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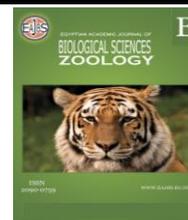
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***Patella caerulea* (Mollusca, Gastropoda) as Bio-Indicator for Certain Pollutants at El-Mex Bay, Alexandria, Egypt**

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**ABSTRACT**

The dominant molluscan species *Patella caerulea* was selected as a trace metals bio indicator. During winter and summer 2016, its specimens were scraped from El-Mex Bay. Concentrations of heavy metals in the water, sediments and *Patella caerulea* (shells and soft tissues) were determined. Cadmium (Cd), lead (Pb), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn) and zinc (Zn) concentrations (conc.) during summer were higher than winter except for shells which had Cd conc. in summer lower than winter, water showed Cu conc. in winter more than summer, Fe appeared higher conc. in water and *Patella caerulea* during winter more than summer, Mn had higher conc. in water and sediments than summer, Ni had higher conc. in water and soft tissues during winter than summer and Zn in water during summer is lower than winter. The bioaccumulation factors (BAFs) of Cd, Pb, Cu, Fe in *Patella caerulea* shells were more than soft tissues, also they were more in winter than summer except that of Cu in winter was lower than summer, BAF of Fe in soft tissues was higher than shells also that of Mn and Zn in *Patella caerulea* during winter were lower than summer, also BAFs of Mn in soft tissues and shells was nearly similar. The highest metal pollution index (MPI) for the studied species appeared in shells (105.95) followed by that of soft tissues during summer and winter (80.54 and 74.64, respectively). While MPI in shells during winter (46.13) came to the last.

**INTRODUCTION**

Ecosystems are complex and dynamic. This makes linking any one effect to a specific cause very difficult and conditions cannot be controlled (Islam and Tanaka, 2004). One of the major environmental problems in Alexandria city is seawater pollutions. Various pollutants are dumped daily by industrial, agricultural and domestic sources over Alexandria coasts through several outfalls, El-Mex Bay one of these disposal sites (El-Mex Pumping Station). It receives a heavy load of waste water ( $2.6 \times 10^9 \text{ m}^3 / \text{y}$ ) both directly from industrial outfalls and indirectly from Lake Mariut via El- Mex pumping station. The main outfalls are; Misr Chemical Industries, Mex pumping station on El-Umum drian combined wastewater from Tanneries and slaughterhouse, El-Noubaria Canal and Mahmoudeya Canal (Shaltout, 2008 and Abdel-Rhman, 2013). El-Mex Bay is characterized

by the presence of two water layers overlaying one on other (Mahamoud *et al.*, 2008).

El-Mex Bay is a part of Alexandria coast on the Mediterranean Sea. It is subjected to effluents contaminated with several anthropogenic materials including trace metals. One of these effluents is called El-Umum agricultural drain (rate  $8 \times 10^6 \text{ m}^3/\text{d}$ ). The elevation in levels of trace metals concentrations in marine environment is a worldwide problem and the discharge of trace metal wastes has many obvious impacts on water, sediments and organisms, led to decrease in productivity, and increase in exposure of humans to harmful substances. The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility, solubility, extractability and many other critical properties were found to depend on the form and nature of the chemical species (Lores and Pennock, 1998).

Metals exist in our natural waters in different labile, but the labile ones are the most important in the environment. They are responsible for bioaccumulation of toxic metals in sediments, biota, animals and finally in humans. The aim of the present work is to establish the levels of some heavy metals (Fe, Cu, Pb, Ni, Mn, Zn, and Cd) in sediments of El-Mex Bay.

## MATERIALS AND METHODS

### The Study Area:

It is located in front of El-Umum drain, south of El-Mex Bay, at 29° 50' Longitude and 31° 88' latitude. Its sediments are sandy fine, with turbid water. (Locations determined by the Geographical Position System (GPS) model C53.

### Sampling of Marine Invertebrates:

During winter and summer 2016, specimens of marine invertebrates were scraped from El-Mex Bay using a metal knife. The dominant molluscan species namely *Patella caerulea* was selected as a trace metals bio-accumulator.

### Sampling Sediments Analysis:

After collection, the sediment samples were transferred to the laboratory in plastic bags.

### Determination of Heavy Metals in the Sediments:

Concentrations of heavy metals in the sediments were determined by using the method suggested by Oregioni and Aston, (1984) as follows:

Amounts of concentrated nitric acid, hydrofluoric acid and perchloric acid (3:2:1, respectively) were added to 0.5 gm dry sample of sediments into Teflon crucible. The latters were covered and placed aside for several hours, then evaporated on a hot plate at 180°C until nearly all the residue was dissolved and left near dryness. After cooling at room temperature, the mixture was completed to 25 ml by 1 N HCl in Deionized distilled water (DDW), then filtered using Whatman No.1 filter papers. The digested samples were stored at 4°C until further analysis.

Heavy metals were measured by Atomic absorption spectrophotometer (FAAS) model (SHIMADZU-AA-6800). The results were expressed in  $\mu\text{g/g}$ . After calibration of standard solution series of standard metal salts.

### Determination of Heavy Metals in The Water:

Heavy metals occur in seawater at a concentration below the sensitivity limits of atomic absorption spectroscopy, so a pre-concentration step was necessary before measurement using cationic exchange chelex-100 technique (Riley and Taylor, 1968) and (Abdullah and Royle, 1974).

Where, preparation of column, 1.4 cm diameter ion exchange column was filled to a depth of 6 cm with chelex-100 resin (50-100 mesh). The resin was cleaned by passing about 70 ml of 2N nitric acid then washed with 100 ml deionized distilled water (DDW). Passing

about 30 ml of 2N ammonia finally washed with 70 ml (DDW). Four liters filtered water samples with 0.45 µm membrane filter paper flowed through the column with flow rate did not exceed 300 ml/hr. heavy metals were eluted with about 70 ml 2N nitric acid and 10 (DDW). The mixture was evaporated to near dryness. The residue was re-dissolved with 1 ml 6N nitric acid and 10 ml (DDW), cooled and completed to 25 ml with (DDW). The reagent blank was performed in the same manner. Stock standards were prepared for each metal in ppm. All samples and standards were kept in the tightly stoppered polyethylene bottles to avoid evaporation. The concentration of metals (Cd, Cu, Fe, Pd, Ni, Mn and Zn) was determined using flame atomic absorption spectrophotometer (FAAS) model (SHIMADZU-AA- 6800). The results were expressed as µg/l.

**A- Determination of Heavy Metals in *Patella caerulea*:**

The concentration of heavy metals in the target molluscs were measured according to method suggested by APHA (1992) as the following:

The weight of sample (triplicate, each of 0.4 - 0.5 g) was placed in Teflon vessel and 4 ml of nitric acid was added. The vessels were tightly covered and allowed to predigest at room temperature overnight. The digestion block was placed on preheated hot plate at 80°C for three hours. After complete digestion, the digested samples were cooled, then transferred to 25 ml volumetric flask and the residues washed several times with deionized water and completed to 25 ml mark at the volumetric flask. The final solution filtered using filter paper (Whatman No.1) and then samples were stored at 4°C for analysis.

Heavy metals were measured by the Atomic absorption spectrophotometer (FAAS) model (SHIMADZU-AA-6800). The results were expressed in µg/g after calibration of standard solution series of standard metal salts.

**B-The Bioaccumulation Factors (BAF):**

$$BAF=C_m/C_w \quad (\text{Gobas } et al., 2009).$$

Where:

C<sub>m</sub>= mean metal concentration in tissues (mg/kg.dry wt).

C<sub>w</sub>= mean metal concentration in water (mg/L).

**C-Metal Pollution Index (MPI):**

$$MPI=(M_1 \times M_2 \times M_3.....M_n)^{1/n} \quad (\text{Usero } et al., 1997)$$

Where:

M<sub>1</sub> x M<sub>2</sub> x M<sub>3</sub>.....M<sub>n</sub> are the overall metal contents in examined organ

**Statistical Analysis:**

In the present study, SPSS for Windows, Version 15, was utilized for the multivariate analysis and for correlation analysis.

**RESULTS AND DISCUSSION**

Data in Tables (1&2) show the concentrations of the studied heavy metals in water, sediments and *Patella caerulea* (shells and soft tissues). While Table (3) appears the bioaccumulation factors of *Patella caerulea* (shells and soft tissues).

**Cadmium (Cd)**

It has been considered as a toxic element for aquatic organisms (Rao and Saxena, 1981). It's polluting effects on organisms cause serious problems on a global scale (Satarug *et al.*, 2003 and Kazuo, 2007). Agricultural activity is a possible source of Cd (from phosphate fertilizer used in agricultural fields) that enters the coastal marine ecosystem (Kazuo, 2007).

In the present study, the value of Cd concentration in El-Mex water during summer (0.71µg/g) is slightly higher than that during winter (0.38µg/g), this may be due to the increase of temperature which increases evaporation then, Cd concentration increase in

water. This is in agreement with that reported by (Medani, 2018). (Masoud *et al.*, 2012) reported that the high content of Cd at El-Mex is mainly attributed to the discharge wastewaters from El-Umum drain which directly discharged to this region, they showed a positive correlation between Cd and Fe ( $r= 0.771$ ).

**Table, 1:** Concentrations of heavy metals in water and sediment during this study.

Elements	<i>P. caerulea</i>			
	Winter		Summer	
	Water	Sediment	Water	Sediment
<b>Cd</b>	0.38	25.10	0.71	28.57
<b>Cu</b>	2.19	16.44	1.05	52.97
<b>Fe</b>	12.99	931.68	9.21	1132.26
<b>Pb</b>	4.53	164.80	10.46	186.42
<b>Ni</b>	3.27	9.42	2.35	22.02
<b>Mn</b>	2.63	77.08	2.35	51.07
<b>Zn</b>	7.73	78.83	4.38	246.30

**Table, 2:** Concentrations of heavy metals in *Patella caerulea* (shells and soft tissues) during this study

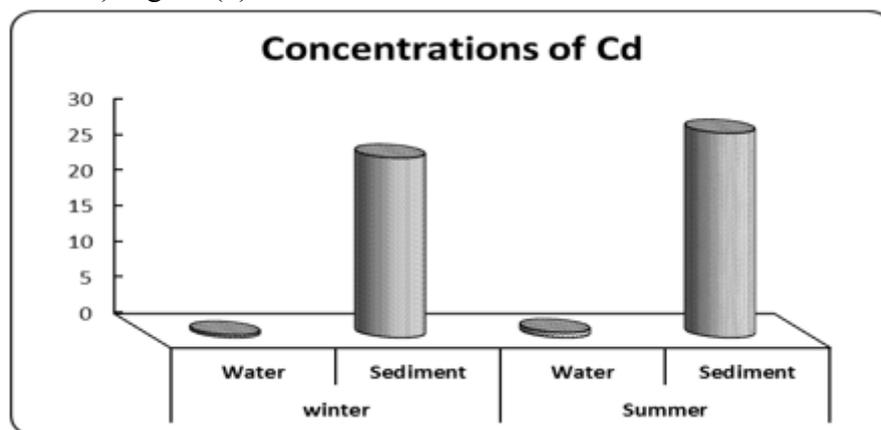
Elements	<i>P. caerulea</i>			
	Winter		Summer	
	Shells	Soft Tissues	Shells	Soft Tissues
<b>Cd</b>	25.32	18.99	24.24	24.57
<b>Cu</b>	160.31	20.15	574.57	59.47
<b>Fe</b>	377.46	1729.18	365.50	654.27
<b>Pb</b>	169.95	139.81	217.81	168.42
<b>Ni</b>	2.46	27.16	6.22	16.70
<b>Mn</b>	71.03	72.00	124.46	98.77
<b>Zn</b>	95.60	71.33	174.60	82.83

**Table, 3:** Bioaccumulation factors of *Patella caerulea* (shells and soft tissues) during this study.

Elements	Bioaccumulation factor of <i>P. caerulea</i>			
	Winter		Summer	
	Shells	Soft Tissues	Shells	Soft Tissues
<b>Cd</b>	66.63	49.97	34.14	34.61
<b>Cu</b>	73.20	9.20	547.21	56.64
<b>Fe</b>	29.06	133.12	39.69	71.04
<b>Pb</b>	37.52	30.86	20.82	16.10
<b>Ni</b>	0.75	8.31	2.65	7.11
<b>Mn</b>	27.01	27.38	52.96	42.03
<b>Zn</b>	12.37	9.23	39.86	18.91

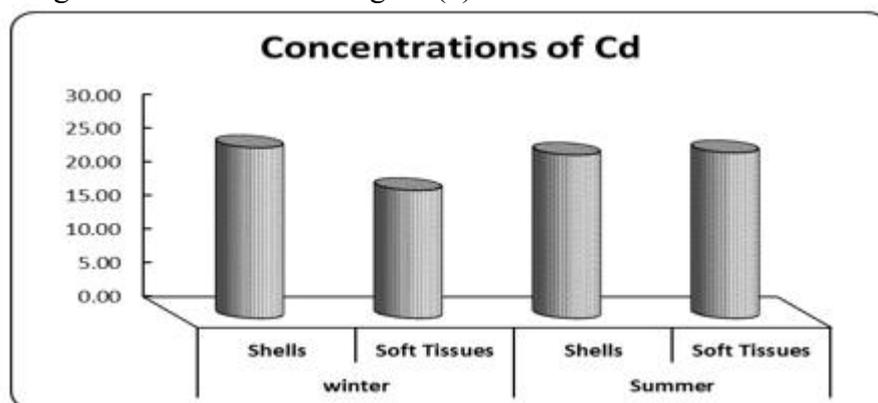
On the other hand, its concentrations in sediments showed the same pattern of that in water (28.57 and 25.10 $\mu\text{g/g}$  in summer and winter, respectively). Generally, the increase in Cd content in the sediments may be attributed to adsorption on the suspended matter leaving

the water body to the sediments. However, the present results appeared positive correlation between Cd and Zn (0.8), Cu (0.48) and Mn (0.49). At the same time, it showed positive correlation with Fe ( $r= 0.52$ ). This cleared the adsorption of Cd on  $Fe(OH)_3$  and  $Fe_2O_3$  (Ahlers *et al.*, 1991) Figure (1).



**Fig. 1:** Cadmium ion concentrations of El-Mex Bay in the water and sediment during this study

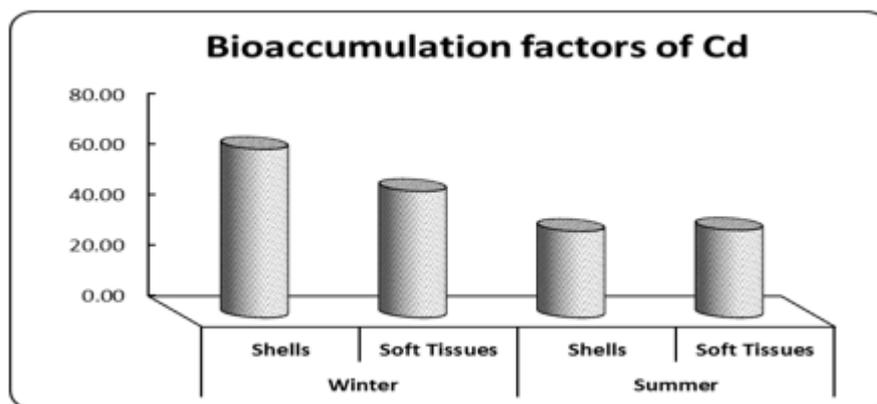
Its concentrations in *Patella caerulea* shells are slightly higher in winter (25.32 $\mu$ g/g) than summer (24.24 $\mu$ g/g) but its soft tissues exhibited more Cd content in summer (24.57 $\mu$ g/g) than winter (18.99 $\mu$ g/g). This is due to the higher Cd concentration in water and sediments during summer than winter Figure (2).



**Fig. 2:** Cadmium ion concentrations in *Patella caerulea* (shells and soft tissues) during this study

**The Bioaccumulation Factors (BAFs):**

Figure (3) Shows the BAFs of Cd in *Patella caerulea* (shells and soft tissues). The shells of the animal had more BAF than soft tissues. During this study, there was a variation in BAF of Cd in *Patella caerulea* (shells and soft tissues). Also, BAF in winter is more than summer, this revealed that *Patella caerulea* has a great potential for rapid accumulation of Cd in water.



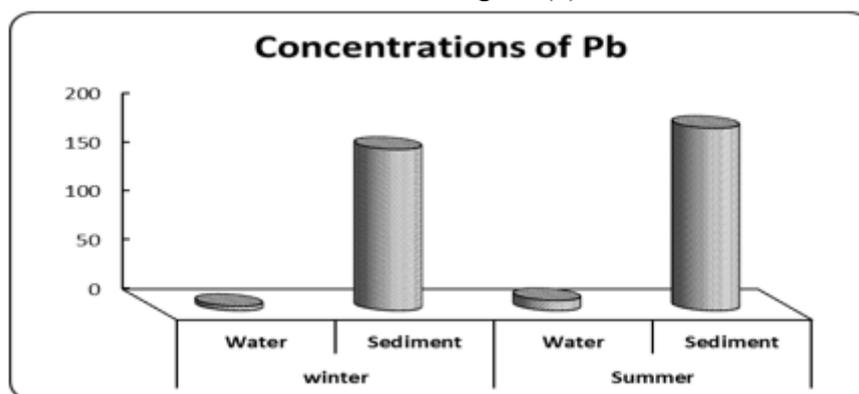
**Fig. 3:** Bioaccumulation factors of cadmium ion in *Patella caerulea* (shells and soft tissues) during this study.

### Lead (Pb):

It is defined by the United States Environmental Protection Agency (USEPA, 2000) as hazardous to most forms of life. The primary sources of Pb include manufacturing processes (particularly metals), atmospheric deposition, and domestic wastewater (Masoud *et al.*, 2012).

The lead concentration in water during summer (10.46 $\mu\text{g/g}$ ) is higher than that in winter (4.53 $\mu\text{g/g}$ ). The high value is due to the effect of different wastes. It was reported that agricultural wastes enriched the sediments with suspended organic matter (Beukemo *et al.*, 1986). Also, its high value in water may be attributed to the reduced volume as a result of high evaporation rate induced by higher water temperature (Obasohan and Eguavoen, 2008).

Its concentrations in sediments took the same pattern as noticed during this work in water (186.42  $\mu\text{g/g}$  in summer and 164.8  $\mu\text{g/g}$  in winter). This may be attributed to the high decomposition rate of organic matter and to lead settlement owing to its positive correlation with other metals. The present work revealed the positive correlation between Pb and Cu (0.79), Mn (0.66), Zn (0.63) and Fe (0.44). However, the positive correlation between Pb and Fe concentrations ( $r=0.147$ ) depicted that Pb is adsorbed from the seawater by ferric oxide, This agrees with that concluded by Masoud *et al.*, 2012) who noticed positive correlation between Pb and Zn, Cu, Mn and Fe Figure (4).

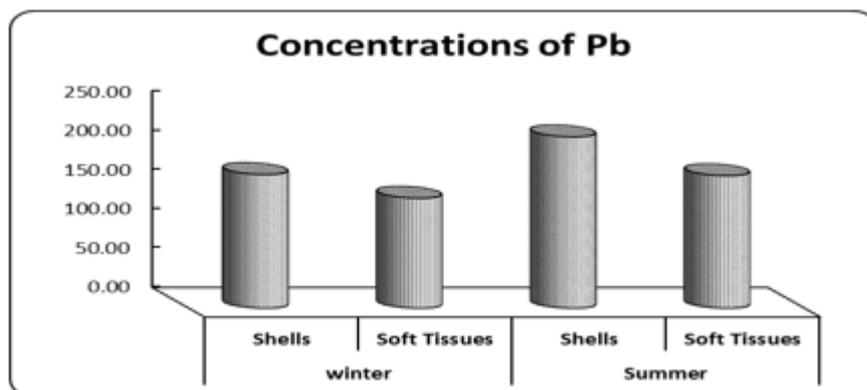


**Fig. 4:** Lead ion concentrations of El-Mex Bay in the water and sediment during this study.

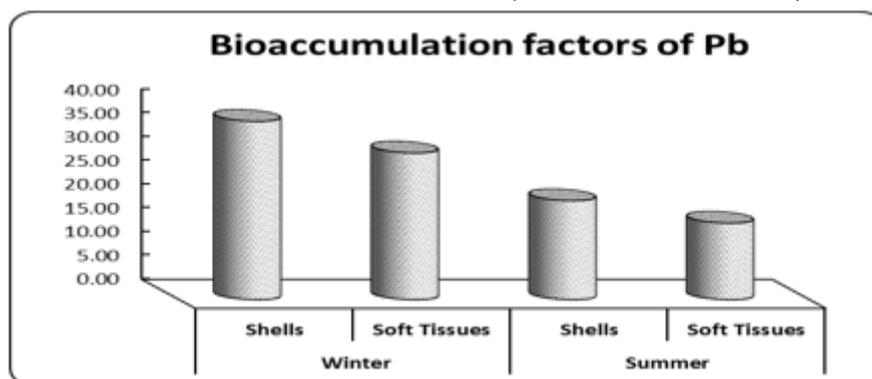
*Patella caerulea* tend to accumulate Pb in its shells (169.75 and 217.81  $\mu\text{g/g}$  during winter and summer, respectively) more than its soft tissues (79.34 and 192.07  $\mu\text{g/g}$  in winter and summer, respectively). The higher Pb concentrations in *Patella caerulea* during summer than winter came to the same pattern of its concentrations in water and sediments Figure (5).

**The Bioaccumulation Factor (BAF):**

The variations in BAF of Pb in *Patella caerulea* (shells and soft tissues) appeared in Figure (6). this revealed that *Patella caerulea* has higher BAF in summer (168.42 and 217.81 for soft and shells, respectively) than winter (139.81 and 169.95 for soft and shells, respectively). This is in coinciding with water and sediments.



**Fig. 5:** Lead ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.



**Fig. 6:** Bioaccumulation factors of lead ion in *Patella caerulea* (shells and soft tissues) during this study.

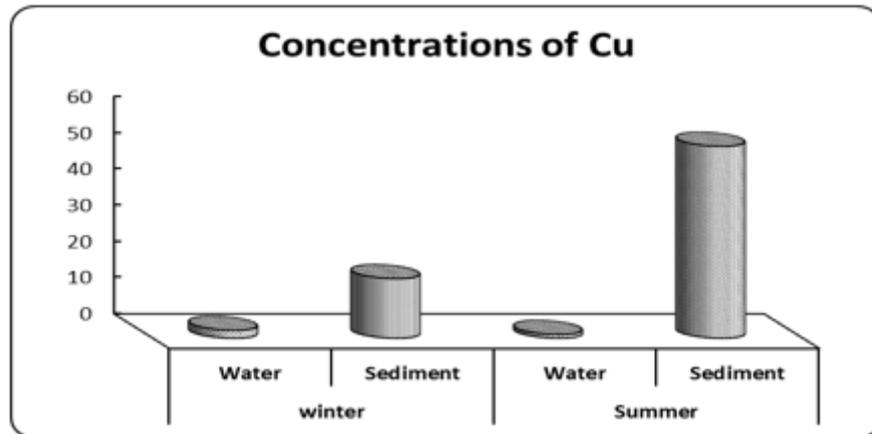
**Copper:**

Copper ion concentrations in water during summer are lower than that in winter (1.05 and 2.19 µg/g, respectively). Generally, the high concentration is mainly due to the discharge from El-Umum pumping station (Masoud *et al.*, 2012).

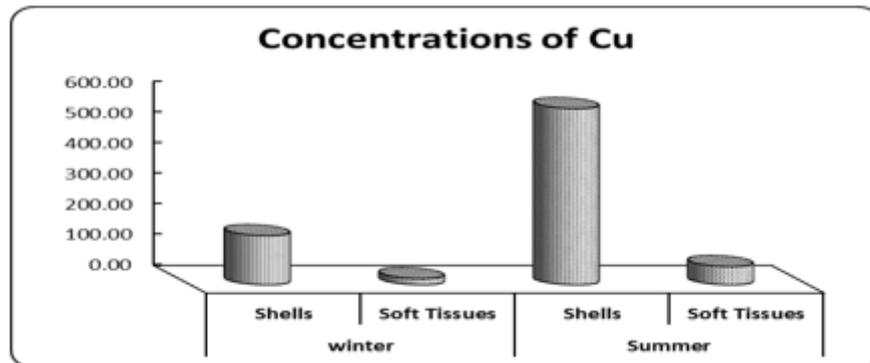
On the other hand, the copper concentration in sediments had the same pattern as Pb, where its concentration was 52.97 µg/g during summer but in winter it was 16.44, µg/g. Its lower concentration in winter is due to low salinity which maintains the metals in solution or suspension (Elfing and Tedegren, 2002). In general, the increase in copper content in the sediments may be attributed to the removal of copper from the water column mediated by the decay of the plankton or due to adsorption on the suspended matter (Borg, 1984). Also, the highest level of copper concentration is related to the input of industrial and agricultural wastes. The high decomposition rate of organic matter and the release of copper from decay organisms by the action of bacteria evolved in the increasing levels of copper at waste-water and seawater (Chester, 1990). The data indicated that there are positive correlations between copper and Mn (0.76), Pb (0.79), Zn (0.69) and Fe (0.63), this showed its precipitation to sediments. Masoud *et al.*, (2012) observed positive correlations with Fe (0.654), Zn (0.842), and Mn (0.947) Figure (7).

The copper concentrations in, *Patella caerulea* soft tissues and shells had the same pattern as that observed of Pb, where its concentrations were 59.47 and 574.57 µg/g,

respectively during summer but in winter it was 20.15 and 160.31  $\mu\text{g/g}$ , respectively. This is congruent with water and sediments Figure (8).



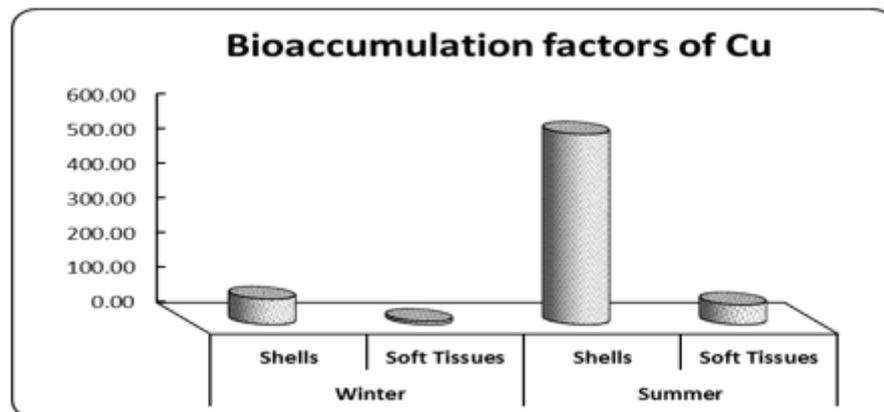
**Fig. 7:** Copper ion concentrations of El-Mex Bay in the water and sediment during this study.



**Fig. 8:** Copper ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.

#### The Bioaccumulation Factors (BAF):

The BAF of Cu in *Patella caerulea* shells is higher than that in soft tissues. Also, it listed higher values during summer than that in winter Figure (9). This is confirmed with water and sediments.



**Fig. 9:** Bioaccumulation factors of copper ion in *Patella caerulea* (shells and soft tissues) during this study.

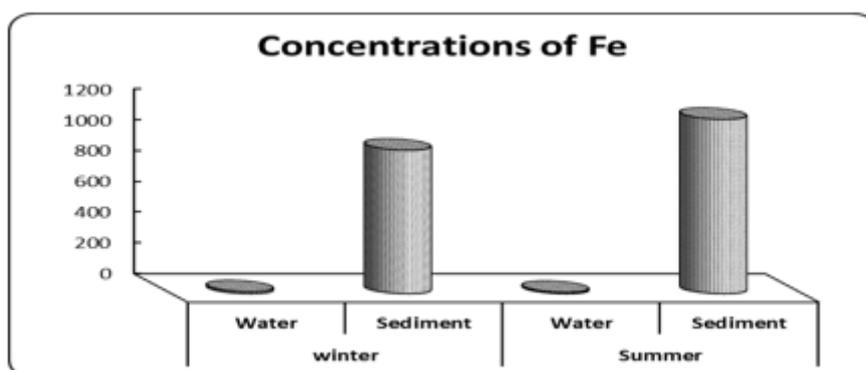
#### Iron:

Iron itself is not toxic but the oxidation of the soluble form to insoluble one leads to form

precipitates that can clog the gills of aquatic organisms (Wyk and Scarpa, 1998). It is considered as one of the elements that are used a lot in the industries and human activities (Okbah *et al.*, 2016).

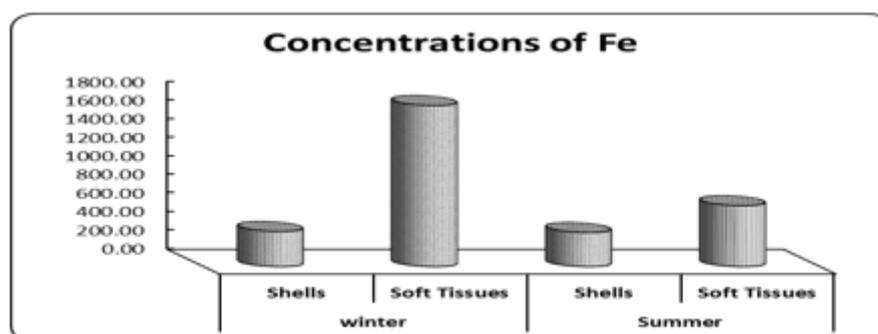
The iron ion concentrations in water are lower in summer (9.21  $\mu\text{g/g}$ ) than winter (12.99  $\mu\text{g/g}$ ), this may be due to its adsorption on organic matter and due to oxidation (Masoud *et al.*, 2005). Its high concentration in winter may be attributed to the release of iron from the sediments, domestic effluents, the breakdown of organic matter and dead microorganisms (Elewa *et al.*, 1996).

Also, its concentration in sediments was higher in summer (1132.26 $\mu\text{g/g}$ ) than winter (931.68 $\mu\text{g/g}$ ), the increase of its concentrations may be due to the adsorption of iron on sediments as iron oxide and due to increasing wastes. Masoud *et al.*, (2012) found that at El-Mex and El-Umum drain the sulphate reducing bacteria produce  $\text{H}_2\text{S}$  to precipitate iron as  $\text{FeS}$ . They reported that oxidation of iron is affected by many factors such as pH and temperature, iron content is positively correlated with manganese ( $r= 0.770$ ). The present data listed positive correlation between Fe and Mn (0.82), Cu (0.63), Zn (0.62) and Cd (0.52). These positive correlations cause co-precipitation of Fe with these metals from water to sediments. Also, (Masoud *et al.*, 2012) found that the oxidation of iron is affected by many factors, such as pH, and temperature ( $r= 0.770$ ) Figure (10).



**Fig. 10:** Iron ion concentrations of El-Mex Bay in the water and sediment during this study.

Its concentrations in *Patella caerulea* soft tissues and shells are higher in winter (1729.18  $\mu\text{g/g}$  for soft and 377.46  $\mu\text{g/g}$  for shells, respectively) than summer (654.27, 527.41 for soft and 365.5 $\mu\text{g/g}$  for shells, respectively), the soft tissues accumulate iron more than shells, this may be due to the physiological and ability of each tissues to accumulate metals Figure (11).



**Fig. 11:** Iron ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.

### The Bioaccumulation Factors (BAF):

The BAF of iron in *Patella caerulea* soft tissues is higher than that in shells; this may be due to the ability of tissues to accumulate Fe. BAF of shells listed higher values (39.66) during summer than that in winter (29.60), this may be due to Fe higher concentration in sediments during summer and the contact between shells and sediments. But that of soft tissues appeared higher values in winter (133.12) than summer (71.04), this may be attributed to the higher Fe concentration in water during winter Figure (12).

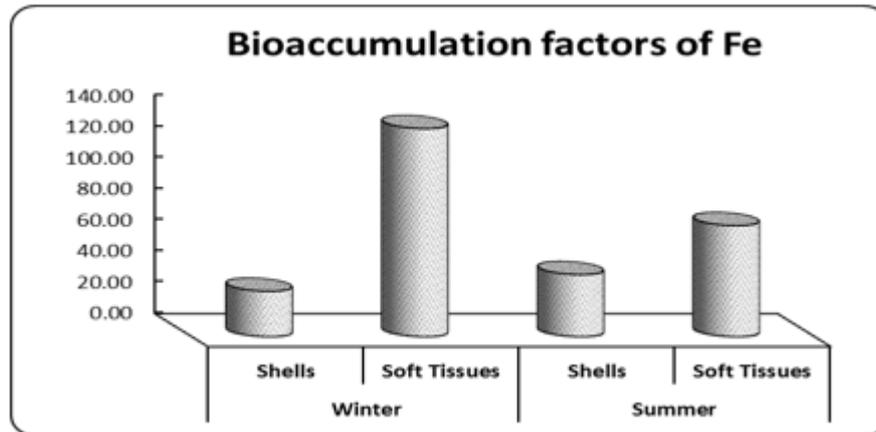


Fig. 12: Bioaccumulation factors of iron ion in *Patella caerulea* (shells and soft tissues) during this study.

### Nickel:

Its concentration in water during summer (9.38  $\mu\text{g/g}$ ) is higher than winter (8.44  $\mu\text{g/g}$ ), this attributed to evaporation caused by high temperature which lead to increase its concentration. Nickel's lower concentration is due to its precipitation from water by hydrous  $\text{MnO}_2$ . Also, nickel is contained in ferromanganese minerals (Lukin *et al.*, 2003).

The concentrations of nickel in sediments are more during summer (22.02  $\mu\text{g/g}$ ) than winter (9.42  $\mu\text{g/g}$ ). The higher value associated with Fe and Mn, where Ni has been scavenged directly from water by hydrous  $\text{MnO}_2$ . Also, nickel is likely to be contained in the clay minerals (Lukin *et al.*, 2003). Also, it is patent from the results; that Ni had positive correlations with Mn (0.508), Zn (0.53), Cu (0.44), Cd (0.43) and Fe (0.3). This congratulated with that reported by (Masoud *et al.*, 2012). Who listed positive correlation coefficients between Ni and both Fe and Mn, ( $r= 0.032$  and  $0.510$ , respectively) which are attributed to Co- precipitation from the water by  $\text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$  to sediments Figure (13).

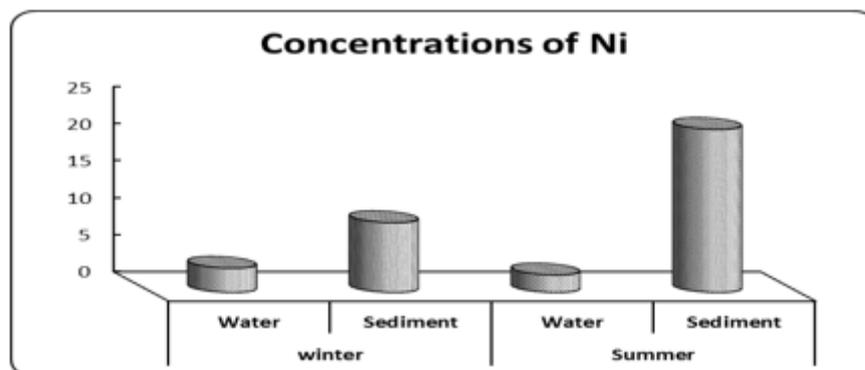
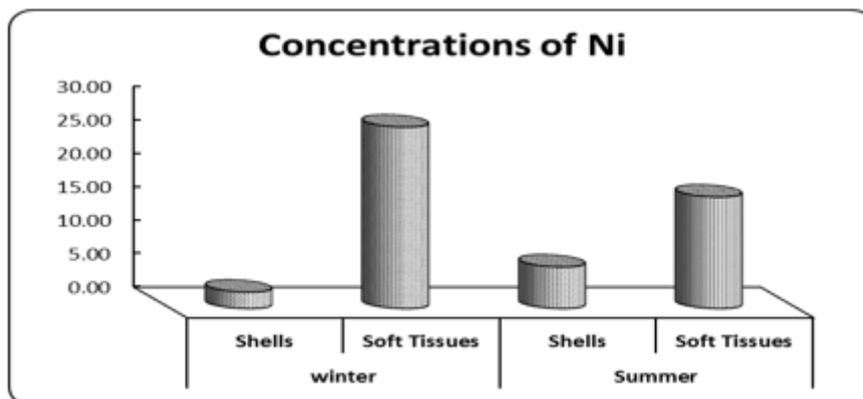


Fig. 13: Nickel ion concentrations of El-Mex Bay in the water and sediment during this study.

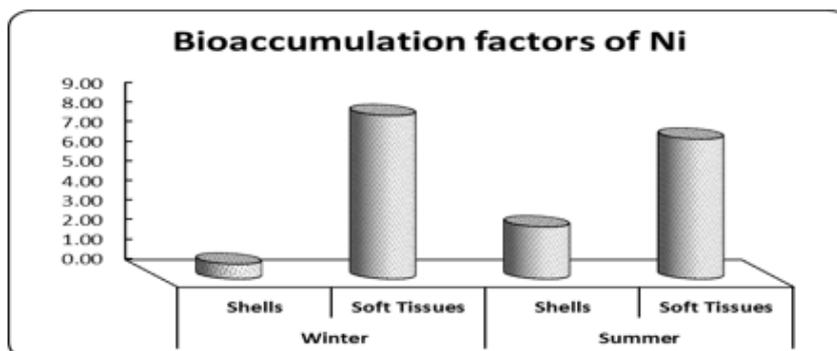
*Patella caerulea* tend to accumulate Ni in its soft tissues more than its shells. The Ni concentration in soft tissues was 27.16 µg/g in winter and 16.70 µg/g in summer, this may be attributed to its high concentration in water during winter. While its concentrations in the shells were 2.46 and 6.22 in winter and summer, respectively. This may be due to its high concentration in sediment during summer Figure (14).



**Fig. 14:** Nickel ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.

**The Bioaccumulation Factors (BAF):**

The BAFs of Ni in *Patella caerulea* soft tissues (8.31 and 7.11 in winter and summer, respectively) are more than that of shells (0.75 and 2.65 in winter and summer, respectively). Also, that of soft tissues in winter is higher than summer but in shells, the BAF in winter is lower than summer Figure (15). this revealed that *Patella caerulea* has higher BAF in winter than summer.

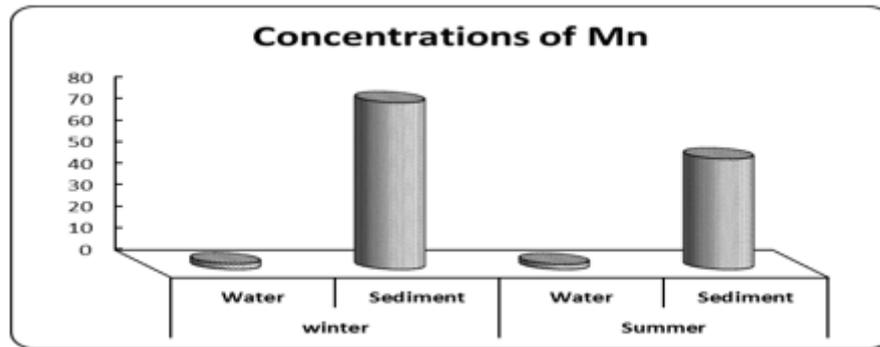


**Fig. 15:** Bioaccumulation factors of nickel ion in *Patella caerulea* (shells and soft tissues) during this study.

**Manganese**

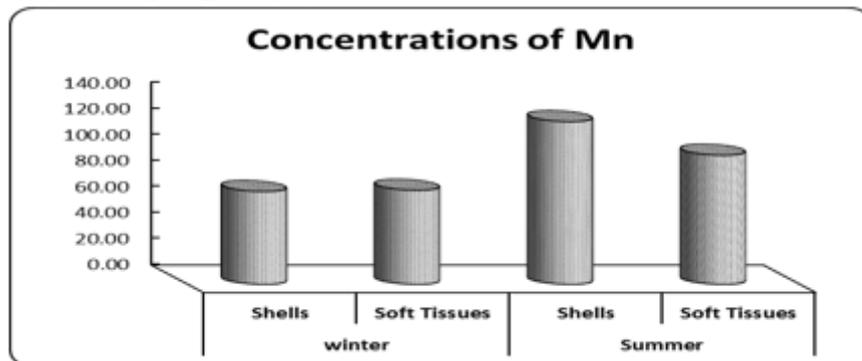
It is seasonally affected by high dust input in water (Okbah *et al.*, 2016). It's concentration in water during winter and summer (2.63 and 2.35 µg/g, respectively). The lower concentration is due to its precipitation from water by hydrous MnO<sub>2</sub>. The high content of Mn may be attributed to the presence of different effluents from El-Umum drain (Masoud *et al.*, 2012).

The concentrations of Mn in sediments are more during winter (77.08µg/g) than summer (51.07µg/g). Manganese is an important micronutrient for marine organisms via its use in photosynthetic and radical scavenging enzymes (Horsburgh *et al.*, 2002 and Kernen *et al.*, 2002). The present work observed positive correlation between Mn and Fe (0.82), Cu (0.76), Pb (0.66), Zn (0.66) and Cd (0.49), this appeared the higher concentrations of Mn in sediments than water Figure (16).



**Fig. 16:** Manganese ion concentrations of El-Mex Bay in the Bay water and sediment during this study

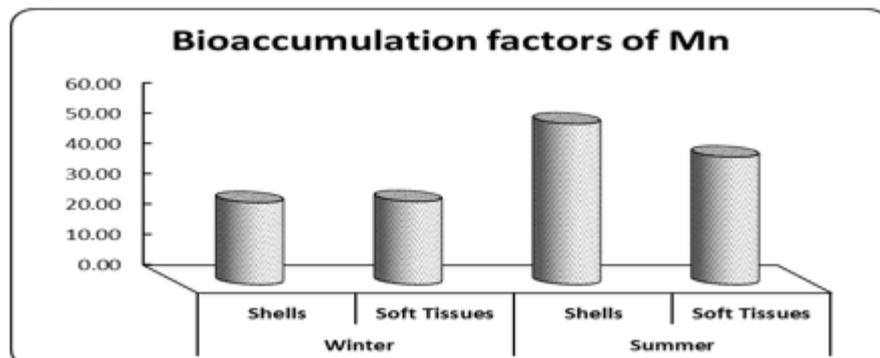
*Patella caerulea* The Mn concentration in soft tissues was 72.0 µg/g in winter and 98.77 µg/g in summer while its concentrations in the shells were 71.03 and 124.46 in winter and summer, respectively Figure (17).



**Fig. 17:** Manganese ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.

#### The Bioaccumulation Factors (BAF):

The BAFs of Mn in *Patella caerulea* soft tissues are nearly similar to that of shells except, BAF of shells in summer is more than that of soft tissues. Also, its BAFs in soft tissues and shells in winter were lower than summer Figure (18). this revealed that *Patella caerulea* has higher BAF in summer than winter.

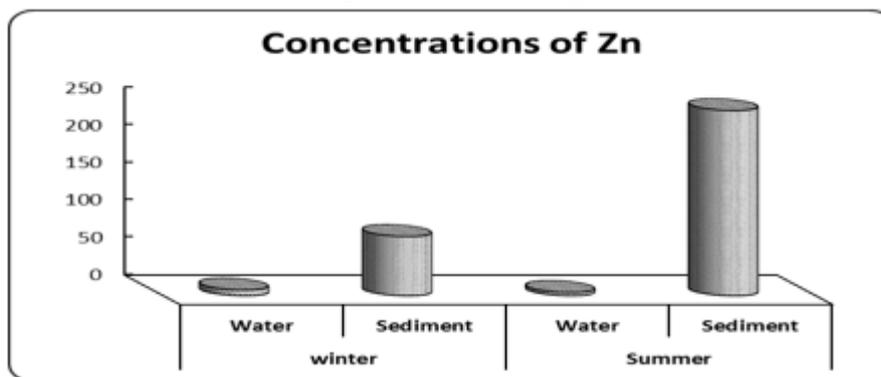


**Fig.18:** Bioaccumulation factors of manganese ion in *Patella caerulea* (shells and soft tissues) during this study.

**Zinc:**

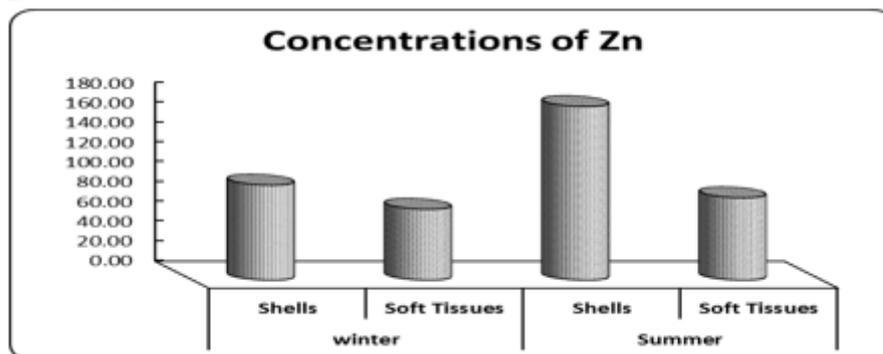
Its concentration in water during summer (4.38 µg/g) is lower than winter (7.73 µg/g). Its lower concentration is due to its adsorption on precipitated Fe (OH)<sub>3</sub> as noticed by Badr et al.,(2006). While the highest zinc concentration at El-Mex is due to the continuous discharges through El-Mex pumping station (Masoud *et al.*, 2012).

Its concentrations in sediments are more during summer (246.30µg/g) than winter (78.83µg/g). It is defined from the results; that Zn had positive correlations with most metals such as Cd (796), Cu (686), Mn (0.664), Pb (629), Fe (0.630) and Ni (527), these positive correlations cause combination of Zn with these metals which facilitate its precipitation from water to sediments. Masoud *et al.*, (2012) noticed that zinc had positive correlation coefficients with iron (0.511) and manganese (0.656) Figure (19).



**Fig. 19:** Zinc ion concentrations of El-Mex Bay in the water and sediment during this study.

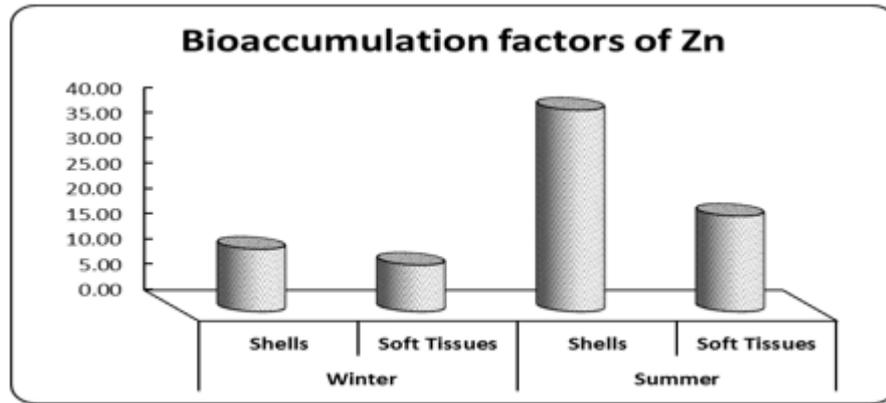
*Patella caerulea* tend to accumulate Zn in its shells (95.8 and 174.6 µg/g in winter and summer, respectively) more than its soft tissues (71.33 and 82.83 µg/g in winter and summer, respectively). Aquatic invertebrates take up Zn directly by gills and mucous (El- Naggar et al., 2016) Figure (20).



**Fig.20:** Zinc ion concentrations in *Patella caerulea* (shells and soft tissues) during this study.

**The Bioaccumulation Factors (BAF):**

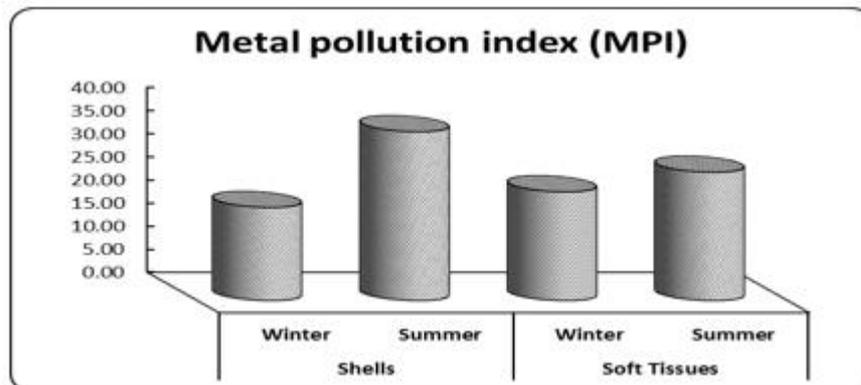
The BAF of *Patella caerulea* shells (12.37 and 39.86 in winter and summer, respectively) is more than that of soft tissues (9.23 and 18.91 in winter and summer, respectively). Also, BAFs in summer is higher than winter Figure (21). this revealed that *Patella caerulea* has higher BAF in summer than winter.



**Fig. 21:** Bioaccumulation factors of zinc ion in *Patella caerulea* (shells and soft tissues) during this study.

#### Metal Pollution Index (MPI) for the Studied Species:

The highest MPI appeared in shells (105.95) during summer, followed by that of soft tissues in summer and winter (80.54 and 74.64, respectively). While MPI in shells during winter (46.13) came to the last. This is due to the high bioaccumulation factors in shells of Cu (574), Mn (52.96), Zn (39.86), Fe (39.66) and Cd (38.14) during summer. On the other hand, soft tissues during summer had high bioaccumulation factors of Fe (71.04), Cu (56.73), Mn (42.03) and Cd (34.6), also in winter they had high bioaccumulation factors of Fe (133.12), Cd (49.97) and Pb (30.86). While, shells had high bioaccumulation factors of Cu (73.2), Cd (66.63), Pb (37.52) and Fe (29.6) in winter (Fig. 22).



**Fig. 22:** Metal pollution index (MPI) for this studied.

**Table 4:** Correlation coefficient between different heavy metals in El Mex Bay during 2016.

	Cd	Cu	Fe	Pb	Ni	Mn	Zn
Cd	1.00						
Cu	0.48	1.00					
Fe	0.52	0.63	1.00				
Pb	0.43	0.79	0.44	1.00			
Ni	0.11	0.44	0.30	0.28	1.00		
Mn	0.49	0.76	0.82	0.66	0.51	1.00	
Zn	0.80	0.69	0.62	0.63	0.53	0.66	1.00

### Conclusion

1-Concentrations of the studied heavy metals in water, sediments and *Patella caerulea* (soft tissues and shells) during summer were higher than winter except Cd and Fe in shells, Fe in Soft tissues, Mn in sediments and Cu, Fe, Mn and Zn in water during summer were lower than winter.

2-(BAFs) of Cd, Pb, Cu, Fe in shells were more than soft tissues except BAF of Fe in soft tissues was higher than shells while BAFs of Mn in soft tissues and shells were nearly similar.

3- Also, BAF in winter was more than summer except that of Cu, Fe, Mn, Zn in winter was lower than summer.

4-The highest metal pollution index (MPI) for the studied species appeared in shells (105.95) followed by that of soft tissues during summer and winter (80.54 and 74.64, respectively). While MPI in shells during winter (46.13) came to the last.

### Recommendations:

1-Sediments are important hosts for trace metals and then they should be included in environmental monitoring programs.

2- Few routine monitoring sites, especially near the major sources of pollution must be done.

3-Prevention, reduction and control of pollution caused by discharges from land-based activities and shipping activities could be greatly helpful in the improvement and the future management of the El-Mex Bay, Alexandria City.

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