

TRACE METALS IN SEDIMENTS FROM
EL-RYAH EL TWFIKY AND SOME OF ITS EXTENSIONS

By

I. GAR AL-ALM RASHED, (PhD)
Physical Science Department,
Faculty of Engineering, El-Mansoura
University, El-Mansoura, EGYPT.

M. M. EL-DESSOUKY, (PhD)
Military Technical College,
Cairo, EGYPT.

HODA. A. ASHRY, (PhD)
National Center for Radiation
Research and Technology,
Nasr City, Cairo, EGYPT.

SALAH M.EL-BEGAWY, (Eng.)
Armed Forces, EGYPT.

خلاصة

اثر الفلزات نسي، واسب الرياح التوفيقى وبعض تفرعاته

د. محمد محمد الدسوقي
قسم الهندسة الكيميائية
الكلية الفنية العسكرية

د. إبراهيم جابر العلم راشد
قسم العلوم الطبيعية
كلية الهندسة - جامعة المنصورة

م. صلاح الدين مصطفى البيجاوى
القوات المسلحة

د. هدى مشرف
المركز القومى لبحوث وتكنولوجيا الإذاعة
مدينة نصر - القاهرة

في هذا البحث تم تحديد تركيزات عناصر الثنائيوم والكروم والمنجنيز والحديد والنيكل والزنك والنحاس في الرواسب المأخوذة من لاج مجرى الرياح التوفيقى وبعض تفرعاته التي تدهى خلال محافظات القليوبية والدقهلية وبهايت حيث تعتبر هذه المجرى - محل الدراسة - هي المصدر الرئيسي لياه الشرب والرى والإستخدام الصناعى في المحافظات الثلاث .
ولقد تم ربط النتائج المتحصل عليها التركيزات للمناسم مع المساحة المسطحة النهرية للرواسب ، ومع الكروم المعنى والجزء من الرواسب ذات الحجم اللى من ١٠٠ ميكرومتر وكذلك مدى إرتباط تلك العناصر بعضها بالبعش .
ولقد قورلت تركيزات العناصر المختلفة مع المستويات الموجودة في رواسب انهار اخرى من العالم . ولقد عنى إرتفاع قيم تركيزات العناصر المختلفة إلى إلقاء الملثبات المعدنية المختلفة بالقرب من المجرى وكذلك إلقاء الملثبات الصناعية والمخرلية في أماكن عديدة في المجرى وكذلك نتيجة مياه الصرف الزواى التي تحول في بعض المناطق إلى المجرى بما تحمله من بفايا الأسمدة الكيميائية .

ABSTRACT

The trace concentrations of a number of elements including: Ti, Cr, Mn, Fe, Co, Zn and Ag have been determined in sediments taken from El-Ryah El Twfiky and some of its extensions through El-Kallobia, El-Dakahlia and Dainietta Provinces, Egypt, where these water streams are considered the main source for drinking, irrigation and industrial waters, to the three mentioned provinces. The concentration values of the trace elements have been determined and associated with the specific surface area, organic carbon, fraction of particles ($< 100 \mu m$) and with each

other. The levels of metal concentration are compared generally with levels found elsewhere in some river sediments. The high values and trends in metal content of the sediments compared with natural levels may be ascribed to the dumping of metallic waste materials nearby the water course, industrial and domestic effluents discharged into the stream from a number of outfalls within the area, in addition to fertilizers washed down from cultivated land.

1. Introduction :

Since the Industrial Revolution, the efforts of removing man-made pollutants from the natural environment have been unable to keep pace with the increasing amount of waste materials and a growing population that further aggravates the situation. With the growth of technology, two groups of substances in particular have a lasting effect on the natural balance in aquatic systems: (i) Nutrients, which promote unrestricted biologic growth and, in turn, oxygen depletion and (ii) Sparingly degradable synthetic chemicals and other waste substances which often constitute multiple effects on the aquatic ecosystems.

The introduction of metal contaminants into aquatic systems have various sources, including : smelting processes and fuel combustion via atmospheric fallout, pollution from leaks, effluents and dumping activities, from run off of terrestrial systems-where accumulation has occurred by atmospheric input-land application of sewage materials and leaching of garbage. On the other hand, polluted water bodies lead over many pathways to metal contamination of terrestrial ecosystems, for example, by way of irrigation, dredging activities and biota flux [1].

Investigation into the distribution of trace metal concentration in water, sediments and biological matter are important items of research in water pollution because they are highly persistent and can be toxic to life in only trace level. It is generally believed that the pattern of accumulation or dispersion of metal pollutants over an extended period may be revealed by measuring the trace element concentration of sediments in the particular area of interest. The general level of trace metal pollution in an area cannot be adequately described by analysis of water samples unless the detailed monitoring programme is carried out over an extended period of months or even years, which may be extremely time-consuming and expensive. Wide fluctuations in dissolved metal concentration are to be expected where the chemical and physical conditions of the water vary, and where there are changes in the nature and volume of discharges of sewage and industrial effluent. Monitoring the level of trace metal pollution by analysis of metals in biological specimens is complicated by the wide diversity in the accumulating power with different species for the various metals and the effects of specimen age on the metal levels [2]

Trace metal surveys of bottom sediments from Nile River area were very scarce. Emelyanov et al [3] calculated the mass of some elements (expressed by 10^6 tonns/year) delivered to the Mediterranean annually based on their average concentrations and amounting to 120×10^6 tons/year deposits as follows; CaCO_3 (7), C organic (1.43), Fe (7.1), Mn (0.13),

Ti (1.48), Na (1.46), K (1.2). The mass of the trace elements expressed by 10^3 tons/year are as follows : Cr (16.2), Cu (6.2), Zn (12.9) and Ni (15.1). Draz [4] in her investigation of the physical and textural properties of the sediments covering the bottom of the Rosetta branch of the Nile, showed some enrichment with heavy metals such as Fe, Mn, Cu and Zn.

The objectives of the present study is to investigate the bottom sediments from El Rayah El Twfiky (a sub-branch from Nile River in Eastern Delta, Egypt) and its extensions in El-Kaliobia, El-Dakahlia and Damietta provinces for a preliminary trace element survey, since this water course is considered a vital source for drinking, irrigation, fishery and industrial use in these three provinces.

2. Sampling and Method of Analysis:

2.1. Description of the investigated water course :

El-Ryah El Twfiky, (ET) is a sub-branch from the Nile River, starting at El-Kanater El-Khairia Barrage passing through El-Kaliobia and El-Dakahlia provinces, it is supported with other tributary at Meit Ghamer Town. Its extension after Meit Ghamer to El-Mansoura City is known as El-Mansouria Canal (Tereit El-Mansouria), where it is supported another time from Damietta Branch of the Nile at El-Mansoura. After El-Mansoura City till Damietta City it is called El-Sharkawia Canal, as illustrated in Fig. (1). The stream goes through areas of large population densities and many industrial activities have been, recently, established near its banks. From Banha City to the end at Damietta, the stream is going beside a crowded high-way road. It is usually seen near its banks a dumps of industrial and domestic wastes.

2.2. sampling :

Twenty sampling stations were chosen for this investigation. Sediments of the area undertaken are chiefly muds, though they were substituted by silty sand in some regions and by sand in another. Core samples were collected by cutting a block of material out from 15-20 cm depth [5], by using a sharp edged plastic pipe of 7.5 cm diameter forced into the sediments. Samples were collected during the time of drying of the stream, (Winter closing of irrigation canal). The sample were transferred to plastic jars that had been prewashed with concentrated nitric acid rinsed well with distilled water. Samples were dried in air for about four days and analysed within two weeks after collection.

2.3 Laboratory Investigation :

The particle size distributions of the samples were obtained on the wet untreated samples by a combination of : (i) wet sieving using a nest of sieves 1000 μm (16 BS mesh) to 63 μm (250 BS mesh) ; and (ii) sedimentation analysis by using the fixed position pipette method on fines less than 63 μm , according to the British Standards No. 3406, [6].

The organic carbon content of samples was determined by a modified procedure of the rapid chromic acid oxidation method of El-Wakeel and Riley [7]. In an investigation of their method, by Jaffé and Walters [2], it was established that the procedure gave rise to anomalous values for the organic carbon content of estuarine sediments. The procedure was modified by using a larger aliquot of chromic acid (20 ml) and extending the oxidation period from 15 to 45 minutes.

weight-loss data were obtained by quasistatic thermogravimetric analysis, and the results were obtained by heating up a sample weight of about 300 mg to 1000°C at a rate of 10°C/min.

The element concentrations of sodium, potassium, calcium, magnesium, silicon, phosphorous, titanium, chromium, manganese, iron and cobalt were determined in samples by using X-ray fluorescence analysis technique, using ORTEC 6110 TEFA Tube Excited Fluorescence Analyzer. Silver and zinc were extracted from sediments by digestion with concentrated HNO₃, (8N), for two hours and the filtered extract diluted to constant volume [5], then they were determined spectrophotometrically using a single-beam spectrophotometer (Bausch & Lomb, U.S.A. model Spectronic 20). Ag and Zn were determined according to the procedure outlined in Standard Methods for Examination of Waters and Wastewaters [8].

3. Results and Discussion :

The particle size distribution of the muds and silty sands fall into two distinct groups as expected from their very nature, with the exception of sample No. 12 which is pure sand with mean particle size of 600 µm and this is clearly shown in Fig. (2). The silty sands have a narrow particle size distribution around a mean between 190 and 450 µm whilst the means of the comparatively broad particle size distribution of the muds in the 90-120 µm range. Although the silty sands are represented by very similar size distributions, they differ significantly in the fraction of their particles below 63 µm. The cumulative percent undersize varies close to zero to 9% by weight and as a result the specific surface area of the silty sands will be significantly different. The size distributions of the muds also broadly resemble each other, but differ from the case of silty sands. There is no significant change in the fractions of particles in the colloidal range (<1-2 µm) which will not give rise to pronounced differences in surface area.

The familiar interdependency of grain size and specific surface area of sediments is used here for the indirect determination of relative grain size values. Specific surface area was determined for samples by the following equation[9].

$$S = \frac{6}{\gamma} \left(\frac{1}{d} \right) \quad \dots (1)$$

Where :

S : Specific surface area, (cm^2/gm)

γ : Density of particles, (gm/cm^3)

d : The average diameter of the particles, (cm).

Grain size seems to play a negligible role as predicted from the values of the correlation coefficients between the mean particle size or the specific surface area and the metal concentration in the sediments as given in Table (2), indicating the predominant effect of rapid sedimentation of highly polluted suspended solids at reduced flow velocities within some parts of the stream, where some obstacles are found at different positions across the water course for controlling water discharge as weirs and locks. These results are in contrast with the mixing theory [10], which assumes a good correlation coefficient between particle size and metal concentration for low sedimentation rate, (greater than 0.7).

Loss on ignition of each sample was carried out by heating the sample at increased temperatures for one hour. The thermogravimetric analysis (TGA) curves of samples, illustrating their weight loss on ignition up to 1000°C , are shown in Fig. (3). Weight loss on heating the sediments may arise from the dehydration and decomposition of a multitude of constituents. Commonly, however the contributions to weight loss will be dominated by the decomposition of a few phases: The oxidation of organic matter in the region of 400°C , (correlation coefficient between organic carbon and weight loss at 400°C was found to be 0.51), the dehydroxylation of one or two clay minerals such as kaolin, montmorillonite or hydrous mica at various characteristic temperatures and the decomposition of calcite or dolomite in the region of 750 to 900°C [2].

In all cases the major loss in weight from samples was completed before a temperature of 750°C was reached. Above this temperature, in some cases there is a slight inflection in the TGA curves at about 803°C reflecting the presence of a significant amount of calcite in sediments. This is in accord with the positive correlation coefficient ($r = 0.76$) obtained between % Ca as CaCO_3 and the difference between weight loss at 1000°C and that at 400°C , where the values of samples No 2, 6, 7 and 11 were excluded due to that they contain large quantities of shells. The major loss in weight is most likely attributable to the presence of one or two clay minerals in varying proportions depending upon the sample. In the case of the mud and silty sand samples, the high percent weight loss in the region of 400 to 700°C and the low loss in weight below 200°C suggests that the major proportion of these samples consist of a kaoline mineral. Prior to the dehydroxylation of the clay minerals, the weight loss up to 400°C , in some cases moderately high, is considered to be predominately associated with the oxidation of the carbonaceous matter in the muds and sands [2].

The organic carbon content of the sediments cover a range from 0.14 to 2.6% , the highest values being given by the muds, the lowest by the sands. These values are comparatively low with that obtained from Rosetta branch sediments which was found to be ranged

from 0.4 to 10.4%, with an average of 4.64%, [4]. Draz in her study on Rosetta Branch [4] showed that the high values of organic carbon come from two major sources: which are the terrestrial origin from inland and disposal of domestic sewage along the Nile branch. In this study the situation is different due to the annual cleaning of the stream bottom after winter close. Values of correlation coefficients between organic carbon and the loss on quasistatic heating to 400° and to 1000°C were found to be 0.511 and 0.44 respectively. This suggests that the loss in weight is predominantly the result of oxidation of organic matter in the sediment. The relatively lower value of the correlation coefficient between the organic carbon% and the weight loss at 1000°C indicates that the major portion of the weight loss up to 1000°C is considered to be the result of the dehydroxylation of the clay minerals in addition to the oxidation of the organic matter [2].

Calcium and magnesium contents of the sediments are determined as oxides and the equivalent calcium and magnesium carbonates are calculated. The sum of both calcium carbonate and magnesium carbonate are roughly considered as the total carbonate content in sediments, and are given in Table (3). CaO content varies between 0.42 to 32.64% with an average of 7.63%. The calculated calcium carbonate ranges from 0.75 to 58.28% with an average of 13.6% . The magnesium oxide content in sediment fluctuates between 0.73 and 3.2% with an average of 1.5%. The calculated magnesium carbonate fluctuates between 1.53 and 6.69% with an average of 3.13% . Therefore, the sediments under investigation are generally more richer in calcareous matter than found in Rosetta branch of the Nile [4]. The average total carbonate value is 16.73% compared with 6.78% found in Rosetta branch.

The phosphorus content in the sediments ranges from zero to 0.955% . The value of P is nearly constant, (about 0.12%), from station 1 till station number 12 then it suddenly increased at stations number 13 & number 14 then drops to zero for all the remaining stations. The source of phosphorus may be due to either the untreated domestic sewage which is discharged directly into the stream or due to the phosphate fertilizers washed down from the cultivated land especially, in some parts on the banks, directly drains to the stream.

The sodium oxide value in the sediments range between 0 and 13.76% with an average of 3.09%. While the potassium oxide content ranges from 1.30 to 4.25% with an average of 2.38%. Values of potassium and sodium are associated with silicon indicating that they present mostly as silicates, (correlation coefficient between Si and Na was found to be 0.5; between Si and K as 0.67 and between Na and K to be 0.77).

The analysis of the samples for the determination of Fe, Ti, Cr, Mn, Co, Zn and Ag is given in Table (1). Pollution reconnaissance can be carried out in stream sediments in the same manner as in mineral exploration. Two effects, however, must be considered when chemical data from active stream sampling are used for identification of pollution source: (i) Under conditions of high water discharge, erosion of the river bed takes place,

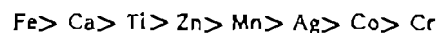
and generally leads to a lower degree of contamination. Laszlo et. al. [11], for example, obtained data from the Sajo River, (Hungary), which indicated that, three months after a flood, the mercury concentration in the bottom sediment had been reduced to approximately one-quarter of the values found immediately before flood. For this reason the samples, of the undertaken work, have been collected in the winter closing of the stream to obtain the true degree of contamination. (ii) It is usually imparative in stream sediment studies to base metal analysis on a standardized procedure, due to a preferential occurrence of the heavy metals in the finest grain-size fraction. In Fig. (4) a plot of element concentrations and the fraction of particles $<100 \mu\text{m}$. According to de Groot et.al [12], such a plot makes it possible to characterize the content of a specific metal of a whole group of co-genetic sediments by a single value, the content obtained by extrapolation to 100% of the fraction $<100 \mu\text{m}$ are given in Table (4).

The sediments in El-Ryah el Twfiky and its extensions show some enrichment with heavy metals. The iron content varies between 0.28 and 14.35% with an average of 8.66% which is very high compared with the average value of 1.6% found in Rosetta Branch [4]. These high values are attributed to mettalic chips and wastes dumped on the banks of the stream, especially, near Benha, Meit Ghamer and Aga. The contents of manganese varies from 9 to 25.4 ppm with an average of 15.66 ppm which is much lower than the average value of 104.2 ppm obtained from the sediments of Rosetta Branch [4]. The zinc content ranges from 1.07 and 1.96% with an average of 1.35%. The content in Rosetta Branch has an average value of 0.0144% [4], which is too much lower than the value found in El Rayah el Twfiky. Zinc is associated with potassium as indicated from their correlation coefficient of 0.48, The high values of zinc may be attributted to the drainage water from the cultivated lands in addition to metal chips dumped on the banks. The content of titanium in the sediments varies from 0.36 to 1.95% with an average value of 1%. Titanium is associated with calcium and iron as indicated from the correlation coefficient between them. Correlation coefficient between titanium and calcium was found to be 0.8 and between titanium and iron 0.84. Cobalt was found in seven stations only and ranges from 65 to 360 ppm, where in the other stations cobalt was undetectable. Silver in sediments ranges from 0.06 to 0.25% with an average 0.08%. Silver associated with fine particles where the correlation coefficient between it and fractions $<63 \mu\text{m}$ equal to 0.6 and associated also with Mg with a correlation coefficient of 0.5. Chromium ranges from zero, where it is undetectable at 7 stations, and 50 ppm. It is associated with iron where their correlation coefficient is 0.54.

4. Conclusions :

Relatively high levels of the trace elements have been found in the sediments taken from El-Rayah el Twfiky and its extensions in comparison with those of the "average" shale and other river sediments especially for Ti, Co, Zn and Fe. Levels of Mn and Cr are in the same range as those given in Table (5).

The relationship between the trace element concentration, in sediments, and the fraction of particales less than $< 100 \mu\text{m}$ indicates that these elements existed according to the following descending order :



Strict restriction are to be put, from the govermental authorities, against dumping of any waste materials such as metal chips, domestical and industerial effluents even water drains from cultivated lands into or near this vital water course.

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Table (1): A comparison of data on specific surface area, weight loss at 400 & 1000°C, organic carbon, mean particle diameter and elements concentration (ppm).

Sample No.	Na	Mg	Si	P	K	Ca	Ti	Cl	Mn	Fe	Co	Zn	Ag	Specific surface area cm ² /gm	Weight loss at 400°C%	Weight loss at 1000°C (%)	Organic carbon content (%)	Mean particle diameter (µm)	Sediment type
1	19310	28340	1160	10260	17700	14870	40930	163310	163310	12670	2510	396.3	7.04	1.17	0.38	90	mud		
2	40730	7930	208930	1160	12330	23130	18460	83980	139900	11630	690	110.46	0.97	2.72	0.28	200	sand		
3	6010	4410	604730	1160	9350	3010	•	•	320	2800	360	10740	680	92.18	0.36	1.40	0.14	250	sand
4	51040	6920	271030	1170	13690	12740	9400	20940	44790	180	13800	673	14.98	3.58	8.00	0.36	1200	sand	
5	28320	7230	139370	1160	12740	14700	3650	23760	36120	703	13860	650	122.39	3.03	9.79	2.63	90	sand	
6	•	14020	212230	1160	9340	76140	14330	83869	120680	•	13900	620	249.67	7.17	12.92	1.01	20	mud	
7	20735	13810	211660	1158	11770	94960	13380	80930	94290	•	13350	700	208.09	1.77	6.00	0.65	120	silty sand	
8	•	12890	228340	1170	9720	10760	12360	10930	114330	•	14330	370	114.94	3.13	9.38	0.93	200	sand	
9	22170	12720	228350	1160	12513	48330	8340	22930	70570	63	14340	670	204.22	3.37	10.83	1.05	120	silty sand	
10	39190	8940	334190	1160	17630	33230	3330	•	930	62400	110	19380	990	162.36	4.52	8.74	0.72	150	sand
11	•	12900	231480	1160	9033	109240	16290	180890	93410	•	12690	705	176.30	1.36	5.57	0.73	140	silty sand	
12	6330	14020	220660	1160	13270	65410	9970	24710	111405	•	13080	660	40.60	10.44	17.41	1.30	600	sand	
13	•	6037	33213	9350	8345	33410	12832	37860	101310	•	11010	700	60.40	6.92	11.83	1.04	500	sand	
14	•	3344	•	43380	9490	22430	3270	•	730	33480	100	13300	480	163.18	4.48	7.16	1.00	110	silty sand
15	•	5679	•	•	6770	31830	9420	20740	9460	•	13340	900	80.32	7.30	11.38	0.79	130	silty sand	
16	•	3074	•	•	6430	38230	4820	•	1422	54410	160	11330	830	322.23	7.34	13.08	0.98	90	mud
17	•	3810	•	•	7560	30830	9340	•	1002	12210	•	12600	500	96.63	3.16	7.40	1.16	190	mud
18	•	6060	•	•	3401	23290	9140	•	600	81220	•	14330	790	268.7	6.51	10.16	2.04	100	mud
19	2320	3900	•	•	3440	27790	9730	•	1032	114030	•	12410	680	232.6	9.44	14.51	1.23	120	mud
20	2340	3490	•	•	3440	28370	9900	75	810	100510	•	13000	660	223.96	8.31	13.85	1.62	100	mud

* Undetectable concentration.

Table (3): Content of major cations alkali metals and calculated CaCO_3 and MgCO_3 in sediments.

Sample No.	CaO (Wt.%)	CaCO_3 (Wt.%)	MgO (Wt.%)	MgCO_3 (Wt.%)	Total carbonate (Wt.%)	Na_2O (Wt.%)	K_2O (Wt.%)	$\text{Na}_2\text{O}/\text{K}_2\text{O}$
1	10.32	18.43	3.20	6.69	25.12	0	2.47	0
2	32.64	58.28	1.32	2.76	61.04	10.84	3.02	3.59
3	0.42	0.75	0.73	1.53	2.28	1.62	2.25	0.72
4	4.58	8.18	1.15	2.41	10.59	13.76	3.30	4.17
5	2.06	3.68	1.20	2.50	6.19	7.77	3.07	2.53
6	10.66	19.04	2.66	5.56	24.60	0	2.39	0
7	13.29	23.73	2.29	4.79	28.52	5.58	2.83	1.97
8	7.11	12.70	2.14	4.48	17.18	0	2.34	0
9	6.14	10.96	1.79	3.74	14.70	8.67	3.02	2.87
10	4.65	8.30	1.48	3.09	11.39	10.56	4.25	2.48
11	15.36	27.43	2.14	4.48	31.91	0	2.18	0
12	9.19	16.41	2.32	4.85	21.26	1.71	3.20	0.53
13	7.80	13.93	1.00	2.09	16.02	0	2.01	0
14	3.14	5.61	0.89	1.86	7.47	0	2.28	0
15	4.39	7.84	0.94	1.97	9.81	0	1.63	0
16	5.36	9.57	0.84	1.76	11.33	0	1.55	0
17	4.32	7.14	0.96	2.01	9.15	0	1.82	0
18	3.26	5.82	1.01	2.11	7.93	0	1.30	0
19	3.89	6.95	0.98	2.05	9.00	0.62	1.31	0.47
20	4.03	7.20	0.91	1.90	9.10	0.63	1.31	0.48

Table (4): Concentration of different elements at 100% particle size <math><100 \mu\text{m}</math> as extrapolated from Fig. (4).

element	concentration of element (ppm), at 100% particle size <math><100 \mu\text{m}</math> (wt.%)
Cr	45
Zn	12500
Fe	115000
Ag	800
Mn	980
Co	200
Ca	41500
Ti	17000

Table (5): A comparison of maximum values of metal concentrations in sediments from El-Ryah el-Twliky and its extensions with other locations and "average" background level.

Location of sediments and reference.	Metal concentration (ppm)					
	Ti	Cr	Mn	Fe	Co	Zn
Ottawa River [13]	----	22	118	9200	11	84
Rhine River [14]	----	1195	---	----	34	2061
Ems River [14]	----	206	----	----	68	1403
Conway River [15]	5000	100	8500	----	130	1300
Conway Estuary [15]	6000	85	3000	----	40	2000
Firth of Clyde-sludge deposit area, [16]	----	308	1000	61000	40	826
New York Bight-Sludge deposit area, [5]	----	209	----	----	----	415
Humber, Immingham-Grimsby Area, [2]	12000	235	1098	99000	30	519
Nile River, Rosetta Branch, [4]	----	----	330	32100	---	340
El-Ryah el Twliky and its extensions (our results)	19000	50	1400	114000	360	19600
Average Shale [17]	4500	100	850	4700	20	80

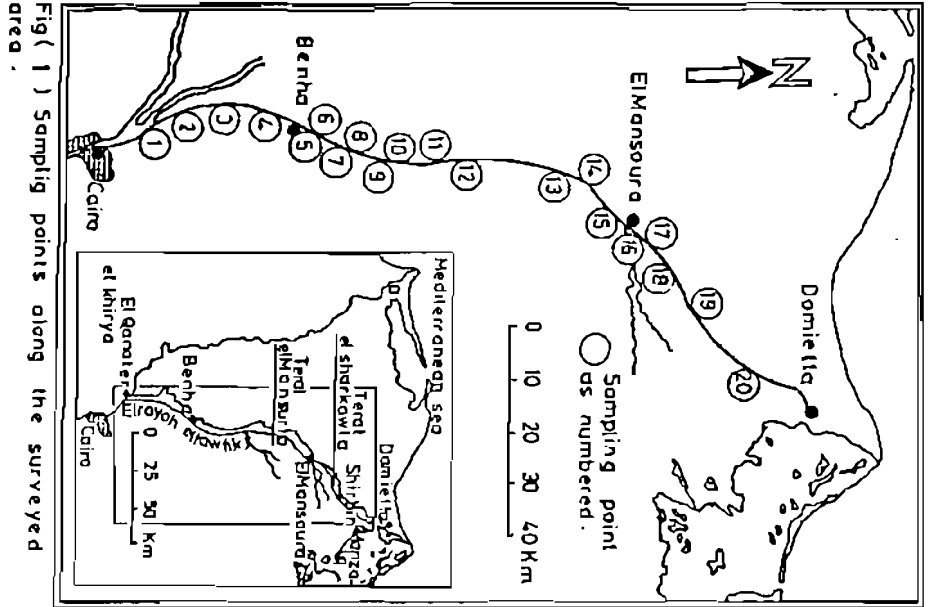
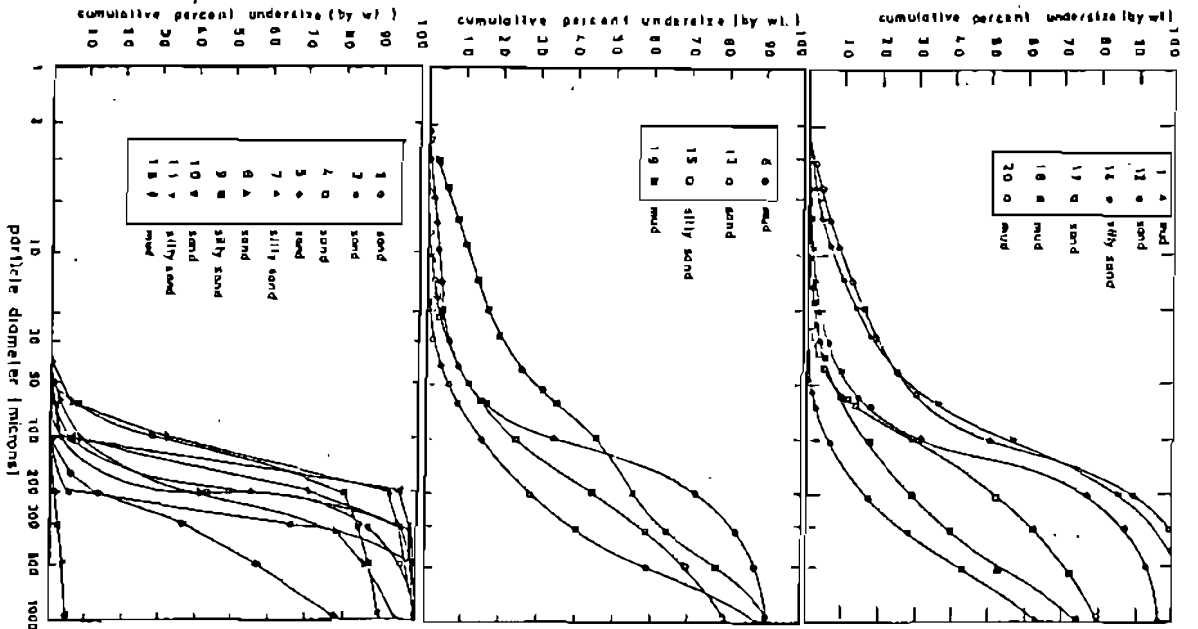


Fig (1) Sampling points along the surveyed area .

- (1) El-Kanater El-Khayria, (2) Barshom, (3) Beltan, (4) Beniha (South A),
- (5) Beniha (South B), (6) Beniha (North), (7) Kafir Shokr (South), (8) Kafir Shokr (North),
- (9) Sahragt El Kobra (10) Kafir El Naeim, (11) Meit Chamri, (12) Beniha (13) Aga,
- (14) Sandoub (15) El-Mansoura (south A) (16) El-Mansoura (south B), (17) El-Mansoura (North), (18) El-Baranoun (19) Shirkein (20) Bosat karrem El Dein



Fig(12): The particle size distribution of sediments

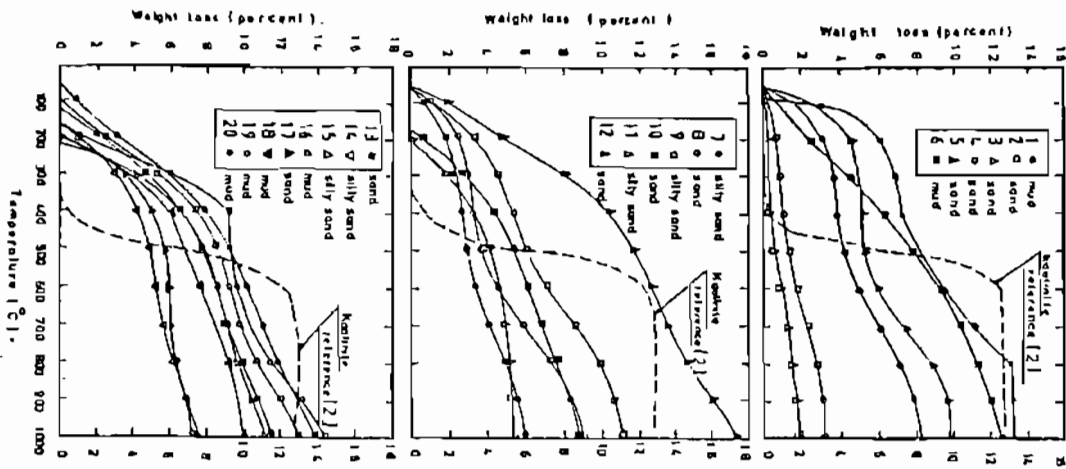


Fig. (3): The TGA curves for sediments

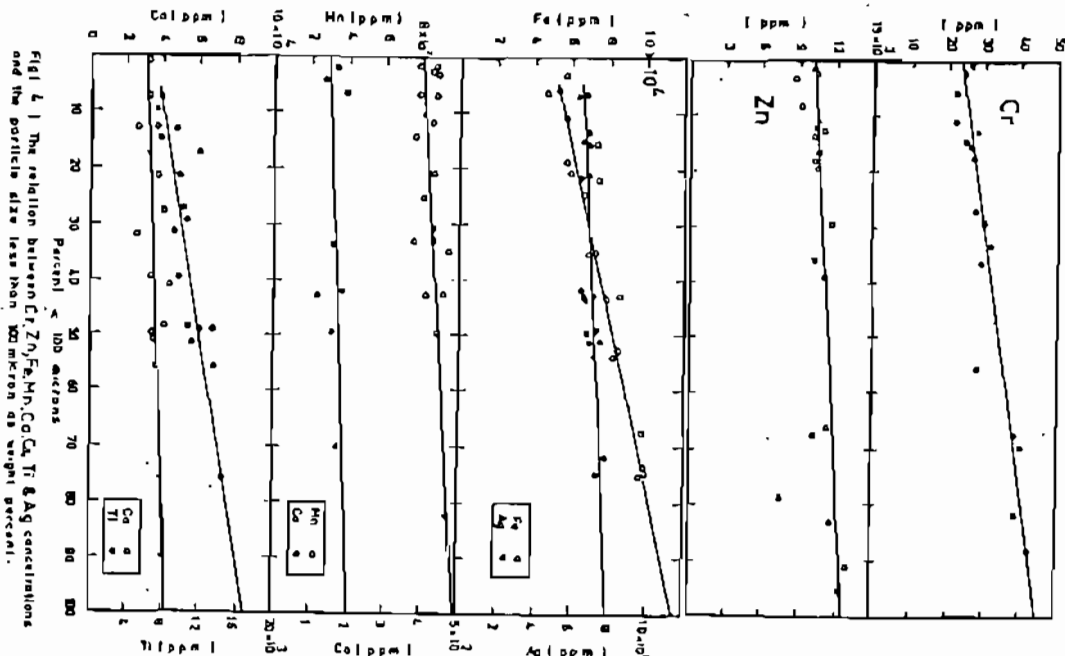


Fig. 4 | The relation between Cr, Zn, Fe, Mn, Cd, Ca, Ti & Ag concentrations and the particle size less than 100 micron as weight percent.