Bull. Inst. Oceanogr. & Fish. ARE, 14 (1) 1988: 283-292.

THE ION-ANOMALIES IN THE WATER OF ALEXANDRIA WESTERN HARBOUR

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ABSTRACT

The main components of sea water in Alexandria Western Harbour were measured at different depths during the four seasons of 1985. Also, the same components were analyzed in the interstitial water of the surficial sediments of the same selected stations.

All Cl-ratios of the investigated ions show strong deviations from the constant ocean ratios. In the water, calcium, sulphate and bromine Ca^{2+}/Cl, SO_4^{2+}/Cl and Br^-/Cl ratios of 0.0186, 0.117 and 0.00281 respectively, show strong negative deviations from the Ocean ratios. In the interstitial water, these three chlorinity ratios, on average, are much lower than in the water above. The average value of Mg^{+2}/Cl ratio for water on interstitial water samples of 0.0669 is similar to the ocean ratio. Specific alkalinity of the water samples, on the other hand, shows strong positive deviation from normal, being 0.143.

Different equations were deduced between the concentration of the studied ions in water and chlorinity but can not be applied on a wide scale owing to the high standard deviations.

The continuous disposal of domestic, industrial, drainage and fresh waters into the Harbour affects the constancy of most ions in the sea water and consequently the correlation coefficients between these ions tend to be weakend ($r < \pm 0.52$).

INTRODUCTION

In spite of the great economical importance of Alexandria Western Harbour, no detailed studies on its main components in the water have been done.

The Harbour lies along the Mediterranean coast of Egypt to the west of Alexandria town between lat. 31° 07⁻ and 31° 13⁻ and long. 29° 47⁻ and 29° 53⁻ (Fig. 1). It is a shallow semielliptical basin, situated in a subtropical area and almost completely surrounded by lands and artificial breakwaters. The Harbour has an area of about 1,862 acres, maximum depth of 16 m and opens to the sea by a relatively narrow mouth "El-Boughaz".

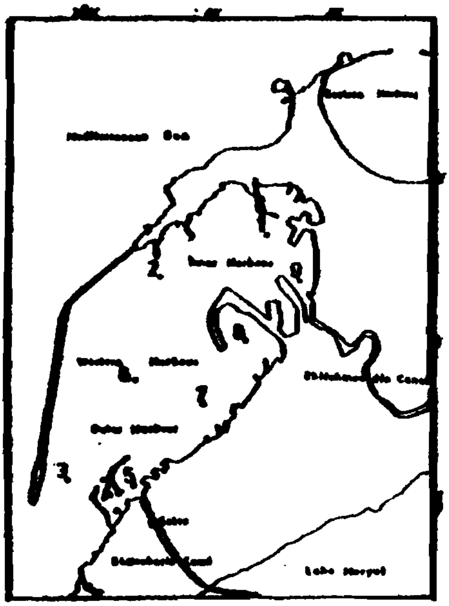

FIG. 1
Location of sampling stations.

About 90,000 m^3/day of domestic, industrial and drainage waters loaded with suspended materail, discharge into the Harbour through El-Noubaria Canal. Another Canal, El-Mahmoudia, was once opened into the Harbour through a water gate but recently it is seized to flow in. The Harbour receives also many pollutants directly from the neighbourhood, in addition to the different human activities and vessels reamins.

The dominant constituents of the Harbour bottom sediment are silt, colloidal clay, carbonate shells, domestic and complex industrial wastes as well as solid pollutants, rubbish crude oil, vessels remains and sinking materials (Rifaat, 1982).

The present work aims at determining the chemical changes in the ionic composition of the Harbour water and interstitial water, particularly the major constituents, caused by pollutants. Deviations of ions-chlorinity ratios from the oceanic ratios reflect the influence of pollutants input on the water composition. Different relations and correlations between the studied ions and chlorinity of water were also deduced.

MATERIALS AND METHODS

Nine stations were chosen to represent the different regions of the Harbour (Fig. 1). Water samples were collected seasonally from different depths at each station during the year 1985. Interstitial water was also obtained from sediments at these stations using an efficient centrifuge. Samples were filtered through a fine textured filter paper G.F.C. to free them from any filamentous algae, sediment and any solids. 155 samples were analysed to estimate calcium, magnesium, sulphate, bromine contents and alkalinity of water as well as salinity.

Salinity was determined by measuring the electrical conductivity of water samples using induction salinometer, Beckman model R-5-7 B. The conductivity ratio was converted to salinity using the standard tables and making temperature corrections. Chlorinity was calculated from salinity according to the following formula:

$$S‰ = 1.80655\ Cl\ ‰.$$

Calcium and magnesium were determined titrimetrically according to the method of Heron and Mackereth (1960) using Eriochrome black T as an indicator. Calcium was also determined against EDTA using another indicator (Murexide). Sulphate was determined gravimetrically according to the method of Bather and Riley (1954) and revised by Grasshoff (1967). Bromide was analysed following the method of Morris and Riley (1966) and subsequently revised by Grasshoff (1967).

RESULTS AND DISCUSSION

Salinity:

Water: The open water of the Mediterranean Sea has a normal salinity between 38 and 39‰. Morcos and El-Rayis (1973) found salinities around 39‰ to the north of Alexandria. At El-Mex, west of Alexandria, the salinity varied from 38.43 to 39.10‰ (Asaad, 1981). Values below 38‰ were recorded mainly in coastal water and semi-enclosed areas, in the Eastern Harobour of Alexandria (Megally, 1970) and Shriadah (1982) found averages around 37‰.

Salinity is affected by several factors such as rate of renewing, rate of sewage and fresh water inflowing, rate of evaporation, precipitation and other physical and climatic conditions. In the Western Harbour, owing to the disposal of domestic and drainage water into it, salinity can be decreased to 20‰ at El-Mahmoudia area. El-Awady (1972) found values below 5‰ at this area.

The effect of dilution on the salinity of the Harbour water showed seasonal trend. 30% of samples above 38‰ was found during spring, increasing to 45% in summer and to 78% in autumn. When the Harbour renewed most of its water during winter, values below 38‰ were rarely detected. Surface water, particularly near outlets, showed relatively lower salinity than bottm water.

Interstitial Water: Salinity widely fluctuated in the interstitial water (22.14-48.16‰) but its average value of 38.13‰ is closely similar to that of water above. The following table shows the proportion of salinity (Interstitail water/Water) for different localities which varied from 0.86 to 1.11 at stations 1 and 5, respectively.

The variation of salinity in the interstitial water was largely correlated to sediment type. Relatively high salinity was found in the muddy bottom samples in front of El-Noubaria Canal. The low salinity values recorded at most stations indicate dilution by fresh water which is usually polluted.

Stations	1	2	3	4	5	6	7	8	9	10
S‰ (Water)	38.41	38.27	37.85	38.07	37.91	38.28	38.31	38.61	36.55	38.03
S‰ (Interstitial water)	33.14	35.21	34.94	37.77	42.19	35.80	38.60	41.47	36.34	38.13
S‰ Interstitial water / water	0.86	0.92	0.92	0.99	1.11	0.94	1.01	1.07	0.99	1.00

Calcium:

The calcium content reached its maximum of 0.487 g/kg in the surface water at station 8 as well as in the bottom water at St. 1, both were recorded during winter. Only these two samples gave positive deviations in Ca/Cl ratios (0.0227 and 0.0224) when compared with the oceanic ratio (0.0216) of Culkin and Cox (1966). The rest of the values lie below normal, being between 0.0215 and 0.0124.

Except the relative high calcium chlorinity ratios of winter samples (average 0.0202), there were no significant seasonal variations during the rest of the year where the averages are around 0.0180 (Fig. 2). The total average of calcium content, 0.392 g/kg met a chlorinity average of 0.0186.

In front of El-Noubaria Canal, where a large amount of drainage water and industrial wastes rich in calcium flow into the Harbour, calcium content and its chlorinity ratio attained maximum annual averages being 0.4091 g/kg and 0.01955, respectively. The area at El-Mahmoudia Canal, St. 9, which receives mainly domestic water, reflects minimum annual average of calcium content (0.360 g/k) which meets a chlorinity ratio of 0.01784.

The vertical distribution of calcium in water follows more or less that of chlorinity where the values tend to increase slightly downwards, while Ca/Cl ratio showed a rise of 1×10^{-5} each 5 m depth.

Calcium content and its chlorinity ratio in the interstitial water widely differ both seasonally and regionally. Interstitial water is relatively poorer in its calcium content than the water column above. The concentration ratio (interstitial water/water) for calcium content was 0.79, 0.75 and 0.71 for winter, summer and autumn, respectively and the calcium chlorinity ratio in the interstitial water did not exceed 0.80 that of the water.

Regionally, El-Noubaria area, which receives drainage water rich in its calcium content, gave maximum annual average for water and interstitial water. Interstitial water of the sediment near the Harbour-Sea opening contains calcium content only 0.55 that of the water above.

Magnesium:

Magensium content varied from 1.7139 g/kg in the subsurface water of St. 7 to 0.7479 g/kg in the surface water of St. 9, both values in autumn. According to seasonal averages, autumn samples showed minimum magnesium content while the summer ones gave maximum, being 1.3763 and 1.4669 g/kg, respectively. Winter and spring averages are nearly similar and occupy intermediate values around annual average (1.4080 g/kg)

Inspite of the wide variation of Mg/Cl ratio (0.0481-0.0804), the annual average calculated for water or interstitial water samples was similar to oceanic ratio (0.669) of Culkin and Cox (1966).

Mg/Cl ratio showed seasonal variations similar to magnesium. Spring and summer ratios were mostly high and positively deviating while winter and autumn ones were found below normal (Fig. 2).

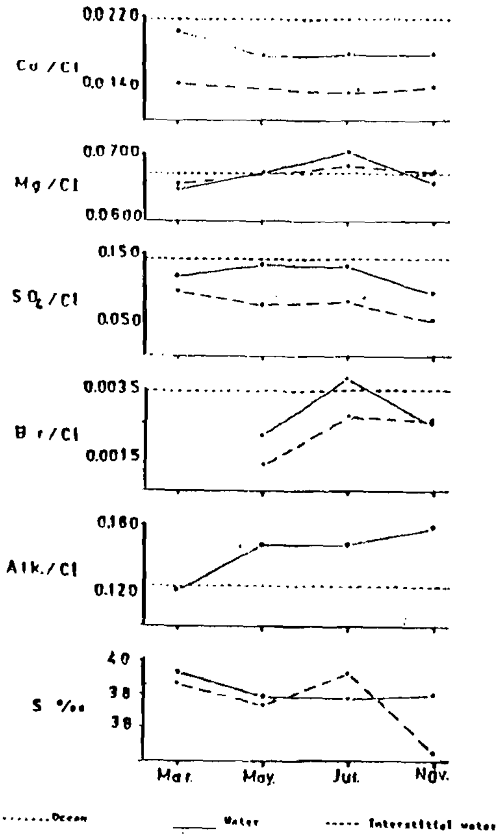

FIG. 2
Seasonal variation of ions/chlorinity ratios in water and interstirial water (1985) compared with salinity values and Oceanic ratio.

Regionally, St. 8 showed the highest annual average for Ca and Mg ratios while St. 3 gave the lowest averages.

It is noticed that the average concentration of magnesium in the interstitial water did not differ greatly from that in the corresponding water above, Consequently the chlorinity ratio shows the same trend as given in the following table:

Stations	1	2	3	4	5	6	7	8	9	1-9
Water	0.0637	0.0650	0.0625	0.0675	0.0688	0.0679	0.0690	0.0692	0.0708	0.0669
(Interstital water)	0.0669	0.0653	0.0699	0.0662	0.0653	0.0669	0.0656	0.0689	0.0670	0.0669

Sulphate:

Sulphate content in the Harbour water showed narrow range of concentrations closely to its annual average of 2.465 g/kg.

Summer and spring averages represented the highest values while autumn reflected the lowest ones and winter samples gave intermediate sulphate content. The mixing of poor oxygenated bottom water, created stagnation during summer with well oxygenated surface water under the effect of fall turbulence diminishes most of sulphate from the water column.

Sulphate ions showed irregular vertical variations; at St. [illegible]. The content tends to decrease upwards. the domestic water poor in oxygen content inflowing near this area may be responsible for sulphate reduction throughout the surface water layer.

Sulphate/chlorinity ratio follows more or less salinity and its average is lying below the oceanic ratio, 0.4100, of Morris and Riley ([illegible]). Only 4 water samples showed slightly positive deviations from normal.

Interstitial water, as expected, contains lower sulphate concentration than the water column above as shown in the following table, taking the annual average in consideration:

Stations	1	2	3	4	5	6	7	8	9	1-9
(Water)	2.706	2.475	2.532	2.374	2.345	2.452	2.477	2.431	2.389	2.437
(Interstital water)	1.462	1.315	1.577	1.168	1.891	1.829	0.783	1.533	1.063	1.493
Interstital water / Water	0.54	0.53	0.62	0.49	0.81	0.75	0.32	0.63	0.44	0.61

The concentration proportion (interstitial water/water) reached its maximum at El-Noubaria area (0.81), as in calcium condition, which is affected with fresh drainage water, where the proportion drooped to its minimum of 0.32 at St. 7.

SO_4/Cl ratio in interstitial water shows strong negative deviation from normal. It reached 0.009 at El-Mahmoudia area influenced with anoix condition occurred during most of the year in the surficial sediment where hydrogen sulphide gas could be easily smelled.

Alkalinity:

The water alkalinity ranged between 4.34 m.e./l in autumn and 2.16 m.e./l in winter, both were surface samples collected at stations 9 and 1, respectively.

Except the low winter average of 2.8 m.e./l, the alkalinity showed slight seasonal variation around an annual average of 3.00 m.e./l.

High alkalinity measured in the surface water at El-Mahmoudia area was associated with a sharp drop in salinity casued by domestic water input which increases specific alkalinity to its maximum value of 0.153.

Alkalinity/chlorinity ratio, specific alkalinity, with an annual average of 0.132 is higher than that of the Alexandria Eastern Harbour water estimated by Shriadach (1982). However, the ratios average for both Harbours are slightly lower than that recorded in front of El-Mex pumping station near the sea opening of the Western Harbour (Mahlis et al., 1970). Both Harbours ratios are lying above normal when compared with the oceanic ratio of 0.123 (Wattenberg, 1933) or even of 0.126 (Koczy, 1956).

Bromine:

The bromide content was widely fluctuated in the water (0.0269-0.0762 g/kg) with an exceptional maximum of 0.1784 g/kg detected at El-Mahmoudia area during summer. The surface water, in general, is slightly lower in its bromide content than the subsurface water.

According to the constant oceanic chlorinity ratio of 0.00347 (Thompson and Korpi, 1942) most of the summer values showed positive deviations while the rest of samples were mostly below normal. Only two chlorinity ratio values, recorded at stations 2 and 6 during summer, are similar to normal. The relative high rate of paint leaching from the vessels landed in the harbour, ships exhaustion and other pollutants in addition to human activity may be responsible for the summer maximum.

The concentration of bromide ions in interstitial water follows that in the corresponding water, showing also maximum summer average.

The proportion of ions concentration (interstitial water/water) varied from 0.46 in front of El-Noubaria gates to 1.21 at St.8. The chlorinity ratios for interstitial water or water above at the latter station are identical (0.00249). The chlorinity ratio in the interstital water is higher than that in water above only at St. 6 as given in the following table:

Stations	1	2	3	4	5	6	7	8	9	1-9
(Water)	0.00275	0.00264	0.00262	0.00269	0.00290	0.00283	0.00263	0.00249	0.00404	0.00281
(Interstitial water)	0.00230	0.00204	0.00168	0.00182	0.00125	0.00289	0.00174	0.00249	0.00261	0.00214

It is clear from the table that the annual averages of chlorinity ratios in the water or interstitial water are storngly negatively deviated from the oceanic ratio. The water samples at El-Mahmoudia area, the highly polluted station, reflect chlorinity ratio above normal.

DISCUSSION AND CONCLUSIONS

1- Chlorinity Ratios Deviation:

Water: In respect of the ocean ratios, the average Ca/Cl ratio of 0.0186 lies below normal, meanwhile, the mean Mg/Cl ratio is similar to the oceanic value. Sulphate/chlorinity as well as Br/Cl ratios, on average, are very low if compared with ocean, being 0,117 and 0.00281, respectively. Specific alkalinity, on the other hand, is higher than normal, being 0.143.

Interstitial water: Except Mg/Cl ratio, all the studied ions showed chlorinity ratios, on average, lower than that in the water column above, and consequently deviate strongly negative from the oceanic ratios. Mg/Cl ratio, on average, is similar to that in the Harbour water or in ocean ([illegible]. The other ratios are; 0.0139 for calcium, 0.071 for sulphate and [illegible] for bromide.

2- Ions- Chlorinity Relations:

Many attemps have been done to calculate certain relationships between different ions concentrations and chlorinity in the Western Harbour water whose summaries as follows:

$$Ca^{2+}\ (g/kg) = 0.0203\ Cl‰ - 0.0356$$
$$Mg^{2+}\ (g/kg) = 0.0635\ Cl‰ + 0.0718$$
$$SO_4^{2-}\ (g/kg) = 0.130\ Cl‰ - 0.280$$
$$Br^-\ (g/kg) = 0.102 - 0.00277\ Cl‰$$
$$Alkalinity\ (m.e./l) = 5.83 - 0.135\ Cl‰.$$

Unfortunately, the standard deviations in all the above equations is too high with great scattering of some data and consequently these relations could nor be applied on a large scale for the different regions of the Harbour.

3- Ions-Correlations

Correlation coefficients between the studied ions, in general, are small, being $< \pm 0.52$. Calcium, magnesium and sulphate showed positive correlations with chlorinity while alkalinity is negatively correlated.

Calcium is also negatively correlated to each of bromide of alkalinity $r > -0.45$. The weak correlation coefficients between the different ions reflect the deviation of the Harbour water from normal sea water under the effect of pollution.

4- Seasonal Variation:

Since the Harbour water undergoes pronounced changes in salinity a seasonal variation in the ions chlorinity ratios might be expected. A good agreement was found between water salinity and Ca/Cl ratio during winter (maximum).

In the interstital water maximal Mg/Cl and Br/Cl average ratios meet maximum salinity average during summer while minimum SO_4/Cl ratio average is corresponded to minimum salinity in autumn.

Contrary to the trend of salinity, the minimum Mg/Cl ratio together with the maximum salinity occurred during winter while the maximale averages of Mg/Cl and Br/Cl ratios were accompanied by minimum salinity in the water during summer.

5- Regional Variation:

The continuous discharge of drainage water loaded with suspended materials into the Harbour, particularly in front of El-Noubaria Canal, enriched the Harbour water with different ions. Silts and other wastes tend to precipitate at this area and make a muddy deposits (El-Awady, 1972) with high efficiency to adsorb ions from the water above. Interstital water exhibits at this area maximum concentrations of chloride, calcium, magnesium and sulphate ions.

At the Harbour-sea opening, on the other hand, the sediment tends to be much coarser and then its interstitial water exhibits minimum calcium and magnesium contents. The water column at this area showed minimal Ca and Mg-chlorinity ratios.

Near El-Mahmoudia area, the strong polluted region in the Harbour, the average concentration of bromine in the water is about 1.5 times greater than the average other stations. The specific alkalinity and Br/Cl ratio at this area are strongly positive deviated from ocean, being on average, 0.153 and 0.00402, respectively. Maximum Mg/Cl ratio is mainly attributed to the dropping in salinity caused by dilution.

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