J. KAU: Mar. Sci., vol. 5, pp. 25-34 (1414 A.H./1994 A.D.)

Humic Substances in the Sediments of Lake Edku, Egypt: I – Occurrence and Distribution

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ABSTRACT. Humic substance (HS) as humic and fulvic acids were determined in the surface sediments of Lake Edku (Egypt). Their sources, distribution and behavior were assessed. The lake is geographically subdivided into eastern, central and western sub-basins; subdivision is based on the presence of natural barriers and proximity to the drains or to the sea-lake connection. The central basin showed the highest concentrations of HS, which is attributed to intensive development of macrophytes and to enhanced phytoplankton primary production. In the eastern basin, high turbidity and water turbulence downstream from the drains limit primary production. In the western basin, however, 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 consists of humic substances (Schnitzer and Khan 1972), which may constitute as high as 70% of the organic matter in the lake sediments (Kemp 1971). This 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 & Kaplan 1972; Prakash *et al.*, 1973; Stumm & Brauner 1975; Frimmel & 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 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 constitute the building units of marine humus (Gagosian & Lee 1981).

In lake water and sediments, HS are derived from the autochtonous organic matter produced within the lake by the aquatic plants and from the allochtonous organic matter washed into the lake from the surrounding soils. Generally, the chemical characteristics of lake water dissolved HS indicate that they are mainly autochtonous (Duursma 1963; Duce & Duursma 1977; Wangersky 1978; Mopper & 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 was undertaken to study the occurrence and distribution of humic and fulvic acids in the sediments of Lake Edku; one of the coastal lagoons of the Nile Delta.

Study Area

Lake Edku (Fig. 1), is one of the shallow coastal lagoons of the Nile Delta. It lies to the west of the Rosetta branch at 30° 15 N and 31° 15 E. The lake is 115 km^2 in area, it has an average depth of 1m and communicates with the Mediterranean Sea (Abu Qir Bay) through a narrow 2m deep channel (Boughaz El Maadia) situated at its north-western extremity. Satellite images taken in 1981 indicate a loss of over 20% of the lake area through land reclamation since 1923. The lake basin is naturally subdivided to separate sub-basins by small belts of islets (Fig. 1). The bottom sediments are mostly composed of clay, with small proportion of sand and are enriched with calcareous shell fragments and plant debris.

The eastern part of the lake receives a considerable amount of agricultural drainage water $1.0 \times 10^9\ m^3\ y^{-1}$ through 3 main drains (Edku, Bousily and Barzik). The drainage water introduces into the lake large amounts of nutrients and terrestrial 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 enters into the lake during stormy days in autumn and winter and mixing with the lake water occurs in the most western basin. The limit of seawater intrusion is governed by wind direction and sea level fluctuations (El-Samra 1973). Several studies have been undertaken on Lake Edku to describe its ecology, water chemistry and hydrography and bottom sediments (Samman 1974; El-Samra 1973; El Sarraf 1976; Aboul Naga 1990).

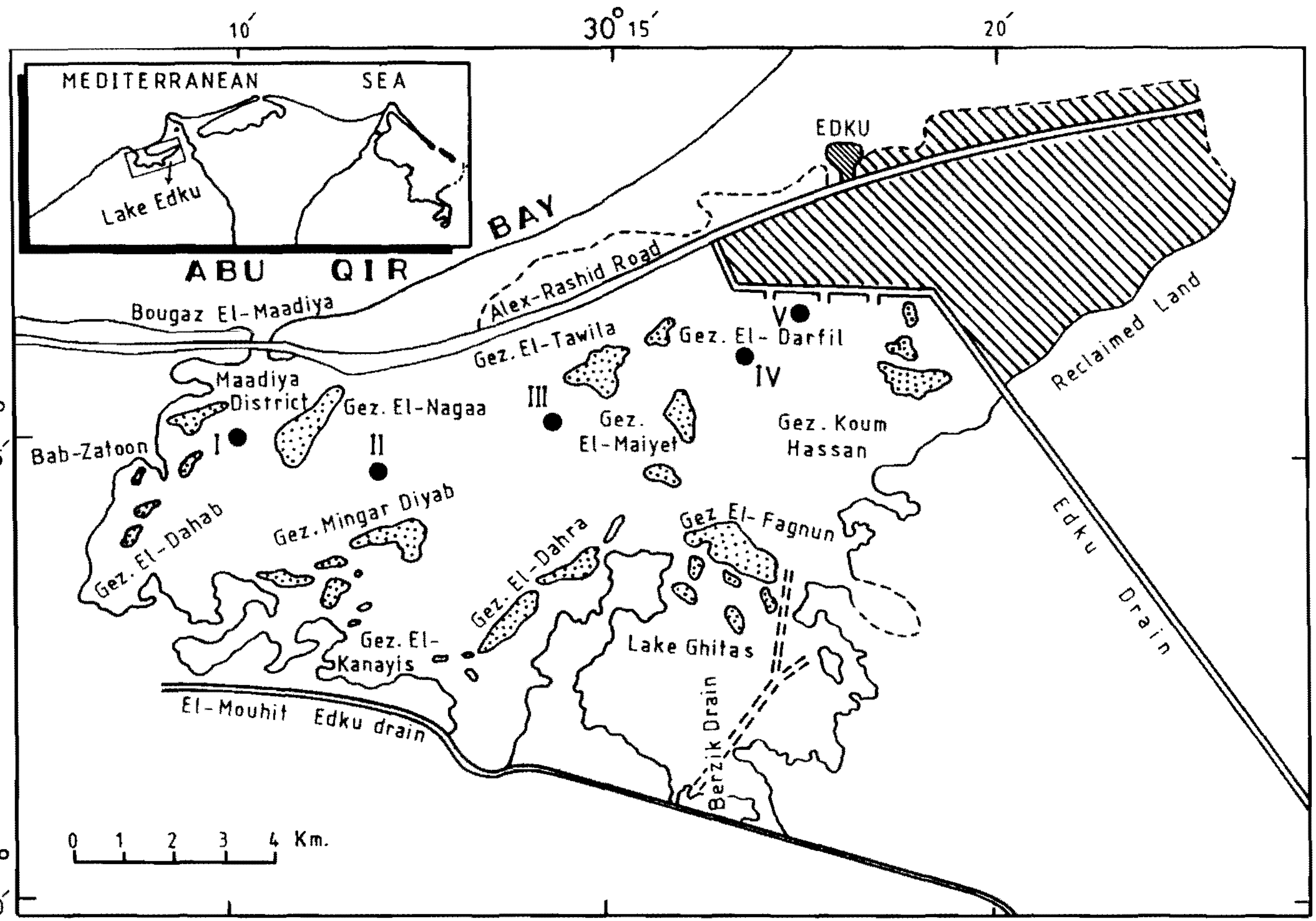

FIG. 1. Lake Edku and position of sampling stations.

Materials and Methods

Five sampling stations were selected to represent the main three 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 directly influenced by the drainage water discharge. This partitioning is based on the presence of physical frontiers (belts of islets) and on the relative influence of the sea and drains on the western and eastern extremities of the lake respectively. Surface sediment samples (0-20 cm) were collected using an Ekman grab sampler. Sediment samples were transferred into polyethylene bags and refrigerated at 4°C until processing after 24 hours. Separate portions of the samples were kept for the determination of organic matter and mud content.

Humic substances were extracted from the wet samples by successive shaking with 0.5 M NaOH according to the method described by King (1967) and Rashid & King (1969). The bulk extract was acidified to pH < 2 to precipitate humic acid. Humic acid was separated from fulvic acid (FA) by centrifugation at 15000 rpm. Redissolution and precipitation were undertaken several times to eliminate impurities. Purification was achieved by the passage of humic acid on the resin Dowex 50 WX8 in the H^+. The solution was finally acidified and centrifuged at 15000 rpm and the separated humic acid was washed several times with MilliQ water and freeze dried and weighed. Fulvic acid was separated as barium fulvate at pH 4.5-4.8 using the method described by (Majumdar & Rao 1978). After thorough washing with MilliQ water, the precipitate was freeze dried and weighed.

Total organic matter was determined as loss on ignition for 4 hours at 525°C. It should be emphasized that this method is accompanied by a small error due to the loss of the lattice water from clay minerals (Mook and Hoskin 1982). Mud content (fraction < 63 um) of the samples was determined by wet sieving. Water content was estimated as the weight loss after drying at 105°C over night.

Results and Discussion

Sediments characteristics in the different sub-basins

Results of mud content and total organic matter (TOM) 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 were mainly composed of coarse sand, the mud content represented only 9.8%. The sand fraction was mostly composed of calcareous shell fragments, but with appreciable quantities of quartz grains. This area, in connection with Abu-Qir bay, is influenced by wind induced waves and residual currents reflecting a high energy depositional environment.

The mud content increased gradually to reach its maximum value at Station 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 the inflowing

TABLE 1. Percentage of total organic matter (TOM) and mud in sediment samples.

Stations	% TOM	% Mud
I	2.2	9.8
II	4.4	32.8
III	8.8	79.4
IV	2.5	50.9
V	2.7	49.2
mean	4.1	44.4
S.D.	2.5	22.9

waters and mainly due to the proliferation of the macrophytes which reduce the water velocity and favors deposition of the fine sediments.

In the eastern sub-basin (stations IV, V), mud gave a large proportion of the sediments (about 50%). Evidently, most of the coarse fraction carried by the drain, sediments in this basin which is still under the influence of the water current generated by the inflowing water. Calcareous shell fragments contributed also to the coarse fraction.

TOM varied approximately in the same way, peaking in the central basin (8.8% at Station III) and decreasing in both the eastern and western basins. Evidently, organic carbon co-varied with the mud content, decrease in the mean particle diameter, due to the increase of the mud content, results in the increase of the exposed surface, which favors surface reactions like sorption (Bordovskii 1965).

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

Distribution of total humic substance

Concentrations of total humic substances (THS), as well as THS/TOM FA/THS ratios in the different sediment samples are given in Table 2. The average of THS concentration in the lake sediments was 25.27 ± 31.14 mg g^{-1}, ranging between 4.37 and 85.54 mg g^{-1}. Obviously, a considerable variation existed between the sampling sites.

The highest THS concentration was associated with the sediments having maximum mud and TOM content. Fig. 2 and Tables 1 and 2 show that THS is well correlated with TOM and mud content which agrees with the observations of Bojanowski & Pempkowiak (1980). It seems that the macrophytes represent an im-

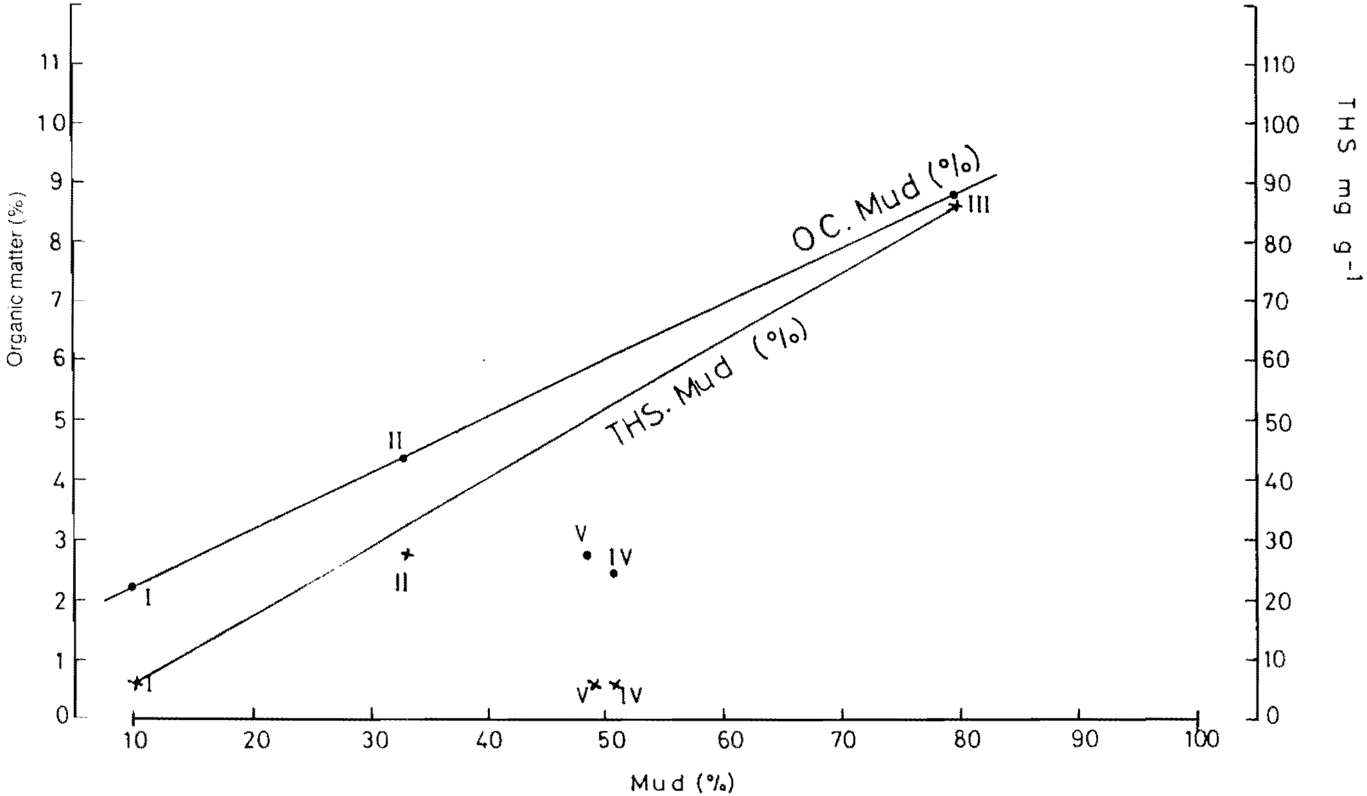

FIG. 2. Plot of total humic substances, total organic carbon against mud content of sediment samples.

TABLE 2. Total humic substances (THS), humid acid (HA), fulvic acid (FA), THS/TOM and FA/THS in sediment samples.

Stations	THS*	HA*	FA*	THS/TOM	FA/THS
I	6.4	1.0	5.5	0.3	85.3
II	26.8	14.9	11.9	0.6	44.4
III	85.5	38.4	47.2	1.0	55.2
IV	4.7	1.0	3.8	0.2	78.9
V	4.4	1.1	3.3	0.2	75.5
Mean	25.6	11.2	14.3	0.5	68.1
S.D.	31.1	14.6	16.7	0.3	15.6

*THS, HA and FA in mg g^{-1} sediment (dw).

portant source for sedimentary humic substances. Mayer (1985) stated that macrophyte debris may serve as an important site of alteration/humification process. Humification is also enhanced in muddy sediments (Cauwet 1985).

It is surprising that the sediments at station I contained almost the same content of THS as those at stations IV and V, despite the fact that the mud content of the later stations was about 5 times higher than that in the sediments at station I. This might result from the flocculation/precipitation of dissolved humic substances due to the increase in salinity in the area of fresh water/seawater mixing (Sholkovitz 1976). It has also been demonstrated that 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). THS/TOM ratio increased regularly from 0.3 at station I to almost 1.0 at station III, then decreased 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/TOM 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 showed an increasing extractability with the increase in the fine fraction. Despite the high mud ratio in the eastern basin, the degree of extractability was very low (6-7.5%). It has been stated (Cauwet 1985) that, 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 concentrations of humic and fulvic acids, as well as FA/THS ratio in the humic extracts are given in Table 2. Humic substances in Lake Edku sediments were characterized by 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

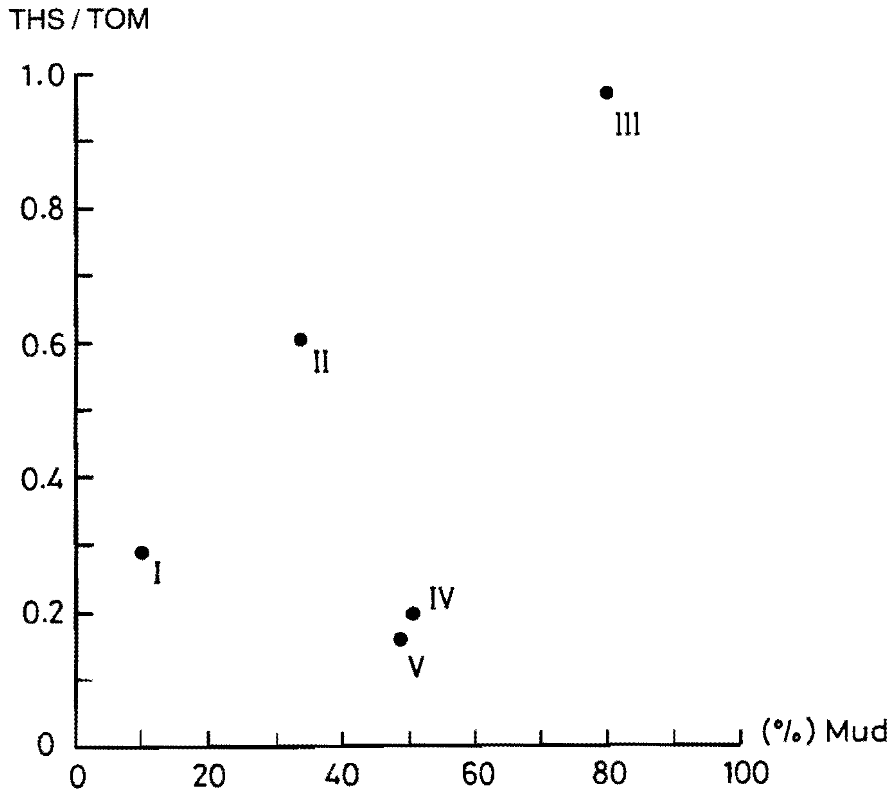

FIG. 3. Plot of THS/TOM ratio against % mud of sediments.

sedimentary humic substances (Riley 1963; Bordovskii 1965; Brown 1975). The mean FA/THS ratio for the lake sediments was 68.05% + 15.61, ranging from 44.39-85.25%. No definite trend has been observed between samples. However, humic acid proportion increased as the humic substances increased which may be given as a result of an increasing probability of condensation and polymerization processes.

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

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المـــواد الهيوميـــة في رواسب بحـــيرة إدكو – مصر :
١ – تواجدهـــا وتوزيعهـــا

محمد عبد الخالق السيد ، وفيقة محمد أبوالنجاة ، يوسف حليم* و علي إبراهيم بلتاجي
معهد علوم البحار والمصائد ، الاسكندرية
و *قسم علوم البحار ، كلية العلوم ، جامعة الاسكندرية ، جمهورية مصر العربية

المستخلص . تم تعيين المواد الهيومية في صورة أحماض فولفية وأحماض هيومية في رواسب بحيرة إدكو (مصر) ودرست مصادرها وتوزيعها في البحيرة وسلوكها . وقد قسمت البحيرة إلى ثلاثة أحواض فرعية هي الشرقي والأوسط والغربي . وقد بنى التقسيم على تواجد فواصل طبيعية بين الأحواض المختلفة والقرب أو البعد عن المصبات الزراعية أو منطقة الاتصال بالبحر .

وقد اتصف الحوض الأوسط بأعلى تركيزات للمواد الهيومية وأُعزيَّ ذلك للنمو الوفير للنباتات المائية وكذا الهائمات النباتية . وفي الحوض الشرقي تعمل العكارة المرتفعة والتيارات المائية الناتجة عن المصبات الزراعية في الحد من الإنتاجية الأولية مما يؤثر على معدل الإمداد بالمادة العضوية ويسبب انخفاض تركيزات المواد الهيومية . كما أن التيارات المائية الناتجة عن التبادل بين البحر والبحيرة وطبيعة القاع الرملية ونقص الأملاح المغذية نسبيًا وكذا ارتفاع الملوحة تشكل مجموعة العوامل التي تؤدى إلى الحد من إنتاج المواد العضوية في الحوض الغربي .

كما بينت الدراسة أن الأحماض الفولفية هي المكون الرئيس للمواد الهيومية في جميع رواسب البحيرة حيث شكلت ما بين ٥٠ و ٨٠٪ من إجمالي المواد الهيومية .