Egypt. J. Aquat. Biol. & Fish., Vol.7, No.4 :283 - 312 (2003) ISSN 1110 – 6131

SEASONAL VARIATIONS OF TRACE METALS LEVELS IN WATER AND THE LIMPET *PATELLA CAERULEA* OF ALEXANDRIA COAST, EGYPT.

Sabry S. El-Serafy[1], Mona M. El-Gamal [2] and Dalia S. El-Sayed[1]

1-Zoology Department. Faculty of Science, Zagazig University. (Benha branch). Egypt.

2-Zoology Department, Faculty of Science, Tanta University, Egypt.

Keywords: trace metals; seasonal variations; rocky shores; *Patella caerulea*

ABSTRACT

The whole soft tissues of the *Patella caerulea* from Abu-Qir, El-Anfushi and El-Mex stations in Alexandria were seasonally analyzed during the period from Autumn 2001 to Summer 2002, to determine the levels of Cd, Co, Cu, Fe, Pb and Zn to reveal their patterns of accumulation throughout different seasons. The correlation between seasonal variations and the nature of investigated stations in metal concentrations was significant. Summer recorded the highest concentrations of Cu and Zn and the lowest one for Pb. Winter recorded the lowest concentrations of Fe, Zn and Cd, while Co recorded its highest concentration in the same season. Fe recorded its highest concentration in Spring, while Autumn recorded the highest concentrations for both Cd and Pb.

On the other hand, Cd, Pb and Zn concentrations in water and tissues revealed highly significant differences for stations and seasons. Co, Cu and Fe concentrations in water revealed marked differences for both seasons and stations. There were no marked differences between seasons for Co, Cu and Fe that accumulated in the soft parts of *Patella* tissues, while stations were significant. The highest values of Cd and Pb was reported for samples collected from El- Mex in Autumn, while the highest ratio of Cu was revealed for the same station but in Summer. The highest concentration of Co appeared in Autumn from El-Anfushi, while its lowest concentration during the same season was in Abu-Qir. Fe recorded its highest concentration in Abu-Qir station in Spring. While El- Anfushi presented the highest concentration of Zn in Summer.

So it can be concluded that the concentrations of the studied metals associated with the soft tissues of *Patella caerulea* varied over the seasons and sampling sites. Summer and Autumn showed higher accumulation of trace metals in *Patella* tissues than the other seasons. There was a positive correlation between trace metals and levels of salinity and seasons, where the concentration of some trace metals increased in Summer with lower salinity as in El-Mex station. Finaly the soft tissues of *P. caerulea* can be considered as a potential indicator, reflecting the environmental pollution by the present trace metals.

INTRODUCTION

Despite the low concentration of heavy metals in the surrounding medium, aquatic organisms take ; accumulate them up in their soft tissues to concentrations several folds higher than those of the ambient levels (Bryan, 1979 & Rainbow, 1990). The usefulness of molluscs as sentinel organisms in metal biomonitoring studies is widely recognized (Rainbow, 1990 , 1997; Langston and Spence, 1995; Brown and Depledge, 1998). Generally, metal concentrations in the soft tissues show greater variability due to seasonal weight changes (associated with physiological conditions and reproductive state). Due to this fact, some authors tried to avoid seasonal variations. When considering metal concentrations in the soft tissues of marine mollusks, they are correlated with shell weight, using metal/ shell weight indices (Soto *et al.*, 1995 & 1997; Carvo *et al.*, 2003). Lingard *et al.* (1992) and Cravo *et al.* (2003) have postulated that shells have important practical advantages over the soft tissues to monitor metal contamination of the aquatic environment to avoid seasonal variations and that shells integrate elemental concentrations over the life of the animal. Also uptake of heavy metals from solution by seaweed is influenced by factors such as light , temperature, salinity, season and presence of other pollutants in the surrounding water (Lobban and Harrison 1997). Rice *et al.* (1973) stated that, the order of metal toxicity to algae varies with the algal species and the experimental conditions. Due to the above reasons, the creatures may not accurately reflect metal concentration in water, beside the nature of the rocky intertidal habitat between the lowest and highest tidal levels. Organisms living in that area must be able to withstand periodic dessiccation. high temperature and light, low salinities and strong wave action (Nybakken,1982). However, insufficient information was available to comment further on the particular sensitivity of any species within the biotope.

This study aimed to examine the effect of the seasons on the concentrations of Cd, Co, Cu, Fu, Pb and Zn in water and *Patella caerulea* taken from three different stations and to detect which season is preferred to use this species as food by other animals and to establish the sensitivity of *Patella caerulea* to such pollutants within the biotope.

MATERIALS AND METHODS

1- Study areas:

Three stations (Abu-Qir, El-Anfushi and El-Mex), were selected to collect limpets. These stations represent different habitats on the Mediterranean coast. Rocky shores were visited seeking for *Patella caerulea* during Autumn 2001 to Summer 2002 .

2– Ecological investigation:

Physico-chemical parameters of water, as water temperature (°C), salinity (‰), Hydrogen ion concentration (pH) and Dissolved Oxygen (DO) were determined seasonally. The latter was determined by using modified Winkler method (APHA, 1992).

3- Determination of heavy metals:

3-1- Heavy metals in water:

Three water samples from each station were analysed for Cd, Cu, Co, Fe, Pb and Zn concentrations, by using Atomic Absorption Spectrophotometer (AAS). Results obtained were expressed in (ppm).

3-2- Heavy metals in limpet tissues:

The heavy metals Cd, Cu, Co, Fe, Pb and Zn were measured in limpet tissues according to Dalziel & Baker (1983) and Dybern (1983). The soft parts of three Patella caerulea individuals from each station were weighed, then 5 ml of freshly prepared 1:1 V/V Hydrogen peroxide/conc. Nitric acid was added to each of them in glass tubes, that were then covered and placed aside for about an hour until the first reaction subsides, then the tubes were placed in sand bath on a hot plate at about 160°C for about 2 hours till complete digestion. The solutions were cooled and diluted to 25 ml by distilled water. Heavy metals were determined in this solution by using AAS. The concentrations of heavy metals in the soft tissues were determined from the following equation:

Element concentration in the sample (µg/gm wet weight) = (CXV) ÷ W
Where: C = conc. of element in the solution.
V = volume of the solution.
W = weight of the sample.

4– Statistical analysis:

The Statistical Package for Social Science (SPSS). Two-way ANOVA were employed to find stations, seasons and stations X season differences. The t-test was used to confirm the differences of heavy metals concentrations between the seawater and limpet soft tissues at different stations and seasons.

RESULTS

1- Physico-chemical parameters of water:

1-1- Temperature (°C):

Surface water temperature recorded a marked seasonal fluctuation as shown in Table (1). It ranged from 18.467±0.033 and 28.633±0.033°C. The average minimum temperature value was recorded in Winter (18.611±0.065°C) and the maximum one in Summer (27.944±0.175°C). Regarding stations variations, minimum temperature was recorded at El-Anfushi (22.942±0.990 °C), while the maximum one was recorded at Abu-Qir (23.525±1.122°C). The mean temperature for stations reached 23.233±0.580°C.

1-2- Hydrogen ion concentration (pH):

The pH values at the studied stations ranged between 7.357±0.009 and 8.067±0.024, with an average value of 7.661±0.036 (Table 2). Seasonal variations showed that, Autumn 2001 and Winter 2002 have the lowest pH values (7.474±0.046 and 7.499±0.011 respectively), while Spring and Summer 2002 recorded the highest pH values (7.842±0.032 and 7.829±0.060 respectively). Regarding to stations, El-Mex and El-Anfushi had the minimum values (7.598±0.055 and 7.627±0.057 respectively) and Abu-Qir had the maximum value (7.758±0.066). Analysis of variance for pH (ANOVA) showed that pH concentrations showed highly significant differences for both stations and seasons.

1-3- Salinity (%o):

As shown in Table (3), salinity varied between 24.400±0.058 and 38.667±0.033%o. Seasonal variations showed that, Winter had the lowest value of salinity (33.056±2.164%o) while Summer had the highest value (33.956±2.103%o). Stations variations showed that, El-Mex had the lowest value (24.992±0.131%o) and Abu-Qir had the highest value (38.092±0.152%o). The mean salinity for stations reached 33.544±1.025%o. Analysis of variance for salinity (ANOVA) revealed that highly significant differences for both stations and seasons.

1-4- Dissolved Oxygen (DO):

Dissolved oxygen throughout studied period at different stations ranged between 4.367±0.088 and 7.933±0.033 mg/l with an average value 5.508±0.165 mg/l (Table 4). Seasonal variations of dissolved oxygen showed the lowest value in Summer (4.689±0.155 mg/l) and maximum value in Autumn (6.478±0.376 mg/l). Stations variations indicated minimum oxygen value at El-Mex (4.842±0.122 mg/l) and maximum value at Abu-Qir (6.325±0.328mg/l).The analysis of variance in dissolved oxygen at the different stations and seasons, revealed highly significant differences for stations and seasons ($P \leq 0.01$).

1-5- Biochemical Oxygen Demand (BOD):

As shown in Table (5), the biochemical oxygen demand (BOD) ranged between 2.167±0.033 and 5.833±0.033 mg/l. The average BOD value being 3.686±0.204 mg/l. The lowest mean value was recorded in Summer (2.678±0.172 mg/l), while the maximum BOD value was recorded in Autumn (4.356±0.383 mg/l). Variation of BOD values at different stations revealed the lowest value at El-Mex (2.692±0.126 mg/l) and the highest value at Abu-Qir (5.025±0.307 mg/l). The analysis of variance in BOD at different stations and seasons revealed that the BOD concentrations recorded highly significant differences for both stations and seasons ($P \leq 0.01$).

2-Trace metals concentrations:

2-1- Cadmium (Cd) :

2-1-A : In sea water

The concentration of cadmium in sea water surface of the studied stations (Table 6 and Fig.1) recorded that the minimum values in Winter and Spring 2002 (0.061±0.007 and 0.066±0.007 μg/ml respectively) and the maximum values in Autumn 2001 and Summer 2002 (0.081±0.009 and 0.078±0.009 μg/ml respectively). Stations variations showed that, Abu-Qir and El-Anfushi had the lowest values (0.058±0.003 and 0.056±0.003 μg/ml respectively) and El-Mex had the highest one (0.100±0.005μg/ml). The average value of cadmium concentration reached 0.071±0.004 μg/ml. Analysis of variance for Cd concentration in water. Analysis of variance (ANOVA), revealed highly significant differences for stations and seasons. $P \leq 0.01$, while non-significant for stations X seasons, $P \geq 0.05$.

2-1-B : In *Patella* tissues

The total mean Cd concentration in *Patella caerulea* reached 0.671±0.021μg/gm (Table 7 and Fig. 1), which recorded the minimum value in Winter 2002 (0.524±0.025μg/gm) and maximum value in Autumn 2001, Spring and Summer 2002 (0.748±0.029, 0.691±0.022 and 0.720±0.042 μg/gm respectively). Stations variations showed that, Abu-Qir and El-Anfushi had the lowest values (0.630±0.028 and 0.628±0.029 μg/gm respectively) while the highest value was recorded at El-Mex (0.754±0.039μg/gm). Stations and seasons revealed highly significant differences, ($P \leq 0.01$), while stations X seasons revealed non-significant differences for Cd concentrations, ($P \geq 0.05$).

2-2-Cobalt (Co):

2-2-A : In sea water

The minimum Co concentration was recorded in Autumn 2001 (0.058+0.003 μg/ml), while the maximum value was recorded in Winter 2002 (0.077+0.005 μg/ml) (Table 8 and Fig. 2). Stations variations revealed a lower Co concentration at El-Mex (0.058+0.004 μg/ml), while the higher was at El-Anfushi (0.073+0.003 μg/ml). The mean stations value of Co reached 0.067+0.002 μg/ml. Analysis of variance in Co concentrations at different stations and seasons,revealed highly significant differences ($P<0.01$) for stations

2-1-B : In *Patella* tissues

The total mean Cd concentration in *Patella caerulea* reached 0.671±0.021µg/gm (Table 7 and Fig. 1). which recorded the minimum value in Winter 2002 (0.524±0.025µg/gm) and maximum value in Autumn 2001, Spring and Summer 2002 (0.748±0.029, 0.691±0.022 and 0.720±0.042 µg/gm respectively). Stations variations showed that, Abu-Qir and El-Anfushi had the lowest values (0.630±0.028 and 0.628±0.029 µg/gm respectively) while the highest value was recorded at El-Mex (0.754±0.039µg/gm). Stations and seasons revealed highly significant differences, ($P \leq 0.01$). while stations X seasons revealed non-significant differences for Cd concentrations. ($P \geq 0.05$).

2-2-Cobalt (Co):

2-2-A : In sea water

The minimum Co concentration was recorded in Autumn 2001 (0.058±0.003 µg/ml), while the maximum value was recorded in Winter 2002 (0.077±0.005 µg/ml) (Table 8 and Fig. 2). Stations variations revealed a lower Co concentration at El-Mex (0.058±0.004 µg/ml), while the higher was at El-Anfushi (0.073±0.003 µg/ml). The mean stations value of Co reached 0.067±0.002 µg/ml. Analysis of variance in Co concentrations at different stations and seasons,revealed highly significant differences ($P \leq 0.01$) for stations and seasons and non-significant differences for stations X seasons ($P \geq 0.05$).

2-2-B : In *Patella* tissues:

The minimum Cobalt concentrations of Patella tissues was at Abu-Qir (0.737±0.069 µg/gm) and the maximum value at El-Anfushi (1.321±0.201 µg/gm), but no marked differences between seasons. (Table 9 and Fig. 2). The mean value for stations reached to 0.985±0.084 µg/gm. Analysis of variance (ANOVA) revealed significant differences for stations, ($P \leq 0.05$) and non-significant for seasons or stations X seasons, ($P \geq 0.05$).

2-3- Copper (Cu):

2-3-A: In sea water:

The concentrations of copper in the three stations (Table 10 and Fig. [illegible]) reached the minimum value in Autumn (0.072±0.002 μg/ml) and maximum value in Summer (0.088±0.002 μg/ml). Abu-Qir had the lowest value of Cu concentration (0.076±0.003 μg/ml), while El-Anfushi and El-Mex had the highest values (0.083±0.003 and 0.083±0.002 μg/ml respectively). The mean Cu concentrations for stations reached 0.081±0.002 μg/ml. Analysis of variance (ANOVA) for Cu concentration revealed significant differences for stations, and seasons ($P\leq0.01$, $P\leq0.05$) respectively, while stations X seasons revealed non-significant differences ($P\geq0.05$).

2-3-B: In *Patella* tissues.

Copper concentration in whole soft tissues of *Patella caerulea* revealed no marked differences between seasons (Table 11 and Fig. 3). The minimum values of Cu concentration were recorded at Abu-Qir and El-Anfushi (4.815±0.308 and 3.603±0.275 μg/gm respectively) while the maximum value at El-Mex station (8.577±1.159 μg/gm). The total mean for stations being 5.665±0.535 μg/gm. ANOVA revealed highly significant differences for stations, ($P\leq0.0$)1 and non-significant for seasons, ($P\geq0.05$) and Stations X seasons.

2-4- Iron (Fe):

2-4-A : In sea water

Fe concentrations ranged between 0.024±0.011 and 0.165±0.022 μg/ml and its total mean for stations reached 0.065±0.006 μg/ml (Table 12 and Fig. 4). Autumn 2001 and Winter 2002 recorded the lowest value of Fe concentrations (0.051±0.007 and 0.037±0.006 μg/ml respectively) and Spring 2002 recorded the highest value (0.102±0.017 μg/ml). Stations variations indicated minimum values of Fe at El-Anfushi and El-Mex (0.044±0.005 and 0.056±0.006 μg/ml respectively) and maximum value at Abu-Qir (0.097±0.014 μg/ml). Analysis of variance (ANOVA) revealed highly significant differences for stations. seasons and stations X seasons,($P\leq0.01$).

Lead concentrations in whole tissues of *Patella caerulea* (Table 15 and Fig. 5), ranged between 0.532±0.078 and 3.553±0.122 μg/gm with an average of 1.738±0.157 μg/gm. The minimum Pb concentration were recorded in Spring and Summer 2002 (1.139±0.196 and 1.232±0.212 μg/gm respectively) while the maximum value was recorded in Autumn 2001 (2.725±0.256 μg/gm). Stations variations revealed the lowest value at Abu-Qir (0.936±0.161 μg/gm) and highest value at El-Mex (2.555±0.213μg/gm). ANOVA recorded highly significant differences in Pb concentration for stations. seasons and stations X seasons ($P \leq 0.01$).

2-5- Lead (Pb):

2-5-A: In sea water.

Winter, Spring and Summer 2002 showed the minimum values of Pb concentrations (0.425±0.109, 0.308±0.087 and 0.345±0.105μg/ml respectively) while Autumn 2001 had the maximum value (0.653±0.178 μg/ml) (Table 14 and Fig. 5). Abu-Qir and El-Anfushi had the lowest Pb concentrations (0.165±0.023 and 0.293±0.077 μg/ml respectively) and El-Mex had the higher value (0.840±0.094 μg/ml). The mean Pb concentrations of all stations reached0.433±0.064 μg/ml. ANOVA revealed highly significant differences for stations and seasons, ($P \leq 0.01$) and non-significant differences for stations X seasons, ($P \geq 0.05$).

2-5-B: In *Patella* tissues:

Lead concentrations in whole tissues of *Patella caerulea* (Table 15 and Fig. 5). ranged between 0.532±0.078 and 3.553±0.122 μg/gm with an average of 1.738±0.157 μg/gm. The minimum Pb concentration were recorded in Spring and Summer 2002 (1.139±0.196 and 1.232±0.212 μg/gm respectively) while the maximum value was recorded in Autumn 2001 (2.725±0.256 μg/gm). Stations variations revealed the lowest value at Abu-Qir (0.936±0.161 μg/gm) and highest value at El-Mex (2.555±0.213μg/gm). ANOVA recorded highly significant differences in Pb concentration for stations, seasons and stations X seasons ($P \leq 0.01$).

2-6- Zinc (Zn):

2-6-A: In sea water

The minimum concentration of Zn was recorded in Winter (0.067+0.003 μg/ml) while the maximum was recorded in Summer (0.123+0.012 μg/ml) (Table 16 and Fig. 6). Stations variations showed that, El-Mex had the lowest Zn concentration (0.077+0.005 µg/ml) while the highest value at El-Anfushi (0.109+0.011 µg/ml). The average Zn concentrations for stations being 0.095+0.005 µg/ml. Analysis of variance (ANOVA), revealed highly significant differences for stations and seasons ($P<0.01$) and non-significant differences for stations X seasons ($P>0.05$).

2-6-B: In *Patella* tissues

The minimum concentration of Zn was recorded in Winter (0.067±0.003 µg/ml) while the maximum was recorded in Summer (0.123±0.012 µg/ml) (Table 17 and Fig. 6). Stations variations showed that, El-Mex had the lowest value of Zn concentration (0.077±0.005 µg/ml), while the highest value was at El-Anfushi (0.109±0.011 µg/ml). The average Zn concentrations for stations being 0.095±0.005 µg/ml. Analysis of variance (ANOVA), revealed highly significant differences for stations and seasons ($P\leq 0.01$) and non-significant differences for stations X seasons ($P\geq 0.05$).

DISCUSSION

The present data indicated that the concentrations of trace metals associated with soft tissues of *Patella caerulea* varied over the seasons and sampling sites.The discussion of this matter needs first to know the physico-chemical parameters of water which are controlled by the seasons, then the quality of sites, (polluted or not), and the type of pollution. For example the Pb concentration in soft tissues of *Patella caerulea* collected from Abu-Qir in Autumn recorded nearly three fold its concentration in Summer. Also the concentration of Pb in El-Mex station was nearly three fold its concentration in Abu-Qir. So, comparison between the published works are insufficient, because many of them have determined the accumulated trace metals related to nature of sites and neglected the seasons affecting those sites (Bargagli *et al.*, 1985; Ramelow, 1985; El- Rayis and Ezzat, 1986; Puel *et al.*, 1987; El-Gamal, 1988; Rifaat, *et al.*, 1997; Farag, *et al.*, 2000 ; Cravo *et al.*, 2003).

The physico-chemical conditions of the rocky shore intertidal zones where *Patella* occurs are extreme. Such habitats seasonally are subject to periodic desiccation, high temperature and light, low salinities and strong wave action (Nybakken, 1982). So it is difficult to put fixed record of trace metals with the seasonal changes of temperature, oxygen partial pressure, salinity and the behavior of animals towards these changes.

The present results showed that the surface water temperature ranged between 18.467± 0.033 and 28.63±0.033 °C. within different seasons. Summer recorded the highest concentration of some metals and the lowest in others. The lowest concentrations of Fe, Zn and Cd were recorded in winter, while Co was high. Autumn recorded the highest concentration of Cd and Pb while the highest Fe was recorded in Spring. Moreover, each season behaves differently towards the concentration of metals. Summer and Autumn recorded the highest concentrations of trace metals than Winter and Spring, that may be due to the effect of temperature and wind on the solubility of these metals.

Salinity values ranged between 24.4±0.058 and 38.667±0.033‰, where the lowest value was recorded at El-Mex station, which may be due to the influence of the major outlet from Umum drain, carrying is mixed agricultural drainage water outflow from Lake Mariut with its industrial wastes. It enriches the bay with detrital material and nutrient salts as well as pesticides and heavy metals (Halim, 1983 and Atta, 1991). The low salinities play a big role in the accumulation of the trace metals in the soft tissues of *patella*. For example, Cu concentration in El- Anfushi and El- Mex were 0.073 (μg/ml) while its accumulation in the soft tissues reached 2.42±0.24 and 6.97±0.64 (μg/gm) respectivily. Lower salinity during Summer gave the highest ratio of Cu accumulation than the other seasons (9.989±0.83 μg/gm). The same results were obtained with other stations, where the salinity, temperature and the accumulation of metals were correlated. This is applied also for Zn and Cd, while for Pb and Co, lower temperature with lower salinities gave the highest accumulation.

Seasonal fluctuation in pH values in the studied sites were limited and ranged between 7.357±0.009 and 8.067±0.024. Spring recorded higher pH value than the rest of seasons, to growth of hydrophytes and phytoplankton (Abdel- Baky & El- Gobashi, 1991). No changes were recorded for pH on the ratio of trace metals accumulation.

The dissolved oxygen depends mainly on the physico- chemical parametrs. Herbst & Dana, (1980) reported that, when the temperature of a salt solution increases, the solubility of oxygen decreases. This coincides with the present data, where Summer recorded the lowest value of dissolved oxygen, while Autumn recorded the highest one.

The dissolved oxygen reflects the pattern of biochemical oxygen demand fluctuation that followed more or less the seasonal and site variations of dissolved oxygen value (Sowyer and McCarty, 1978). So the decrease in dissolved oxygen during summer at El- Mex station was followed by decreasing in biochemical oxygen demand at the same season and station. The lowest O_2 value was recorded in El-Mex which recorded the highest value of pollution. Moreover dissolved oxygen plays an indirect role in the accumulation of trace metals in soft parts of *Patella*.

El-Mex contributed the highest concentration of Cu, Pb and Cd in both water and soft tissues of *Patella caerulea* than those taken from El- Anfushi and Abu- Qir. From this comparison, it is tempting to conclude that Cu, Pb and Cd concentrations associated with El- Mex limpets are a direct reflection of the availability of metals by the impact of untreated industrial, agricultural and sewage contamination. According to Abdel- Moati, (1991), El-Mex station receives annually two tons of Pb through the effluent from ethyl lead unit of Alexandria Petroleum Company. The high concentration of metals were recorded in Summer and Autumn, indicated that. the temperature and wind play a role in the enrichement of these metals. Abu-Qir station at the most eastern part of Alexandria coast line, recives a lot of domestic waste water but no industrial effluents (Atta, 1991), so it was the lowest station in trace metals pollution but only recorded highest concentration of Fe. Many data recorded high concentration of iron in the soft tissues of *Patella caerulea* as other patella species (Bargagli *et al.*, 1985; Ramelow, 1985; El- Rayis and Ezzat, 1986; Puel *et al.*, 1987 and Cravo *et al.*, 2003), which may be ascribed to the fact that iron is a constituent of goethite (J- FeOOH) present in the radula of Patellidae (Runham *et al.*, 1969; Fish and Fish, 1989). El- Anfushi station recorded higher values of Fe, Co and Pb which may be due to repairing of Qaitbay fort during the study period.

A comparison of the present results as mean of all seasons, with the previous studies from a wide range of geographical locations and different environmental regimes is presented in Table(18). The comparison showed that, the concentration of any trace metals associated with the soft tissues vary over a wide range. In all *Patella* species, there is a general tendency for iorn and zinc to be preferably incorporated into the soft tissues as found in investigated species and other marine gastropods (Puel *et al.*, 1987; Depledge *et al.*, 1994 ; de Wolf *et al.*, 2001). However, metal concentrations in soft tissues of *Patella caerulea* affected by sewage discharges when comparable to those of other *Patella* sp.taken from sites influenced by industrial discharges.

REFERENCES

Abdel-Baky, T. and El-Ghobashy, A. (1991). Seasonal variation of mineral contents in four species of cichlid fishes from lake Manzalah, Egypt. J. Egypt. Ger. Soc. Zool., *6*(A): 283-296.

Abdel-Moati, M. A. R. (1991). Biochemical and physiological responses of *Mytilus edulis* to Hg and Pb in the coastal waters of Alexandria region. FAO/UNEP/IOC. Workshop on the Biological effects of Pollutants on Marine Organisms. Athens (Greece): 61-72.

APHA, (1992). Standard Methods for the Examination of Water and Waste Water. Washington, 18th Ed. DC.

Atta, M. M. (1991). Rocky shore fauna of Mediterranean coastline of Alexandria. J. Egypt. Ger. Soc. Zool., *5*:211-224.

Bargagli, R. ; Baldi. F. and Leonzio, C. (1985). Trace metal assessment in sediments, molluscs and reed leaves in the bay of Follonica (Italy). Mar Environ Res, *16*: 281-300.

Brown, M. T. and Depledge, M. H. (1998). Determinants of trace metal concentrations in marine organisms. In: Langston W, Bebianno MJ, editors. Metal metabolism in aquatic environments. London: Chapman & Hall. p. 185-217.

Cravo, A. ; Bebiano, M. J. and Foster, P. (2003). Partitioning of trace metals between soft tissues and shells of *Patella aspera*. Environ Int (in press).

Dalziel, J. and Baker, C. (1983). Analytical methods for measuring metals by atomic absorption spectrometry. FAO Fish. Technical paper, *212*:14-21.

Depledge, M. H. ; Weeks, J. M. and Bjerregaard, P. (1994). Heavy metals. In Calow P, editor. Handbook of ecotoxicology, Vol. 2. Oxford: Blackwell; pp. 79-105.

De Wolf, H. ; Ulomi, S. A. ; Backeljau, T. And Blust, R. (2001). Heavy metal levels in the sediments of four Dar es Salaam mangroves. Accumulationin, and effect on the morphology of the preiwinkle. *Littoraria scabra.* Environ Int; *26*(4):243-9

Dybern, B. (1983). Field sampling and preparation of subsamples of aquatic organisms for analysis of metals and organochlorines. FAO, Fisher Tech. Paper, *212*:1-13.

El-Gamal, M. M. T. (1988). "Studies on marine edible molluscs of Egypt". M.Sc. Thesis, Fac. Sci., Tanta Univ., Egypt.

El-Rayis, O. A. and Ezzat, A. A. (1986). Bioaccumulation of some heavy metals in coastal marine animals in the vicinity of Alexandria: 3. Surveying. FAO Fish Rep. *334*: 67-72.

Farag, E. A. ; Dekinesh, S. I. and El-Odessy, H. M. (2000). Trace elements accumulation in soft parts of six edible bivalve molluscs inhabiting Alexandria coast, Egypt. J. Egypt. Ger. Soc. Zool., *31*(D): 27-36.

Fish, J. D. and Fish, S. (1989). A student's guide to the seashore. London: Unwin Hyman; 473pp.

Halim, Y. (1983). Mid Term. Technical report aquatic environmental pollution project EGY/73/058, University of Alexandria, Research Center Alexandria.

Herbst, D. B. and Dana, G. L. (1980). Environmental physiology of salt tolerance in the alkaline salt lake population of *Artemia* from Mono Lake, California, U.S.A.. In, The Brin Shrimp *Artemia*. Volume 2. Physiology, Biochemistry, Molecular Biology. Wetteren, Belgium, Univera, pp. 157-167.

Langston, W. J. and Spence, K. (1995). Biological factors involved in metal concentrations observed in aquatic organisms. In: Tessier A, Tumer DR, editors. Metal speciation and bioavailability in aquatic systems. New York: Wiley; pp. 407-78.

Lingard, S. M. ; Evans, R. D. and Bourgoin, B. P. (1992). Method for the estimation of organic-bound and crystal-bound metal concentrations in bivalves shells. Bull Environ Contam Toxicol., *48*:179-84.

Lobban, C. S. and Harrison, P. J. (1997). Seaweed ecology and physiology. Cambridge: Cambridge University Press.

Nybakken, J. W. (1982). Marine biology: An Ecological Approach. New York, NY. Harper & Row.

Puel, D. ; Zsurger, N. and Breittmeyer, JPh. (1987). Statistical assessment of a sampling pattern for evaluation of changes in mercury and zinc concentrations in *Patella caerulea.* Bull Environ Contam Toxicol., *38*:700-6.

Rainbow, P. S. (1990). Heavy metal levels in marine invertebrates. In heavy metals in the marine environment (ed. R.W. Furness and P.S. Rainbow), pp.67-79. Boca Raton, Florida: CRC Press.

Räinbow, P. S. (1997). Trace metal accumulation in marine invertebrates: marine biology or marine chemistry. J. Mar. Biol. Ass. U.K., *77*:195-210.

Ramelow, G. J. (1985). Astudy of heavy metals in limpets (*Patella* sp.) collected along a section of the southeastern Turkish Mediterranean coast. Mar Environ Res; *16*:243-53.

Rice, H. ; Leighty, D. A. and McLeod, G. C. (1973). The effects of some trace metals on marine phytoplankton. CRC Critical Review in Microbiology. *3*:27-49.

Rifaat, A. E. : El-Mamoney, M. H. and Draz, S. E. (1997). The organic matter, iron, copper, manganese, zinc and cadmium in 1982 and 1995 in El'Mex Bay sediments, Alexandria, Egypt.

Runham, N. W. ; Thornton, P. R. : Saw, D. A. and Wayte, R. C. (1969). The mineralization and hardness of the radular teeth of the limpet *Patella vulgata* L. Z Zell-forsch, *99*:608-26.

Sawyer, C. N. and McCarty, P. L. (1978). Chemistry for Environmental Engineering, 3 rd Eddition. Mc Graw-Hill Book company, NY, NY. 532 pp.

Soto, M. ; Kortabitarte, M. and Marigomez, I. (1995). Bioavailable heavy metals in estuarine waters as assessed by metal/shell-weight indices in sentinel mussels *Mytilus galloprovincialis*. Mar Ecol, Prog Ser, *125*(1-3):127-31.

Soto, M. ; Ireland, M. P. and Marigomez, I. (1997). The contribution of metal/shell-weight index in target tissues to metal body burden in sentinel marine molluscs: 2. *Mytilus galloprovincialis*. Sci Total Environ.,*189*(2):149-60.

Table (1): Seasonal variations in temperature (°C) of sea water surface at three stations of Alexandria during Autumn 2001 to Summer 2002. (a-k, sequence of temperature values and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3 determinations).

Station	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	24.867±0.033 d	24.033±0.033 f	24.367±0.033 e	24.422±0.122 B
Winter	18.467±0.033 k	18.500±0.000 k	18.867±0.033 j	18.611±0.065 D
Spring	22.133±0.067 g	21.733±0.033 i	22.000±0.000 h	21.956±0.063 C
Summer	28.633±0.033 a	27.500±0.000 c	27.700±0.000 b	27.944±0.175 A
M±SE	23.525±1.122 A	22.942±0.990 C	23.233±0.975 B	23.233±0.580

Table (2): Seasonal variations in hydrogen ion concentration (pH) of sea water surface at three stations of Alexandria during Autumn 2001 to Summer 2002. (a-e, sequence of pH concentrations and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	7.653±0.009 c	7.413±0.012 de	7.357±0.009 e	7.474±0.046 B
Winter	7.497±0.003 d	7.500±0.006 d	7.500±0.036 d	7.499±0.011 B
Spring	7.813±0.088 b	7.887±0.055 b	7.827±0.003 b	7.842±0.032 A
Summer	8.067±0.024 a	7.710±0.006 c	7.710±0.006 c	7.829±0.060 A
M±SE	7.758±0.066 A	7.627±0.057 B	7.598±0.055 B	7.661±0.036

Table (3): Seasonal variations in salinity (‰) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (a-j, sequence of salinity values and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	37.900±0.058 c	37.200±0.058 f	24.833±0.033 i	33.311±2.122 C
Winter	37.367±0.033 e	37.400±0.058 e	24.400±0.058 j	33.056±2.164 D
Spring	38.433±0.033 b	37.967±0.120 c	25.167±0.033 h	33.856±2.174 B
Summer	38.667±0.033 a	37.633±0.033 d	25.567±0.033 g	33.956±2.103 A

Table (4): Seasonal variations in dissolved oxygen concentration (mg/l) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (a-h, sequence of DO concentrations and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	7.933±0.033 a	6.067±0.033 c	5.433±0.033 de	6.478±0.376 A
Winter	5.433±0.033 de	5.333±0.033 de	4.633±0.033 g	5.133±0.127 C
Spring	6.700±0.100 b	5.567±0.033 d	4.933±0.033 f	5.733±0.260 B
Summer	5.233±0.033 e	4.467±0.233 gh	4.367±0.088 h	4.689±0.155 D
M±SE	6.325±0.328 A	5.358±0.182 B	4.842±0.122 C	5.508±0.165

Table (5): Seasonal variations in biochemical oxygen demand concentration (mg/l) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (a-i, sequence of BOD concentrations and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	5.833±0.033 a	3.967±0.033 d	3.267±0.033 f	4.356±0.383 A
Winter	5.367±0.067 c	3.267±0.033 f	2.467±0.033 h	3.700±0.433 C
Spring	5.600±0.000 b	3.567±0.033 e	2.867±0.033 g	4.011±0.410 B
Summer	3.300±0.153 f	2.567±0.033 h	2.167±0.033 i	2.678±0.172 D
M±SE	5.025±0.307 A	3.342±0.155 B	2.692±0.126 C	3.686±0.204

Table (6): Seasonal variations in Cd concentration (µg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (A-C, sequence of total Cd concentrations means at different stations and seasons; M±SE, mean ± standard error of 5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.067±0.009	0.065±0.007	0.111±0.012	0.081±0.009 A
Winter	0.048±0.001	0.048±0.004	0.086±0.003	0.061±0.007 B
Spring	0.052±0.005	0.052±0.005	0.094±0.002	0.066±0.007 B
Summer	0.064±0.002	0.060±0.008	0.109±0.012	0.078±0.009 A
M±SE	0.058±0.003 B	0.056±0.003 B	0.100±0.005 A	0.071±0.004

Table (7): Seasonal variations in Cd concentration (µg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B, sequence of total Cd concentration means at different stations and seasons: M±SE, mean ± standard error of 3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.697±0.022	0.696±0.027	0.850±0.030	0.748±0.029 A
Winter	0.384±0.015	0.485±0.048	0.604±0.021	0.524±0.025 B
Spring	0.654±0.031	0.655±0.026	0.762±0.006	0.691±0.022 A
Summer	0.683±0.030	0.677±0.023	0.800±0.121	0.720±0.042 A
M±SE	0.630±0.028 B	0.628±0.029 B	0.754±0.039 A	0.671±0.021

Table (8): Seasonal variations in Co concentration (µg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B, sequence of total Co concentration means at different stations and seasons; M±SE, mean ± standard error of 3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.064±0.002	0.064±0.006	0.047±0.002	0.058±0.003 B
Winter	0.080±0.006	0.082±0.008	0.069±0.013	0.077±0.005 A
Spring	0.067±0.005	0.078±0.003	0.060±0.003	0.068±0.003 AB
Summer	0.069±0.001	0.069±0.002	0.056±0.003	0.065±0.002 AB
M±SE	0.070±0.003 AB	0.073±0.003 A	0.058±0.004 B	0.067±0.002

Table (9): Seasonal variations in Co concentration (µg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B, sequence of total Co concentration means at different stations; M±SE, mean ± standard error of (3-5 determinations)

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.574±0.101	1.109±0.399	0.767±0.108	0.817±0.146
Winter	0.975±0.131	1.650±0.550	1.041±0.197	1.222±0.203
Spring	0.791±0.112	1.330±0.390	0.944±0.173	1.022±0.150
Summer	0.607±0.117	1.195±0.440	0.836±0.141	0.879±0.162
M±SE	0.737±0.069 B	1.321±0.201 A	0.897±0.074 AB	0.985±0.084

Table (10): Seasonal variations in Cu concentration (µg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (A-C, sequence of total Cu concentration means at different stations and seasons; M±SE, mean ± standard error of (3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M+SE
Autumn	0.071±0.003	0.073±0.001	0.073±0.004	0.072±0.002 C
Winter	0.072±0.004	0.081±0.008	0.082±0.002	0.078±0.003 BC
Spring	0.076±0.008	0.087±0.002	0.087±0.001	0.083±0.003 AB
Summer	0.083±0.005	0.091±0.005	0.090±0.002	0.088±0.002 A
M±SE	0.076±0.003 B	0.083±0.003 A	0.083±0.002 A	0.081±0.002

Table (11): Seasonal variations in Cu concentration (µg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B, sequence of Cu concentration means at different stations; M±SE, mean ± standard error of (3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	3.576±0.212	2.424±0.244	6.974±0.640	4.325±0.714
Winter	4.340±0.202	3.358±0.324	8.224±0..995	5.307±1.626
Spring	5.146±0.312	3.897±0.055	9.121±0.994	6.054±0.843
Summer	6.196±0.148	4.735±0.300	9.989±0.834	6.974±0.825
M±SE	B	B	A	

Table (12): Seasonal variations in Fe concentration (µg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (a-e, sequence of Fe concentrations and A-C, sequence of total means at different stations and seasons; M+SE, mean + standard error of 3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.077±0.006 bc	0.035±0.008 de	0.042±0.004 de	0.051±0.007 C
Winter	0.050±0.002 cde	0.024±0.011 e	0.038±0.013 de	0.037±0.006 C
Spring	0.165±0.022 a	0.062±0.002 cd	0.079±0.005 bc	0.102±0.017 A
Summer	0.095±0.002 b	0.054±0.002 cd	0.063±0.003 cd	0.071±0.006 B
M±SE	0.097±0.014 A	0.044±0.005 B	0.056±0.006 B	0.065±0.006

Table (13): Seasonal variations in Fe concentration (µg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B, sequence of total Fe concentration means at different stations; M±SE, mean ± standard error of 3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	220.498±17.306	233.591±8.810	181.588±22.768	211.892±11.644
Winter	205.875±12.477	223.517±12.484	185.262±25.575	204.885±10.536
Spring	231.809±8.329	252.293±7.884	197.546±26.731	227.216±11.587
Summer	225.329±8.658	236.706±6.647	186.668±23.871	216.235±10.712
M±SE	220.878±5.961 A	236.527±5.014 A	187.766±10.718 B	215.057±5.495

Table (14): Seasonal variations in Pb concentration (µg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (A-B. sequence of total Pb concentration means at different stations and seasons; M±SE, mean ± standard error of 3-5 determinations).

Station / Season	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.239±0.042	0.439±0.254	1.281±0.084	0.653±0.178 A
Winter	0.189±0.033	0.300±0.177	0.784±0.094	0.425±0.109 B
Spring	0.084±0.006	0.205±0.084	0.634±0.026	0.308±0.087 B
Summer	0.149±0.052	0.226±0.106	0.661±0.204	0.345±0.105 B
M±SE	0.165±0.023 B	0.293±0.077 B	0.840±0.094 A	0.433±0.064

Table (15): Seasonal variations in Pb concentration (μg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (a-f, sequence of Pb concentrations and A-C, sequence of total means at different stations and seasons; M±SE, mean ± standard error of 3-5 determinations).

Season \ Station	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	1.820±0.114 c	2.801±0.048 b	3.553±0.122 a	2.725±0.256 A
Winter	0.840±0.030 e	1.907±0.068 c	2.821±0.167 b	1.856±0.291 B
Spring	0.532±0.078 f	1.024±0.012 de	1.859±0.073 c	1.139±0.196 C
Summer	0.554±0.038 f	1.158±0.097 d	1.985±0.112 c	1.232±0.212 C
M±SE	0.936±0.161 C	1.723±0.215 B	2.555±0.213 A	1.738±0.157

Table (16): Seasonal variations in Zn concentration (μg/ml) of sea water surface at three stations in Alexandria during Autumn 2001 to Summer 2002. (A-C, sequence of total Zn concentration means at different stations and seasons; M±SE, mean ± standard error of 3-5 determinations).

Season \ Station	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	0.089±0.001	0.089±0.005	0.073±0.004	0.084±0.003 BC
Winter	0.069±0.005	0.076±0.001	0.056±0.003	0.067±0.003 C
Spring	0.113±0.019	0.124±0.029	0.085±0.003	0.107±0.012 AB
Summer	0.127±0.023	0.148±0.018	0.093±0.004	0.123±0.012 A
M±SE	0.099±0.009 AB	0.109±0.011 A	0.077±0.005 B	0.095±0.005

Table (17): Seasonal variations in Zn concentration (µg/gm) in whole soft tissues of *Patella caerulea* collected from rocky shores of three stations in Alexandria during Autumn 2001 to Summer 2002. (A-C, sequence of total Zn concentration means at different stations and seasons; M±SE, mean ± standard error of (3-5 determinations).

Station / Seasons	Abu-Qir	El-Anfushi	El-Mex	M±SE
Autumn	19.129±0.419	15.088±0.346	23.170±1.323	19.129±1.237 C
Winter	18.181±2.075	13.720±0.117	19.408±2.994	17.103±1.362 C
Spring	21.189±0.100	19.764±0.105	24.236±0.548	21.730±0.679 B
Summer	27.462±0.867	22.088±0.666	30.836±0.529	26.796±1.321 A
M±SE	21.490±1.194 B	17.665±1.037 C	24.413±1.434 A	21.189±0.834

Table (18): Trace metal concentrations (µg g^{-1}) in the soft parts of *P. caerulea* determined in present work and in *Patella sp.* From mediterranean sea and other geograhpical locations.

	Cd	Cu	Fe	Zn	Co	References
Patella caerulea	**0.67**	**5.76**	**215**	**21.2**	**0.99**	present work
Patella caerulea Follonica Bay	0.8	7.7	103	63	2.4	Bargagli *et al.*. (1985)
Patella vulgata (Alexandria water) domestic sewage	0.4	20.9	450	38		El- Rayis and Ezzat. (1986)
Patella vulgata (Alexandria water) domestic sewage	0.5	20.7	504	38		El- Rayis and Ezzat. (1986
Patella vulgata (Alexandria water) industrial sewage	0.9	22.9	1239	63		El- Rayis and Ezzat, (1986
Patella aspra South coast of Portugal (clean site)	0.6	6.1	1022	62.3	4.3	Cravo *et al.*, (2003)
Patella aspra South coast of Portugal (contaminated site)	1.6	8.1	1466	129	4.1	Cravo *et al.*, (2003)
Patella sp. (Turkish coast, sewage influence)	2.5	1.4	891	44.8		Ramelow (1985)
Patella sp. (Turkish coast, not influence by sewage)	1.1	3.1	929	40		Ramelow (1985)
Range of metal concentrations in the soft parts of molluscs	1-5	3-12	110-5000	50-500	1-3	Depledge *et al.*. (1994)

FIG. (1) SEASONAL VARIATIONS IN CD CONCENTRATION OF WATER AND *PATELLA CAERULEA.*

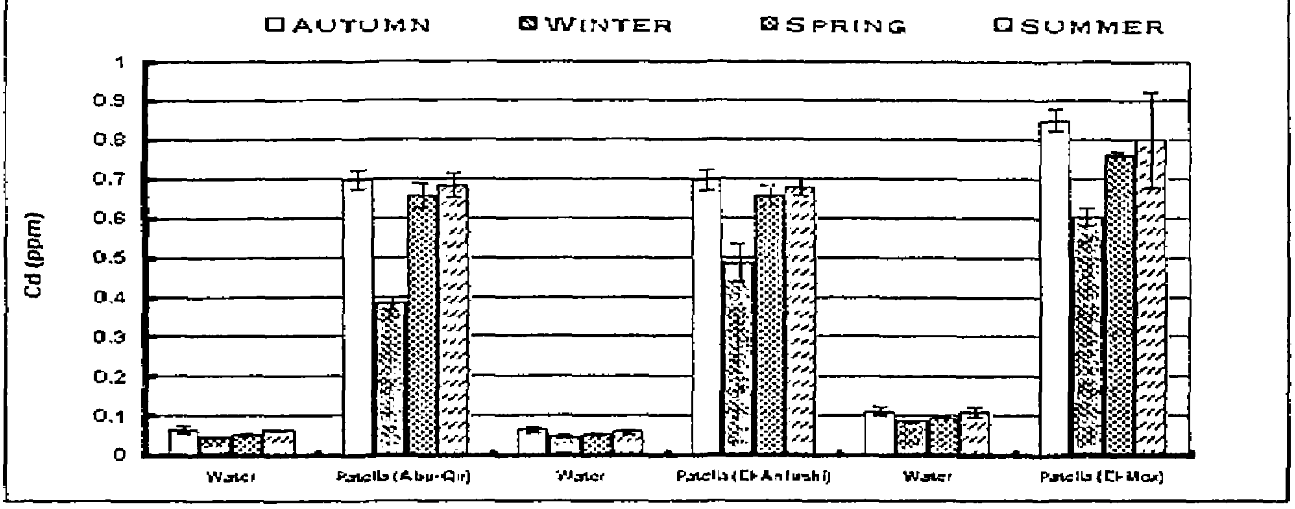

FIG.(2) SEASONAL VARIATIONS IN CO CONCENTRATION OF *PATELLA CAERULEA*

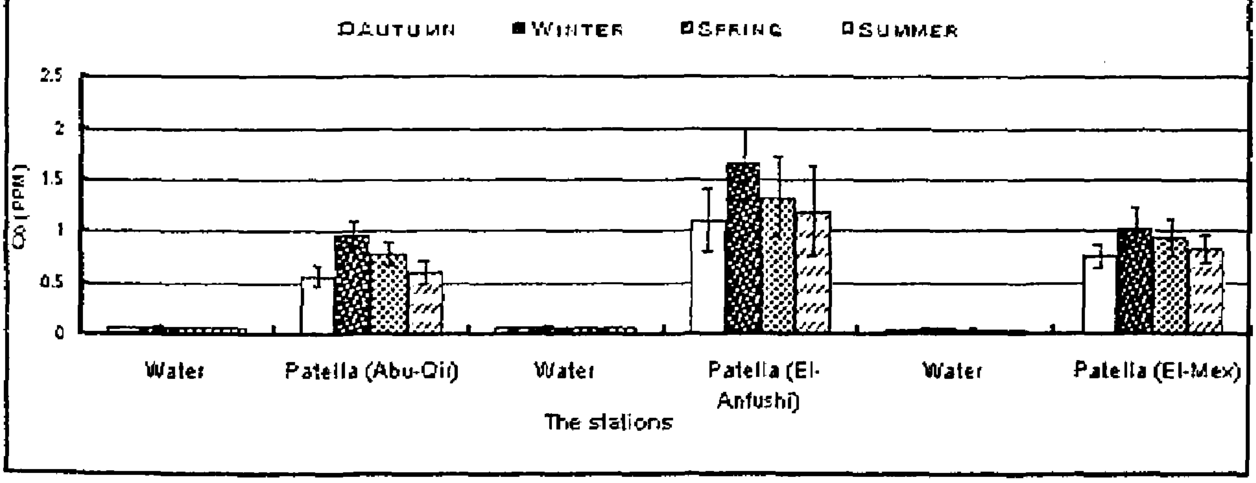

FIG.(3) SEASONAL VARIATIONS IN CU CONCENTRATION OF WATER AND *PATELLA CAERULEA*.

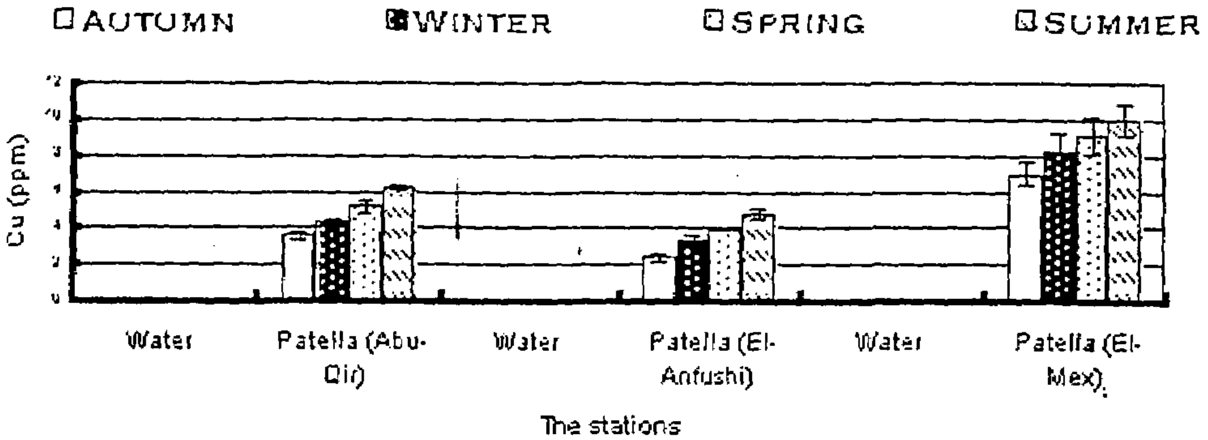

FIG. (4) SEASONAL VARIATIONS IN FE CONCENTRATION OF WATER AND *PATELLA CAERULEA*.

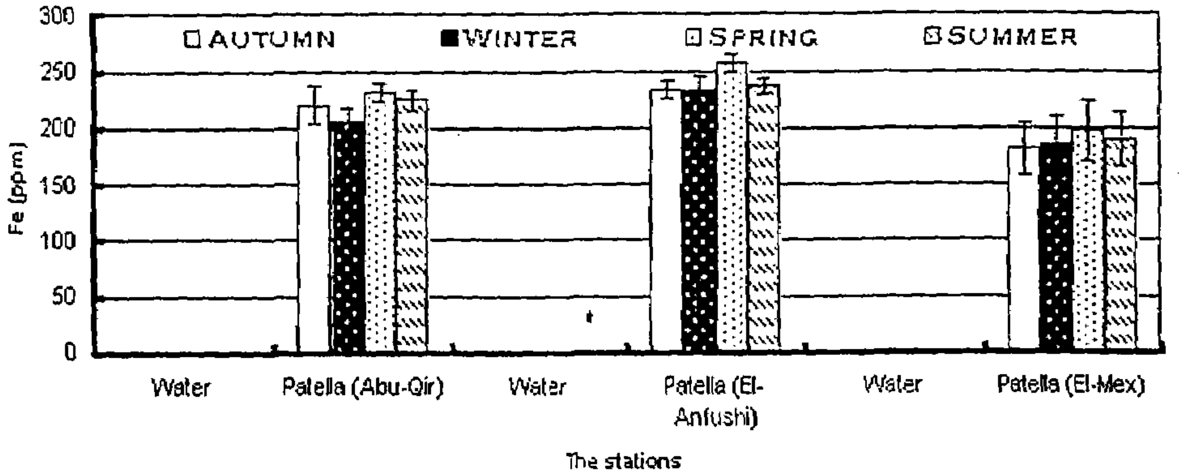

FIG. (5) SEASONAL VARIATIONS IN PB CONCENTRATION OF WATER AND *PATELLA CAERULEA*.

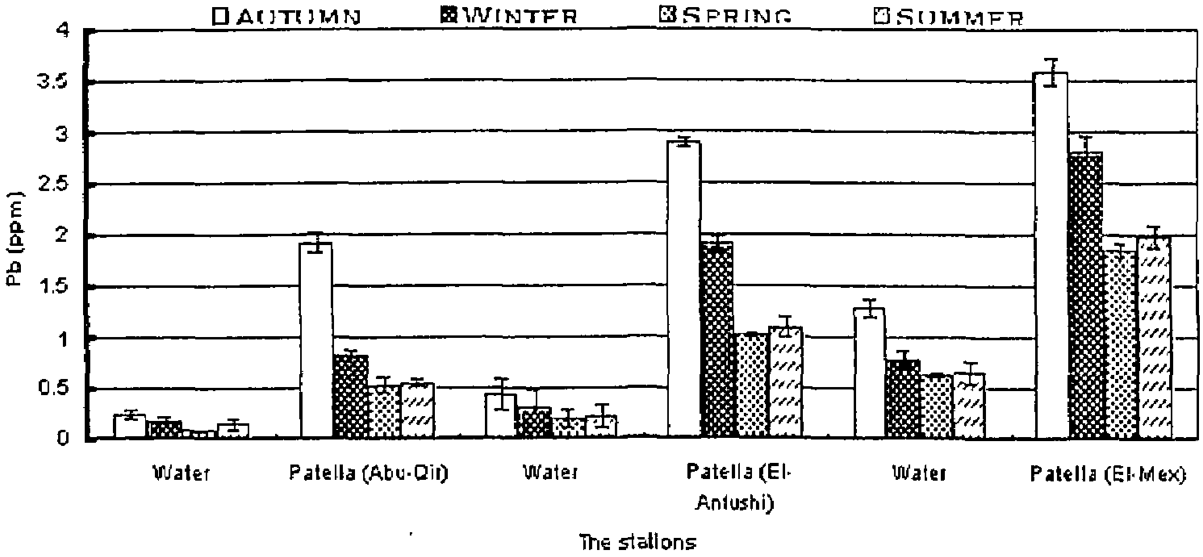

FIG. (6) SEASONAL VARIATIONS IN ZN CONCENTRATION OF WATER AND *PATELLA CAERULEA*.