Invertebrate shells as pollution bio-indicators, Gebel El-Zeit area, Gulf of Suez, Egypt.

Mohamed Youssef1,2,*, Abdelbaset El-Sorogy1,3, Mohamed El-Sabrouty1 & Naif Al-Otaibi1

1Department of Geology and Geophysics, College of Science, King Saud University, Saudi Arabia
2Geology Department, Faculty of Science, South Valley University, 83523 Qena, Egypt
3Geology Department, Faculty of Science, Zagazig University, Zagazig, Egypt

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Sixteen well preserved Pelecypod and gastropod shells were analyzed for their Mn, Ni, Co, Cu, Zn and Pb content. Eight shells are belonging to the Pleistocene of Gebel El-Zeit and eight recent shells were collected from El-Zeit Bay. Average metal accumulation levels in Pleistocene shell of the study area is in the following order Mn < Ni < Cu < Co < Zn < Pb, while in the Recent shell are in the following order Mn < Ni < Co < Zn < Cu < Pb. This is due to the human activities such as: shipping, the oil pollution resulted from the oil industries, where Gabal El Zeit area is one of the important areas of oil exploration in Egypt. Natural sources of heavy metals include: terrigenous inputs from wadis during flash floods that transport terrestrial material into the sea.

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**Introduction**

The detection of pollutants such as petroleum hydrocarbons and heavy metals in the marine environment promote several workers to employ bio-indicators\(^1\). Clams, bivalves and cockles\(^2\)-\(^4\), Barnacles\(^5\) and Gastropods\(^6\)-\(^7\) were employed as bio-indicators to determine the effect of marine pollution. These organisms were considered as appropriate indicators since they were spatially distributed\(^8\), relatively large in size, and easily collected. Heavy metals could be accumulated in soft tissue and calcareous shells of mollusks, however, most metals are generally concentrated many times over within an organism’s soft tissue, rather than the shell\(^9\). Shells can provide a more accurate indication of environmental change and pollution; they exhibit less variability than the living organism’s tissue, and they provide a historical record of metal content throughout the organism’s life time, with this record still preserved after death\(^10\). Concentrations of metals in mollusks depend not only on the levels of elements in the environment but also on size, age, growth, sex and reproductive conditions apart from seasonal variations, hydrological parameters and interaction with other pollutants\(^11\). Bivalves and Gastropods concentrate heavy metals so actively under natural environments through water and food, they are used as biomonitor organisms concerning to aquatic metal pollution\(^12\)-\(^13\). Advantage of gastropods as biomonitoring organisms concerning heavy metals pollution is emphasize on a few species, such Patella\(^14\). Gastropods have been commonly employed in the monitoring of metal pollution\(^15\)-\(^16\) because they have a broad geographical distribution\(^17\).

The major anthropogenic stresses in the Egyptian Red Sea coast in the past were caused by phosphate pollution and oil spills. However, the major recent cause of damage has been the accelerated tourism development and the annual thousands of visitors to thereof. Recent studies have recommended continuous chemical and biological screening on marine environments to rate natural inputs, anthropogenic impacts and treatment\(^18\)-\(^20\). Levels of heavy metals in recent invertebrates of the Red Sea coast is intensively studied\(^21\)-\(^32\).

The present work deals with the study of chemical analysis of eight molluscan species collected from the more recent Pleistocene terrace sediments at Gebel El-Zeit, Gulf of Suez.
which were deposited in a pristine environment unaffected by human activities and compared with their equivalent Recent shells which were collected from El-Zeit Bay, Gulf of Suez recently affected by human activities. Gebel El-Zeit area was selected for the ecologic monitoring because the studied coastal area is linked to pollution by oil resulting from the oil industries, shipping, sewage, tourism activities, phosphate mines along the Red Sea Coast. Main objective of the present work is to evaluate the levels of pollution along Gebel El Zeit area, which is a very important as the main area of oil exploration in Egypt.

**Materials and Methods**

Gebel El-Zeit area (28° 43' N, 33° 42' E) is located on the western coast of the Gulf of Suez, Egypt (Fig. 1). The area is bordered on the west by the northern part of Esh El Malaha range, and on the east by the relatively high topographic features of the Gebel El-Zeit range, which extends about 14 km in the NW-SE direction, parallel to the Gulf of Suez. Gebel El Zeit range reaches a maximum elevation of 465 m and is an exposed granite pluton. Gebel El-Zeit area represents a typical example of a complex structure of the Gulf of Suez region.

Gulf of Suez may be viewed as a great-elongated (400km long) depression separating the central Sinai Peninsula from the mainland of Africa. In fact, the Gulf of Suez region represents one of the most intensively faulted areas of Egypt.

El Zeit bay is considered as the main harbor of Petrojet Oil Company which provides the essential facilities for the petroleum service and cargo oil ships in Red Sea and Gulf of Suez (Fig. 1). Oil pollution from onshore and offshore oil facilities, as well as from passing vessels, is one of the most serious threats to marine habitat in this area. Random tourist developments spreading north from Hurghada are rapidly consuming all natural habitats and are threatening to completely alter the landscape of the region in the near future.

Sixteen well preserved Bivalves and Gastropods shells were analyzed (Plates 1, 2) for their Mn, Ni, Co, Cu, Zn and Pb. Chemical analyses were performed on class gastropoda of *Turbo argyrostomus, Tellinarugosa, Conusvirgo*, and *Cypraeastaphylaea*, and on class bivalvia of *Neritapolita, Anadora (Anadora) antiquate, Glycymerispectunculus*, and *Arcaimpricata*. All
shells were cleaned with a brush and water and/or by immersion in hydrogen peroxide and cut into half using a diamond saw, and polished slices were produced. The remaining shell material was ground into sub-millimeter-sized fragments using an agate mortar and pestle, dry-sieved, and the best-preserved shell pieces were selected under a binocular microscope, briefly immersed in 0.5 N hydrochloric acid to remove traces of diagenetic calcite, washed in ultrapure water and dried. To assess the state of preservation of the shells, the polished slices were examined by cathodoluminescence microscopy. Additionally, the absolute contents of Mn, Ni, Co, Cu, Zn and Pb in the shells were determined by flame AAS(Table 1, 2).

Results and Discussions

The concentrations of Cu, Pb, Zn, Ni,Mn, and Co in the studied bivalves and gastropods in the two studied locations are illustrated in Tables 1, 2. The following is a detailed description of each element within the two groups among the two studied locations.

Measured elements

Manganese (Mn):

Mn is an essential metal in the terrestrial sediments. The main source of manganese to the coastal areas is represented by natural terrestrial contributions by dissolved and particulate Mn derived from the shelf sediments\textsuperscript{36}. Mn has been hypothesized to substitute for Ca in the CaCO\textsubscript{3} lattice, but may also be adsorbed within aragonite as an oxide or in some aragonite phase\textsuperscript{36}. The second source is the human impact such as landfills, pipelines, corrosion of steel construction and marine paints.

Arithmetic mean of Mn content in the studied Pleistocene shells equals to 0.026 ppm while it attains 0.062 ppm in the studied Recent shells (Figs. 2, 8). Manganese is associated with iron in the conditions of accumulation and dissolution. Mn concentration in corals is an indicator of detrital inputs\textsuperscript{37-38} reported that the concentration of Mn as in Zn, in recent coral samples from Red Sea is mostly high comparing to the world samples. However, the foraminiferal tests have the highest values of Mn and Fe compared to coral reefs and molluscan shells in Quseir, Safaga, Hurghada Harbors, and El-Esh area\textsuperscript{29, 31}. Anthropogenic
affected sites and natural input areas have higher Mn values\(^{20}\). Anthropogenic sources of manganese to the marine environment in the study area are: shipment of mineral products from phosphate mines in the Eastern Desert, paints of marine ships, corrosion of the marine constructions, landfilling and construction residuals, in addition to the terrestrial contribution of some wadis nearby.

Nickel (Ni):
The contribution of Ni to the marine environment can be attained through many anthropogenic ways, such as crude oil seepage, diesel fuel, drilling mud, marine paintings, sewage and landfiling. Nickel is enriched in marine organisms relative to seawater to a greater extent than any other trace elements, with the exception of vanadium and iron\(^{39}\).

Arithmetic mean of Ni content in the studied Pleistocene shells equals to 0.045 ppm while reaches 0.083 ppm in the studied Recent shells (Figs. 3, 8). Major source of nickel reported in benthic foraminifera shells in the Red Sea Coast is anthropogenic and also the wadis are important contributors of terrigenous materials\(^{31}\). On the other hand\(^{40}\) showed that Ni do not display trends indicative of large anthropogenic contribution to the sediments. Coral reef species show that bioaccumulation of nickel is species specific and indicates that the main source of nickel is the terrestrial sediments, either naturally by wadis or by human activities due construction and dredging activities\(^{20}\). High uptake of Ni in gastropod *Nerita* species was recorded south of Hurghada and interpreted due to anthropogenic activities such as crude oil seepage, diesel fuel, drilling mud, marine paintings, sewage, and landfiling\(^7\).

Cobalt (Co):
Cobalt is transported into marine environment by seepages of crude oil pollution, landfills and marine paints. Arithmetic mean of Co in the studied Pleistocene shells equals to 0.065 ppm, while it is 0.115 ppm in the studied Recent shells (Figs. 4, 8). The Co analysis is rare in molluscan shells in the Red Sea Coast. In coral reefs the concentrations of Co range from 0.01-2.91 ppm in the different localities of the Red Sea Coast\(^{22, 28, 29}\). Co and Ni are principally derived from ultramafic rocks along the Red Sea Coast\(^{19}\).
Copper (Cu):

The possible sources of contamination by Cu are the tourism activities as in the diving equipment. Arithmetic mean of Cu in the studied Pleistocene shells equals to 0.054 ppm, while it is 0.248 ppm in the studied Recent shells (Figs. 5, 8). Old ships, removing rust, painting the ship bodies can be considered as a possible source of copper. Copper concentrations are high in El-Esh area due to terrigenous influx and the presence of some basic dykes. There is a specific legislation for Cu concentration in bivalves in Spain, which establishes the maximum allowed concentration for Cu (20 mg/kg). Copper toxicity is controlled by its ratio with zinc in the marine ecosystem, it is most toxic in the free ion form prevalent at (pH<7). Foraminiferal tests recorded high values of Cu concentrations compared with coral reefs and molluscan shells in Quseir and Safaga Harbors. They attributed that to the great ability of foraminiferal species to extract this metal from sediment and bioaccumulate it within their structure more than molluscan shells and coral reefs.

Zinc (Zn):

Zinc which accumulated by organisms is necessary for normal cell division and growth in both plants and animals but can be harmful if exist in extreme amounts. Therefore, the bioaccumulation factor will be greater if the availability of zinc is low. The availability of Zn is not directly related to total concentration of the metal in the environmental compartment. In the marine environment, zinc concentration is least influenced by human impacts, but it will continue to rise to lead to ecological damage, where zinc has very long residence time in the environment. However, Zn is transported into marine environment by the construction materials and the ship paints, oil harbor and municipal sewages are also expected sources to be responsible for accumulation of Pb and Zn. Other main sources are metallurgic industry, pyrite mines, galvanic industry, incineration plants and anti-corrosive products, paints, plastic and rubber. In the studied invertebrates, arithmetic mean of Zn in the studied Pleistocene shells equals to 0.124 ppm, while it is 0.200 ppm in the studied Recent shells (Figs. 6, 8). It was suggested that zinc measured in coral mostly have anthropogenic or polluted source and is enriched in the coral skeleton relative to the surrounding seawater.
Coral reefs in natural inputs areas recorded the maximum values of Zn compared with anthropogenic areas\textsuperscript{20}. In the study area the proposed sources of zinc include zinc sulphate used in house construction, air-conditioning ducts, garbage cans, galvanized pipes, batteries and wear of tires\textsuperscript{19}.

Lead (Pb):

The possible sources of pollution by Pb along the Red Sea coast are variable, where leak of oil and its products seems to be the most effective. Arithmetic mean of Pb in the studied Pleistocene shells equals to 0.793 ppm, while it is 1.141 ppm in the studied Recent shells (Figs. 7, 8). The gastropod *Nerita* can be used as an excellent indicator for Pb pollution in the aquatic system because the Pb content in *Nerita* is very high compared with the other gastropod\textsuperscript{7}. Foraminiferal species have high values of Pb concentration compared to coral reefs and molluscan shells in Quseir, Safaga, Hurghada Harbors, and El-Esh area\textsuperscript{29}. Area under investigation represents an oil production area, suggesting that this is the main source of Pb.

\textit{A comparison between Pleistocene and Recent shells in the study area and other areas from Egypt}

The average of concentrations of Mn, Ni, Co, Cu, Zn and Pb are higher in the studied recent shells than their equivalent Pleistocene ones which lived a pristine environment. This increase may be caused by the pollution of human activities as oil resulting from the oil industries, shipping, tourism activities and the construction materials of the new tourism villages along the Red Sea Coast. In the study area the natural and anthropogenic sources of heavy metals may include: terrigenous inputs from wadis during flashfloods that transport terrestrial material into the sea (metals from mineral forming basement and sedimentary rocks all over the coastline), huge desalination plants, agriculture activities, land traffic increase, sedimentation caused by filling and coastal construction and dredging, oil spills and discharges, industrial discharges (fertilizers, plastic stabilizers), ship-based sewage and solid waste, soft wastedumping (alloys, dyes, automobile tires, anti-fouling paints and galvanizing materials),
shipment of mineral products (mainly phosphate) that is considered as possible hazardous increase of suspended matter. Moreover, the development of the tourism sector especially along the northern and the central parts of the Egyptian Red Sea coast, which is considered as an ineffective pollution source through boat mooring, boat grounding, and cans and other metal littering.\textsuperscript{7,20} Also, mining of the hot brine pools in the Red Sea\textsuperscript{46} could yield thousands of tons of Zn, Cu, Ag, and Au with some contamination of the surrounding waters.

The comparison of the concentrations of heavy metals in the study area with other localities either in the Red Sea coast\textsuperscript{26,47} or in the Egyptian Mediterranean coast\textsuperscript{48-52} shows that the study area is not strongly polluted (Table 3) and also the US National Oceanic and Atmospheric Administration (NOAA) and Canadian guidelines (Table 4) were used as interim measures to assess whether the concentrations of heavy metals in sediments could have adverse biological impacts. The results obtained showed that no elements have incurred over the TEC values of Canadians guidelines and the ERL of NOAA (U.S. National Oceanic and Atmospheric Administration). This indicates that current levels of metals in this area are not high enough to cause adverse biological effects.

**Conclusions**

The average metal accumulation levels in Pleistocene shell of the study area is in the following order: Mn < Ni < Cu < Co < Zn < Pb, while in the Recent shell are in the following order: Mn < Ni < Co < Zn < Cu < Pb. Natural sources of trace elements include weathering of rocks, thermal springs, wadi deposits and vegetation. Anthropogenic inputs sources of trace elements include tourist activity, smelting, oil spills, industrial and mining operations, waste disposal, agricultural activities, and domestic sewage. The present work represents a database for future research.

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Figures and tables caption:

**Fig. 1:** Location map for the Gabal El Zeit and Zeit bay After Aboud et al., 2005).

**Fig. 2:** Distribution of Manganese in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 3:** Distribution of Nikle (ppm) in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 4:** Distribution of Cobalt (ppm) in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 5:** Distribution of Copper (ppm) in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 6:** Distribution of Zinc (ppm) in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 7:** Distribution of Lead (ppm) in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Fig. 8:** Average concentration of heavy metal in Pleistocene and Recent molluscan shells in Gabal el Zeit area.

**Table 1:** Concentration of heavy metals measured in Pleistocene molluscan shells collected from Gabal el Zeit area.

**Table 2:** Concentration of heavy metals measured in recent molluscan shells collected from Gabal el Zeit area.

**Table 3:** Comparison of the heavy metals concentrations (ppm) in Mollusca shells, of study area and different areas of Egypt.

**Table 4:** Guiding values for some heavy metals according to the guidelines of the U.S. National Oceanic and Atmospheric Administration(NOAA) and Canadian guidelines Sediment Quality.

**Plate 1:**

1- *Turbo argyrostormus* LINNE (X 1.5), aperture view.

2, 3 - *Neritapolita* LINNE (X 3), 2 = aperture view, 3 = opposite view.
4, 5 - *Anadora (Anadora) antiquate* LINNE (X 1) 4 = external view, 5 = internal view.

6, 7 - *Glycymerispectunculus* LINNE (X 1), 6 = external view, 7 = internal view.

**Plate 2:**

1, 2 - *Tellinarugosa* BORN (X 1), 1 = external view, 2 = internal view.

3, 6- *Cyraeastaphyae* LINNE (X 1.2), 3 = aperture view, 6 = opposite view.

4, 5- *Conusvirgo* LINNE (X 1.2), 4 = opposite view, 5 = aperture view.

7, 8- *Arcaimpricata* BRUGUIERE (X 2), 7 = external view, 8 = internal view.