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MAJOR CATIONS LEVELS STUDIES IN SURFACE COASTAL WATERS OF DERNA CITY, (LIBYA)

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ABSTRACT

Sodium, potassium, calcium and magnesium concentrations and their Chlorinity ratios were measured in the coastal surface waters of Derna City (Libya).Eight stations were sampled during autumn (2006) and winter (2007) from surface water .It was found that increasing in the content of these cations during autumn. The low levels were recorded at the near shore stations comparing with the off share ones. The results gave indication that the content and amount of discharged water largely affect the chemical composition of the coastal surface water. The major cation / chlorinity ratio was calculated for the studied area which consists with the fact that the area affected directly with some sources of pollutions. Different statistical treatments were carried out to calculate the correlation coefficients between the major cations.

1. INTRODUCTION

Chemical pollutants are the major concern in the MEDITERRANEAN area and in several marine environments all over the world. A number of these materials can reach the estuarine, coastal area and open water of the Mediterranean Sea from land- based sources (Abel-Halim 2004).

Derna city lies at the northern east side of Libya (with population about 100,000). Its coastal water is subjected to different pollutants. Most of these pollutants are mainly domestic waste water which discharges to the sea directly from several outlets distributed along the shores.

The present study aims to study the distribution of major cations (calcium, magnesium, sodium and potassium) and their chlorinity ratios (for the first time in this area) in order to asses the change of the chemical composition of coastal water affected by land run- off.

2. MATERIAL AND METHODS

The studied area is located between El-Sahel El-Shargi in the East to El-Bokaria station at the west of Derna city. Eight Stations were selected, the surface water samples were collected during autumn (2006) and winter (2007) along two horizontal sections parallel to the shore line. The first section (Stations I, III, V, and VII) was selected at near shore; the second section (Stations II, IV, VI and VIII) was selected at the off shore of the coast (about 5 km from the shore line), Figure (1).

Calcium and magnesium were determined titrimetrically according to American Public Health Association (APHA 1995) using Eriochrome black-T as an indicator. Calcium was determined titrimetrically against EDTA using murxide as an indicator. Sodium and potassium were determined photometrically using a flame photometer Model CM63LB (JENWAY, DUNMOW. ESSEX, U.K). The salinity was measured by an inductive Salinomater (Model 330 WTW. Germany) and Chlorinity was calculated from salinity values (Grasshoff, 1976).

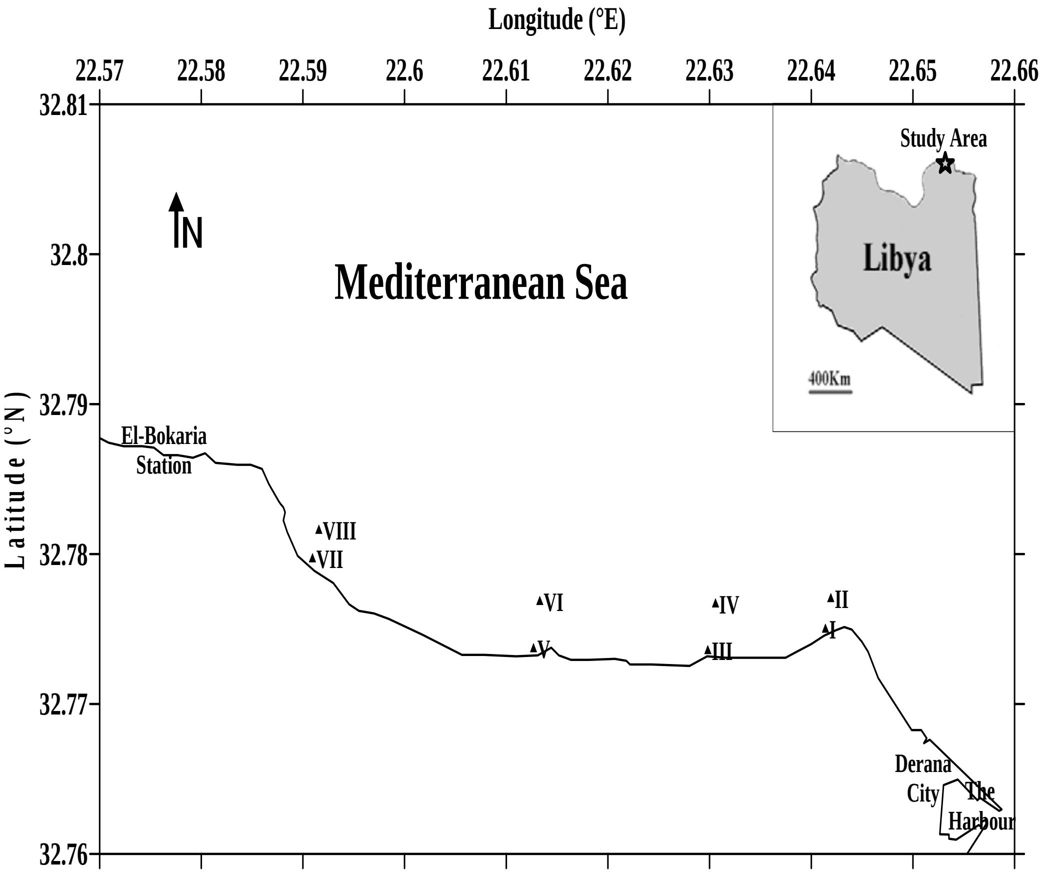

Fig. (1): The area of study.

3. RESULTS AND DISCUSSIOIN

3.1. Calcium:

It is one of the major constituents of the seawater and has a constant ratio to chlorinity (Mahmoud, 1998). Most of calcium is exists in the free form (about 88%). A small part (about 11%) is combined with sulfates and minor parts (0.6% and 0.1%) are present as calcium carbonate and bicarbonate (Mahmoud, 1998).

The variations of calcium concentrations during autumn and winter seasons of area under investigation are given in Tables (1&2) and Figure (2). The contents at different stations were in the ranges of 307.19-531.82 mg/l and 310.80 – 504.30 mg/l, during autumn and winter respectively. The results assianed that, the low values of Ca^{+2} recorded during winter, and may be attributed to the change of temperature with influences the rate of $CaCO_3$ precipitation (Abdel-Halim 2004). The relative increase of Ca^{+2} content during autumn is probably due to some decomposion of organisms containing calcium (Katoh and Keneko 2002).

An increase in calcium concentration with increasing the distance from the shore line is recorded. This may be attributed to dilution caused by the discharged water coming from the out-run off at the coast. The low calcium content value (310.22 mg/l) at station III is mostly coincided with low salinity (30).

A strong positive correlation between Ca and Mg is deduced (r=0.94, n = 16, p > 0.5) which explained the similarity behaviour of calcium and magnesium (Masoud *et al* 2005). The regression equation is given as follow: *Ca= 185.01 +2.81 Mg*

A positive correlation between K^+ and Na^+ is deduced (r = 0.92 and 0.88 n = 16 p > 0.05.

3.2. Magnesium:

It is one of the major constituents in seawater. The chemical speciation of magnesium in seawater is similar to calcium (Masoud *et al.,* 2005). The major species (89%) is free magnesium, about 10% is exists as magnesium sulfate and 0.6- 1% as magnesium carbonate and bicarbonate (Mahmoud, 1998).

The variation of magnesium concentrations during autumn and winter of the area under investigation are given in Tables (1&2) and Figure (2). The contents were fluctuated between 1280.32 –1640.10 mg/l and 1221.19-1650.40 mg/l during autumn and winter seasons, respectively. The lower Mg^{+2} values content were recorded during winter season, (Average 1365.55 mg/l. The lowering of temperature facilitates the precipitation of Mg^{+2} as $MgCO_3$ to the sediment (Abdo 2002).

The relative increase of magnesium concentrations during autumn season, (Average 1424.08 mg/l), may be due to the leaching of the rocks containing magnesium with of high amount of carbon dioxide leading to the magnesium soluble as magnesium carbonate (Hasan, 2006).

The discharge of waste water has also affected on the distribution of magnesium content, when the lower values, (Average 1257.33 and 1289.12 mg/l), were recorded at near-shore stations comparing with that values, (Average 1469.77 and 1559.04 mg/l) , at offshore stations during winter and autumn seasons , respectively .

3.3. Sodium:

It is the most abundant cation in seawater and importance to establish its chlorinity ratio (Mahmoud, 1998)

The seasonal variations of Na^+ values, (Tables 1&2) and Figure (3), showed that the concentrations of sodium were fluctuated between 8.90-11.80 g/l and 8.40-11.70 g/l during autumn and winter seasons, respectively.

The general trend in the horizontal sodium variations was the increase with distance from the shore line. This depends mainly on the amount of brackish water discharged through the out-run off. The high content of Na^+ during autumn, (Average 10.67g/l), may be attributed to release of sodium from sediment into the overlying water (Abdel-satar, 1998). On the other side, the lower values of sodium during winter, (average 10.06g/l), were directly correlated with chlorinity variations, sodium was high positively correlated with potassium (r=0.91 n = 16 p > 0.05). The regression equation is:

K*=64.64* ***Na*** *- 307.08*

Table (1): The concentrations of calcium, magnesium, sodium, potassium and chlorinity in the studied area during autumn (2006)

Parameter / Station	Ca(mg/l)	Mg (mg/l)	Na(g/l)	K(mg/l)	Cl %
I	420.15	1282.32	10.35	390.80	19.66
II	462.28	1447.55	11.75	425.12	20.44
III	307.19	960.37	8.90	230.18	17.16
IV	412.55	1558.09	10.45	408.40	20.22
V	500.07	1435.80	10.21	417.75	20.61
VI	520.64	1590.45	11.40	490.29	20.61
VII	509.20	1480.00	11.55	465.32	20.38
VIII	531.82	1640.10	11.80	480.45	21.22

Table (2): The concentrations of calcium, magnesium, sodium, potassium and chlorinity in the studied area during winter (2007).

Parameter / Station	Ca(mg/l)	Mg (mg/l)	Na(g/l)	K(mg/l)	Cl %
I	345.10	1221.19	9.60	312.20	19.22
II	390.20	1400.27	10.20	340.30	19.55
III	310.80	990.10	8.40	210.19	17.05
IV	374.15	1320.24	9.40	330.15	20.16
V	408.00	1380.39	9.70	361.40	20.11
VI	470.90	1508.20	10.35	370.80	20.77
VII	462.18	1437.65	11.20	390.55	19.88
VIII	504.30	1650.40	11.70	430.15	20.72

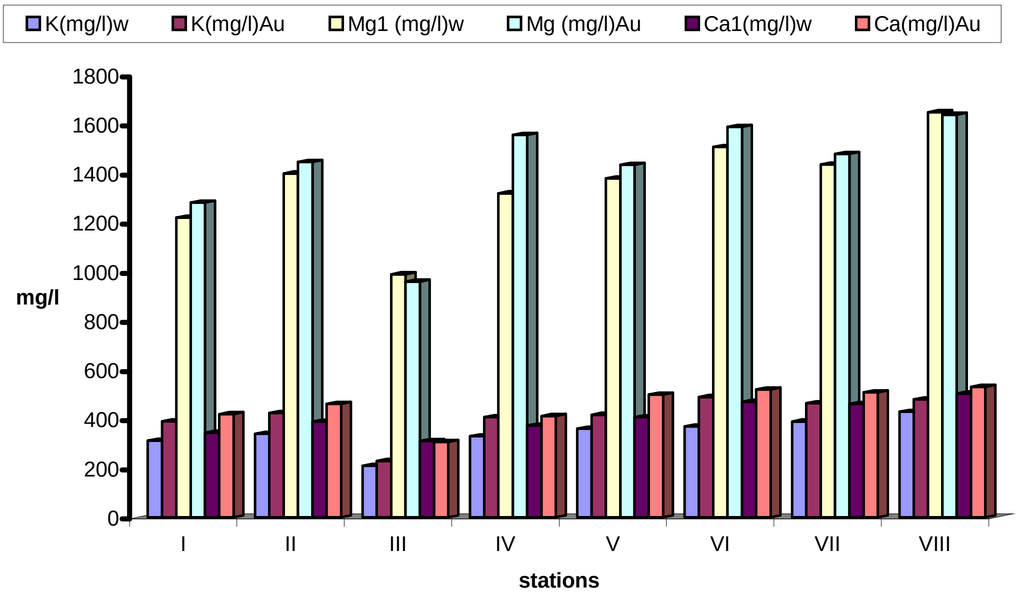

Fig. (2): The concentrations of calcium, magnesium and potassium in the studied area.

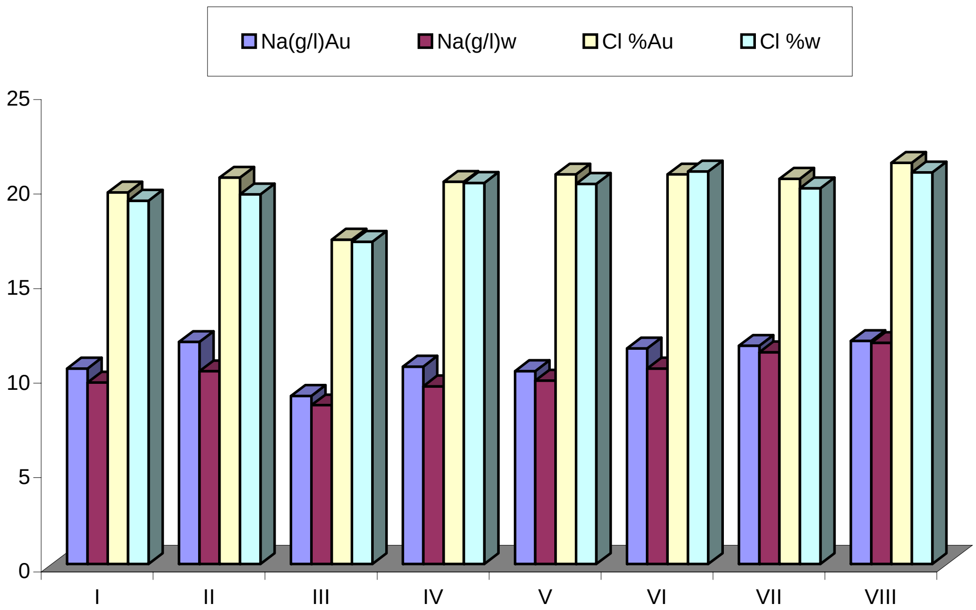

Fig. (3): The concentrations of Sodium and Chlorinity in the studied area.

3.4. Potassium:

Most of potassium in seawater is in the free from (98.8%) and minor part is present as sulfates (Mahmoud, 1998). K^+ is apparently always present in smaller amounts than Na^+, the different tending to increase with salinity.

The variations of K^+ concentrations of the area under investigation, Tables (1&2) and Figure (2), were in the ranges of 230.18-490.29 mg/l and 210.19-430.15 mg/l during autumn and winter seasons, respectively. The low values of k^+ during winter (average 343.15 mg/l) may be related to the precipitation of K_2CO_3 or $KHCO_3$ (Elewa and Latif, 1988) While the high values of potassium contents during autumn (431.53 mg/l) may be due to the dissolution of potassium and release to the over layer waters.

In general, the minimum values were recorded at near shore stations comparing with the offshore ones, this mainly attributed to dilution caused by the discharging of out-run off water.

3.5. (Major Cations / Chlorinity) Ratio:

The average of major cations chlorinity ratios are calculated from the average concentrations of major cations and the average concentrations of chlorinity, Table (3).

The Ca/Cl assesses the change on the chemical composition of coastal water seawater affected by the run- off of the discharged water. The minimum and maximum Ca/Cl values of 0.018 and 0.024 were detected at station III and VIII, respectively. The lowest value of Ca/Cl is probably due to the dilution by discharged water, and / or may be due to the probable precipitation of $CaMg(CO_3)_2$, $CaSO_4$, $Ca_3(PO_4)_2$, ect. (Masoud *et al.*, 2003).

The Mg/Cl ratio for the stations under study is varied between a minimum value of 0.060 at station (II) and a maximum value of 0.078 at station (VIII). The minimum values are mainly due to the effect of brackish water and may be attributed to the precipitation of $MgCO_3$, $MgSO_4$ and $CaMg(CO_3)_2$, ect (Masoud *et al* 2003).

Also, the lower values of Na/Cl ratio are recorded at stations which receive influents of brackish water. While the high Na/Cl ratio value of (0.565) was recorded at station (VII), Table 3. This ratio is higher than that reported for normal seawater (Table 3).

The results showed that, the K/Cl ratio is ranged between (0.013-0.022). The low value, (0.013), at station (III) is mainly attributed to the brackish water (Hemaida et al 2007).

Comparison between the results obtained in the present study with the published data, Table (3), it is concluded that the present values are differ from those given by Culkin and Cox (1966) for normal seawater. It is observed that, the Mg/Cl and Ca/Cl ratios are higher than that reported, except for station III which recorded low value. On the other side, the K/Cl ratio is lower that reported especially station III (0.019).

Also the lower ratios of Na/Cl are recorded at near shore stations and they are lower than published for the normal seawater, probably attributed to the region of study is affected by the discharge of the brackish water.

Table (3): The concentrations of calcium, magnesium, sodium and potassium chlorinity ratio and major cation chlorinity ratios for proper sea (Normal seawater)

Ratio / Station	Ca/Cl	Mg/Cl	Na/Cl	K/Cl
I	0.019	0.064	0.513	0.018
II	0.021	0.071	0.548	0.019
III	0.018	0.060	0.537	0.013
IV	0.019	0.071	0.491	0.018
V	0.022	0.069	0.448	0.019
VI	0.023	0.047	0.525	0.020
VII	0.024	0.075	0.565	0.021
VIII	0.024	0.078	0.562	0.022
Proper seawater	*0.021*	*0.066*	*0.555*	*0.020*

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