

Distribution and Occurrence of Humic Substances in Lake Edku, Egypt.

By

**El-Sayed Mohamed, A. ; Beltagy Ali, I. ; Aboul Naga Wafica, M. and
Halim Yossef ***

National Institute of Oceanography and Fisheries, Alexandria, Egypt

Abstract

Humic substances (HS) as humic and fulvic acids were determined in the surface sediments of lake Edku (Egypt). Their sources, distribution as humic and fulvic acids variability and behavior are assessed. The lake was geographically subdivided into eastern, central and western basins. The central basin showed the highest concentrations of HS which is attributed to intensive development of macrophytes and to enhanced phytoplankton primary production. In eastern basin, high turbidity and water turbulence downstream from the drains limit primary production, while in the western basin, water turbulence, sandy bottom, elevated salinity and decrease in nutrients due to mixing with seawater limit the growth of macrophytes as well as the phytoplankton productivity.

Introduction

Humic substances (HS) are the largest reservoir of organic carbon in the aquatic and terrestrial environments (Gjessing, 1976; Mantoura et al., 1978). The bulk of the organic matter in most soils, waters and sediments consist of humic substances (Schnitzer and Khan, 1972; Gjessing, 1976). Humic substances are the major component of the organic matter, they may constitute as high as 70% of the organic matter in lake sediment (Kemp, 1971). These fairly stable and extremely complex copolymers, have received a great deal of interest due to their active participation in the biogeochemical processes in the aquatic environment (Duursma, 1963; Nissenbaum and Kaplan, 1972; Prakash et al., 1973; Stumm and Brauner, 1975; Frimmel and Christman, 1988).

The origin of the HS is of great importance since it will determine their chemical composition and structural characteristics and both will define their fate and reactivity in the environment, for example vis-a-vis organic and metallic pollutants. According to Stevenson (1982) terrestrial humus is formed through microbial activities from polyphenols and aromatic acids. These compounds arise in soil either by microbial decomposition of lignin of higher plants or by microbial synthesis from non-aromatic carbon

* Oceanography Department, Faculty of Science, Alexandria University, Egypt.

coming from the remains of lower plants (mosses, algae, etc.). On the other hand, many of the important biosynthetic compounds such as amino acids, sugars, amino-sugars and fatty acids consist the building units of marine humus (Gagosian and Lee, 1981).

In lake water and sediments, HS are derived from the organic matter produced by the lake plants and from organic matter washed into the lake from the surrounding soils. Generally, the chemical characteristics of HS derived from lake water indicate that they are mainly autochthonous (Duursma, 1963; Duce and Duursma, 1977; Wangersky, 1978; Mopper and Degens, 1979). However, whenever drainage water is the principal water input to the lake, terrestrial organic matter, resulting from soil leaching and higher plant debris may constitute a considerable proportion of the total organic matter input to the lake and consequently interfere with the characteristics of the in situ produced HS.

The present work aims at the examination of the distribution and occurrence of HS in the sediments of a coastal Egyptian lagoonal environment in Egytu (Lake Edku).

Area of Study

Lake Edku (Fig. 1), a shallow coastal lagoon, communicates with the Mediterranean Sea through a narrow 2 m depth channel (Bougaz el Maadiya). It has an average depth of about 1 m and a surface area of about 115 km². Satellite images taken in 1981 indicate a loss of over 20% of the lake through land reclamation since 1923. Sub-basins in the lake are separated by small belts of islets (Fig. 1). The bottom sediments are mostly composed of clay with small proportion of sand-sized sediments, mainly of calcareous shell fragments and plant debris.

The eastern part of the lake receives considerable volume of agricultural drainage-water ($1 \times 10^9 \text{ m}^3 \text{ y}^{-1}$) through 3 main drains (Edku, El-Bousily and El-Barzik). The drainage water, introduces large amounts of nutrients and terrestrially organic matter. Rooted and floating hydrophytes are flourishing particularly in the central part and eastern side of the lake (El-Sarraf, 1976). Seawater from Abu-Qir Bay penetrates into the lake only during autumn and winter and mixing with lake water takes place in the most western basin. The extinction of penetration is governed by wind direction and sea level fluctuations (El-Samra, 1973). During the rest of the year, the whole lake is occupied by proper lake water.

Materials and Methods

Five sampling stations were selected to represent the different sub-basins in the lake (Fig. 1). Station I represents the lake-sea mixing basin, stations II and III represent the northern part of the central sub-basin and stations IV and V are representative of the eastern sub-basin downstream from the drains. This partitioning is however, without any physical frontiers but based on influence of the sea and drains on the western and eastern extremities of the lake. Surface sediment samples (0-20 cm) were collected during 1987 from the lake.

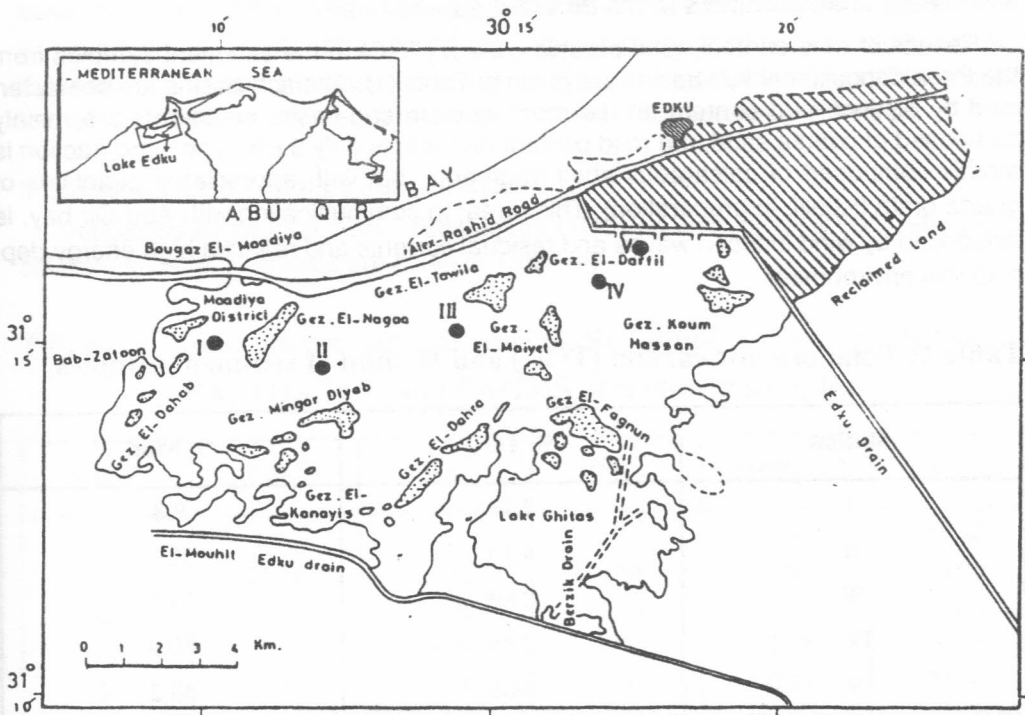


Figure (1)

Lake Edku and position of sampling stations.

Humic substances were extracted and fractionated from the wet samples by successive shaking with 0.5 M NaOH, according to the method described by King (1967) and Rashid and King (1969). The bulk extract was acidified to pH < 2 to precipitate humic acid. Humic acid was separated from fulvic acid by centrifugation, redissolved in 0.2 M NaOH and reprecipitated for purification. Fulvic acid was separated as barium fulvate using the method described by (Majumdar and Rao, 1978). Total organic matter was determined as weight loss by ignition for 4 hours at 525 °C. Water content was estimated by the loss of weight after oven drying at 105 °C over night. Mud content in the samples was also determined by mechanical analysis, separation of the < 63 µm fraction.

Results and Discussion

Sediments characteristics in the different sub-basins:

Results of mud content, total organic carbon (TOC) in the sediment samples from the three depositional sub-basins are given in Table (1). The sub-basins are characterized by distinct mud content. In the most western sub-basin, sediments are mainly composed of coarse sand, the mud content represents only 9.8%. The sand fraction is mostly composed of calcareous shell fragments, but with appreciable quantities of quartz grain (Khalil, in preparation). This area, in communication with Abu-Qir bay, is influenced by wind induced waves and residual currents and reflect a high energy depositional environment.

Table 1: Total organic carbon (TOC) and % mud of sediment samples.

Station	% TOC	% Mud
I	2.18	9.8
II	4.46	32.8
III	8.80	79.4
IV	2.46	50.9
V	2.65	49.2
mean	4.10	44.4
S.D.	2.48	22.9

The mud content increases gradually to reach its maximum value at St. III in the central basin (79%). This seems to be partly due to the geographic position of the basin which is relatively sheltered and far from the direct influence of inflowing water and mainly due to the proliferation of the macrophytes which reduces the water velocity and favours the deposition of the fine sediments.

In the eastern sub-basin (Sts. IV, V) mud still represents a large proportion of the sediment (average 50%). Evidently, most of the coarse fraction carrier by the drains sediments in this basin which is still under the influence of the water current generated by the inflowing water from the drains. Calcareous shell fragments contribute also to the coarse fraction.

TOC varies approximately in the same way, peaking in the central basin (8.8% at St. III) and decreasing in both the eastern and western basins. Evidently, organic carbon covers with the mud content, decrease in the mean particle diameter results in increase of exposed surface, which favours surface reaction like sorption (Bordovskii, 1965).

However, plot of TOC against the mud content (Fig. 2) reveal that the eastern basin is relatively deficient in TOC. It is worthy noting that, TOC in the sediments from the eastern basin (\sim 2.5%) lies in the range found for most of the coastal lagoon which eliminates the possibility of a rapid mineralization of the land derived organic matter. Evidently, the *In situ* primary productivity, particularly macrophytes, contributes largely to the TOC in the central basin, the western basin is consequently affected.

Distribution of total humic substances:

Concentration of total humic substances (THS) as well as THS/TOC ratios in the different sediment samples are given in Table (2).

Table 2: Total humic substances (THS), humic acid (HA), fulvic acid (FA) THS/TOC and FA/THS of sediment samples.

Station	THS*	HA*	FA*	THS/TOC	FA/THS
I	6.44	0.95	5.49	0.30	85.25
II	26.76	14.88	11.88	0.61	44.39
III	85.54	38.36	47.18	0.97	55.16
IV	4.73	0.95	3.78	0.19	78.92
V	4.37	1.07	3.30	0.17	75.51
mean	25.57	11.24	14.33	0.45	68.05
S. D.	31.14	14.59	16.71	0.31	15.61

* THS, HA and FA in mg g⁻¹ sediment.

The average THS concentration in lake sediments is 25.57 ± 31.14 mg g⁻¹ and it varies between 22 and 88 mg g⁻¹. Obviously, great variations exist between the sampling sites. Concentration in sediment from stations near the drains IV, V are surprisingly comparable to the concentration measures in sediment from St. I.

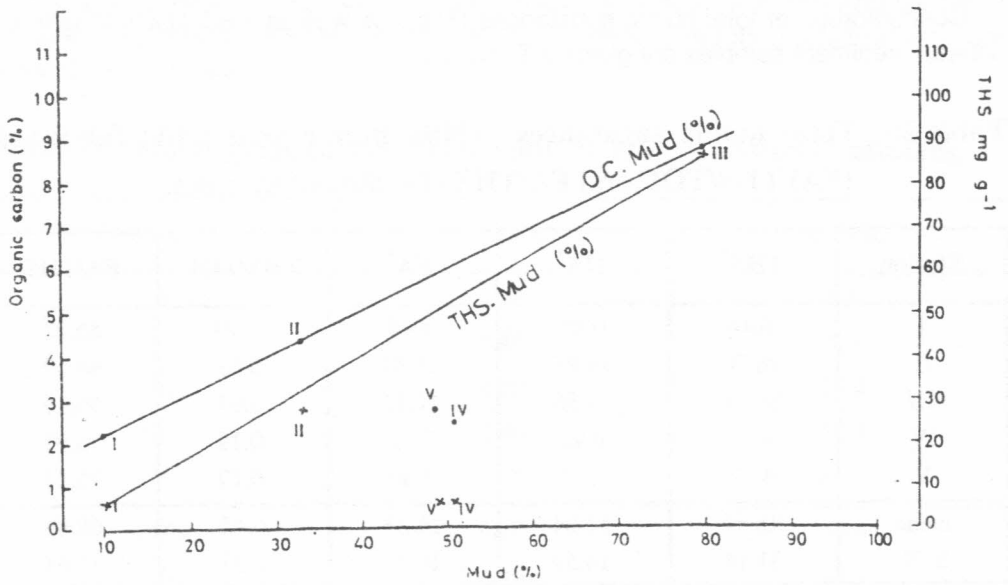


Figure (2)

Plot of total humic substances, total organic carbon against mud content of sediment samples.

The highest THS concentration is associated with the sediments having maximum mud and TOC content. Fig (2) shows that THS is perfectly correlated with TOC which agrees with the observations of Bojanowski and Pempkowiak (1980). It seems that the macrophytes represent an important source of sedimentary humic substances. Mayer (1985) stated that macrophytes debris may serve as an important site of alteration/humification processes. Humification is also enhanced in muddy sediments (Cauwet, 1985).

It is surprising that sediments of station I contains almost the same content of THS as sediments of Sts. VI and V, despite the fact that, the mud content in the later stations is about 6 times that in the sediments of St. I. This may result from the flocculation/precipitation of dissolved humic substances due to the increasing salinity in the area of fresh water/seawater mixing (Sholkovitz, 1976). It has also been demonstrated that the increased salinity enhanced adsorption of humic substances on clay minerals (Rashid et al., 1972).

Whatever is the total organic carbon in the sediments, the extractable organic matter is an important parameter, it may reflect the degree of association between the organic matter and mineral support as well as the nature of the organic matter (Cauwet, 1985). Total humic substances/TOC ratio increases regularly from 0.3 at St. I to almost 1.0 at St. III, then it decreases to almost a constant level of 0.17 and 0.19 in the most eastern part of the lake (Table 2).

The plot of THS/TOC ratio against the mud content reveals the distinct character of the eastern basin and the rest of the lake (Fig. 3). The central and western basins show increasing extractability with the increase of the fine fraction. Despite the high mud ratio in the eastern basin, the degree of extractability is very low (6-7.5%).

The nature of the humic substances particularly the degree of polymerization may be one of the factors controlling the binding of the humic substances to clay particles (Cauwet, 1985).

Humic substances and relative abundance of humic and fulvic acids:

The preparation of humic and fulvic acids as well as FA/THS ration in the humic extracted are given in Table (2).

Humic substances in lake Edku sediments are characterized by the dominance of the fulvic acid fraction whatever the sampling site and consequently the origin of the organic matter. This seems to be a general feature of sedimentary humic substances (Riley, 1963; Bordovskii, 1965; Brown 1975). The mean FA/THS ratio for the lake is 68% and it varies between 44 and 85%. No definite trend has been observed between samples, however, humic acid proportion increases as the humic substances which may be given as a result of an increasing probability of condensation and polymerization processes.

It seems also that HA/THS ratio increases with the increase of the mud and organic carbon content which may indicate that the humification process is enhanced in the muddy sediments rich in organic matter which is the case of the sediments in the central basin of the lake.

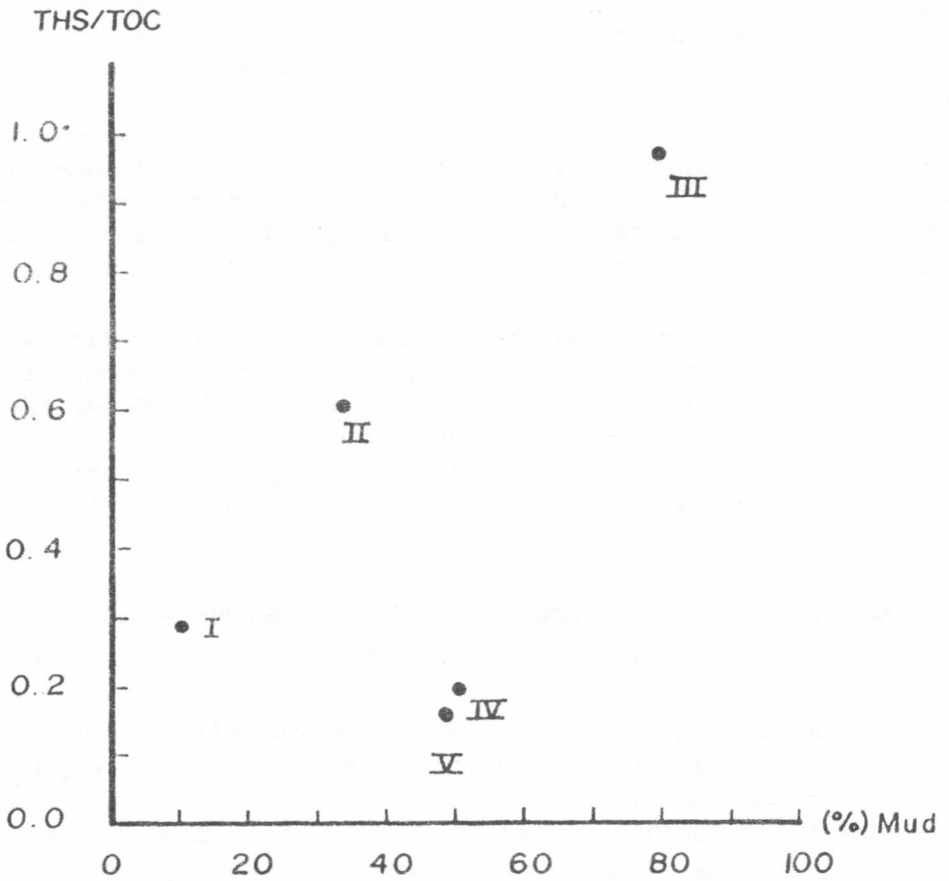


Figure (3)

Plot of THS/TOC ratio against % mud of sediments.

References

- Bojanowski, R. and Pempkowiak, J., 1980.** Humic substances in the Baltic sediments. In Management of Environment., B. Patel (Editor)., New Delhi., Wiley Eastern Ltd., 246-260
- Bordovskii, O.K., 1965.** Accumulation and transformation of organic substances in marine sediments. In accumulation of organic matter in bottom sediments., Marine Geology., 3: 33-82.
- Brown, M., 1975.** High molecular weight material in Baltic Seawater., Marine Chemistry., 3: 253-261.
- Cauwet, G.C., 1985.** Dynamique de la matière organique dans les milieux marins et polyhalins; son rôle dans les processus géochimiques, thèse d'Etat, Université de Perpignan., 178 pp.
- Duce, R.A. and Duursma, E.K., 1977.** Input of organic matter in the ocean. Marine Chemistry., 5: 319-341.
- Duursma, E.K., 1963.** The production of the dissolved organic matter in the sea, as related to the primary gross production of organic matter. Netherland Journal of Sea Research., 3: 391-405.
- EI-Samra, M.A., 1973.** Chemical and physical properties of the water of lake Edku and the mixed waters between the lake and the sea. M. Sc. Thesis. Faculty of Science, Alexandria University., 110 pp.
- EI-Sarraf, W.M., 1976.** Some limnological studies on the submerged macrophytes in lake Edku, with special reference to their value as food of fish., M. Sc. Thesis. Faculty of Science, Alexandria University., 117 pp.
- Frimmel, F.H. and Christman, R.F., 1988.** Humic Substances and their Role in the Environment. Jon Wiley & Sons 1988, New York., 271 pp.
- Gagosian, R.B. and Lee, C., 1981.** Processes controlling the distribution of biogenic organic compounds in seawater. In: Marine Organic Chemistry, (Duursma, E.K & Dawson, R. eds). Elsevier Scientific publication Company Amsterdam., 521 pp.
- Gjessing, E.T., 1976.** Physical and chemical characteristics of aquatic Humus. Ann Arbor Science, Ann Arbor, Michigan.
- Kemp, A.L.W., 1971.** Organic carbon and nitrogen in the surface sediments of lakes Ontario, Erie and Huron., Journal of Sedimentology and Petrology., 41: 537-548.
- Khalil, M. KH., (In preparation).** Geochemical cycle of phosphorus in lake Edku, M. Sc. Thesis, Faculty of Science, Alexandria University.
- King, L.H., 1967.** Isolation and characterization of organic matter from glacial marine sediments on the Scottian Shelf. Bedford Institute of Oceanography. Report No. (4) p. 18.

- Majumdar, S.K. and Rao, C.V.N., 1978.** Physicochemical studies on enzyme-degraded fulvic acid., *Journal of Soil.*, 29: 489-497.
- Mantoura, R.F.C., Dickson, A. and Riley, J.P., 1978.** The complexation of metals with humic material in natural waters. *Estuar. Coast. Mar. Sci.*, 6: 387-408.
- Mayer, L.M., 1985.** Geochemistry of humic substances in estuarine environments. In: *Humic substances in soil, sediments and water.* Jon Wiley & Sons. New York., 211-233.
- Mopper, K. and Degens, E.T., 1979.** Organic carbon in the ocean: nature and cycling. In: *The Global Carbon Cycle*, (Bolin, B., Degens, E.T & Kempe, S., eds). Wiley, New York., 293-316.
- Nissenbaum, A. and Kaplan, I.R., 1972.** Chemical and isotopic evidence for the in situ origin of marine humic substances. *Limnology and Oceanography.*, 17: 570-582.
- Prakash, A., Rashid, M.A. and Rao, D.V.S., 1973.** Influence of humic substances on the growth of marine phytoplankton: Diatoms. *Limnology and Oceanography.*, 18: 516-524.
- Rashid, M.A. and King, L.H., 1969.** Molecular weight distribution measurements from marine clays on the Scottian Shelf., *Geochimica et Cosmochimica Acta.*, 33: 147-151.
- Rashid, M.A., Buckley, D.E. and Robertson, K.R., 1972.** Interaction of humic acids with different clay minerals and natural sediments in ionic waters similar to waters of marine estuaries. *Mezhdunar Geokhim. Kong.*, 4 (Pt. 3.) 125-133.
- Riley, G.A., 1963.** Organic aggregates in sea water and the dynamics of their formation and utilization. *Limnology and Oceanography.*, 8: 372-381.
- Schnitzer, M. and Khan, S.U., 1972.** *Humic Substances in the Environment*, Marcel Dekker., New York.
- Sholkovitz, E.R., 1976.** Foculation of dissolved organic matter during the mixing of river water and sea water. *Geochimica et Cosmochimica Acta.*, 40: 831-845.
- Stevenson, F.J., 1982.** *Humus Chemistry; Genesis, Composition, Reactions*, Wiley-Interscience, New York, 443 pp.
- Stumm, W. and Brauner, D.A., 1975.** Chemical speciation. In: *Chemical Oceanography*, (Riley, J.P. & Chester, R., eds). 2nd ed., Academic Press., 173-234.
- Wangersky, P.J., 1978.** Production of Dissolved Organic Matter. In: *Marine Ecology*, (Kinne, O., ed.). IV, Dynamics. Wiley. New York., 115-220.

Mango Eas

The concentration spectrophotometry of El-Me Bay (Fig. 1) concentrations are sea respectively.

The concentration and near the bottom Mn, Co, Ni and Zn, the surface water. Generally, the ter.

Trace metals charging from U tendency to concentration Mn, Co and Ni sho

The distribution used as a good trac

The appearance correlate with high Zn ($r=0.85$) showed of El-Mexx Bay. T Co ($r=0.60$) for the

The present data higher, probably du