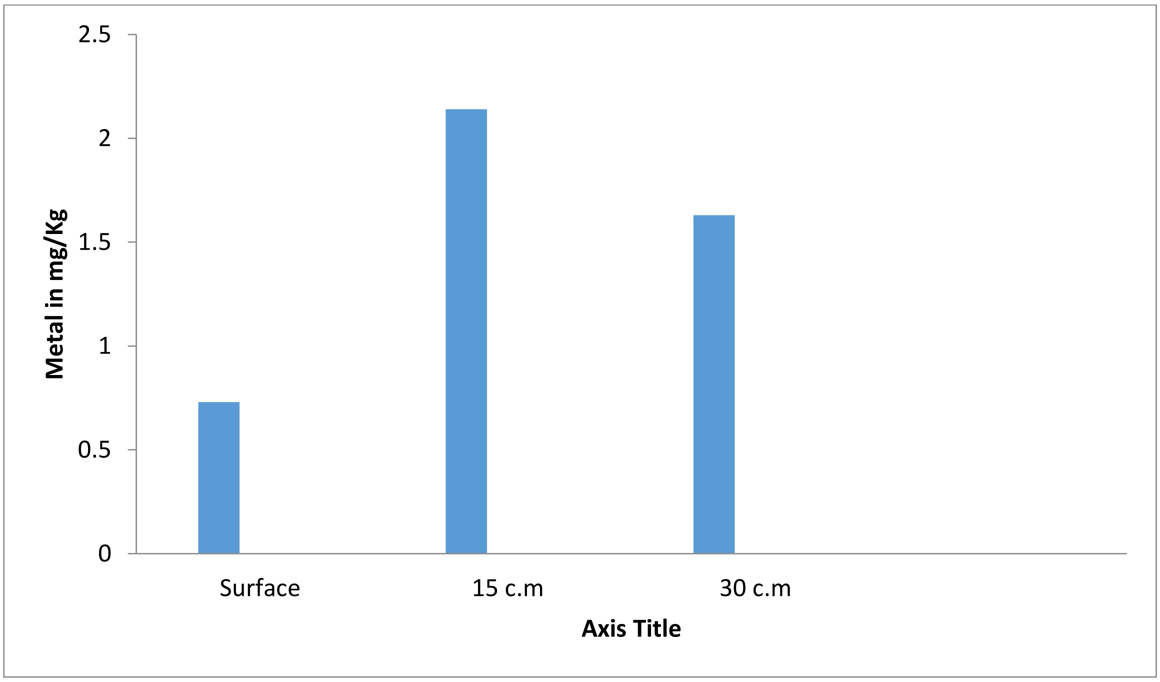


Fig 7-mercury (Hg):

CONCLUSION

From the studies of humic acid from different depth soils of river, significant results have been found which are given below.

[1] From our studies, we have observed that E_4/E_6 ratio decreases from 30 cm depth soil to surface which indicates that HA, at surface contains more aromatic groups compared to other two soil samples.

[2] Copper (Cu) presents in the soil samples is higher than other metals which shows association of Cu in process of formation of humic acid and it also reveal the fact that it has higher affinity to carboxylic group present in the humic substance.

[3] Total concentration of Chromium (Cr) in river sediment is higher than TEL value while Copper is above both TEL and PEL value.

REFERENCES

1. abc Stevenson F.J [1994]. Humus chemistry. Genesis, composition, reactions. New York: John Wiley & sons.
2. Yamauchi, Masashige; Katayama, Sadamu; Todoroki, Toshiharu; Watanable, Toshio [1984]. "Total synthesis of fulvic acid." Journal of the Chemical Society, Chemical communications [23]: 1565-6. Synthesis of fulvic acid was accomplished by a route involving selective ozonization of 9-propenylpyranobenzopyran obtained by a regioselective cyclisation of the 2-methyl 1,3-dione.
3. Baigorri R; Fuentes M; Gonzalez-Vila FJ. [2009]. "Complementary multianalytical approach to study the distinctive structural features of the main humicfractions in solution: Gray humic acid, Brown humic acid and fulvic acid." J Agric Food Chem. 57(8): 3266-72
4. Fiorentino G; Spaccini R; Piccolo A (2006). "Separation of molecular constituents from a humic acid by solid-phase extraction following a transesterification reaction. Talanta 68 (4): 1135-1142
5. a b Ghabbour, E.A; Davies, G (editors) (2001). Humic substances structures models and functions. Cambridge, U.K: RSC publishing.
6. Piccolo, A (2000). "The supramolecular structure of humic substances. A novel understanding of humus chemistry and implications in soil science." Advances in agronomy. Advances in Agronomy 75: 54-134
7. Tipping E (1994) "WHAM-a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete site/ electrostatic molel of ion-binding by humic substances." Computers and Geosciences 20 (6): 973-1023.
8. Oliver, Barry G. (1983). "Dihaloacetonitriles in drinking waters." Algae and fulvic acid as precursors." Environmental science & technology 17(2): 80
9. Peters, Ruud J.B; De Leer, Ed W.B; De Galan, Leo(1990). "Dihaloacetonitriles in Dutch drinking waters." Water Research 24 (6): 797.
10. Lapedes, Daniel N, ed. (1966). McGraw-Hill encyclopedia of science and technology. An international reference work, Volume 12. McGraw-Hill. P. 428. ISBN 0070452652. "The value of adding organic matter to the soil in the form of animal manures, green manures and crop residues for producing favorable soil tilth has been known since ancient times."
11. Pan American Union. Dept. Of cultural Affairs. Division de Fomento Cientifico, Pan American Union Dept. Of cultural Affairs, Organization of American states. Dept. Of scientific Affairs [1984]. Ciencia interamericana: volumes 24-27. "And since plants have shown their ability to absorb and translocate the complex molecules of systemic insecticides, they can no longer discredit the idea that plants are able to absorb the soluble humic nutrients, containing by far-"
12. Arancon, norman Q; Edwards, Clive. A; Lee, Stephen; Byrne, Robert. (2006). "Effects of humic acids from vermicomposts on plant growth." European Journal of soil biology 42: 565
13. Cooper, R J; Liu, Chunhua; Fisher, D .S. [1998]. "Influence of Humic Substances on Rooting and Nutrient. Content of Creeping Bentgrass." Crop Science 38 (6): 1639.
14. Liu, Chunhua; Cooper, R J. (August 1999). "Humic substances Their Influence on Creeping Bentgrass Growth and Stress Tolerance". TurfGrass Trends: 6.
15. Lucas, A; Harris, J.R. [1998]. Ancient Egyptian Materials and Industries. New York: Dover Publications. P. 49. ISBN 0-486-40446-3.
16. Viery. FEM, Palazzi VI, Sanchez de pinto MI, Borsareli CD.
17. Stevension, FJ- Stability constant of Cu, Pb and Cd complexes with humic acid, SoilSci. Soc Ar.J. 1976, 40, 665-671.
18. Melamed, R.; et al.: Mechanisms of physico-chemical interaction of mercury with river sediments from a gold mining region in Brazil: Relative mobility of mercury species. Journal of Geochemical Exploration, vol. 58, Issues 2-3, April 1997, p. 119-124