Libyan Journal of Science & Technology 7:2 (2018) 118–126

Faculty of Science - University of Benghazi
Libyan Journal of Science & Technology
(Formerly known as Journal of Science & It's Applications)
journal home page: www.sc.uob.edu.ly/pages/page/77

Pollution impact on recent mollusks along the Mediterranean coast between Abu Traba and Al Kuwifia, NE Libya

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ARTICLE INFO

Article history:
Received 07 July 2018
Revised 07 August 2018
Accepted 29 August 2018
Available online 02 September 2018

Keywords:
Environmental Geochemistry, Mollusks, Pollution, Mediterranean Coast, Abu Traba and Al Kuwifia, Libya

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ABSTRACT

The current study assessed the levels of pollution on recent mollusks along the Mediterranean coast from Abu Traba to Al Kuwifia, Northeast Libya. Twenty-five molluskan species have been documented in total. However, only thirteen taxa were chemically analyzed in this study. The chemical analysis showed that the *Cerastoderma glacum* and *Venus* sp. are good accumulators for Zinc (Zn), Lead (Pb) and Thorium (Th), while *Cerithium* sp. A and *Cerithium* sp. B are fine collectors for Uranium (U). Most of the analyzed metals have Enrichment Factor (EF)>2 suggesting that they are mainly of anthropogenic origin. We recommend treating the pollution levels of Lead (Pb), Arsenic (As) and Selenium (Se) in different localities of the study area, especially in Abu Traba and Al Kuwifia localities.

1. Introduction

Mollusks as one of the largest invertebrate phylum group are commonly seen along Libyan coastline. They can be used in detecting and monitoring the recent environment in terms of pollution, therefore mollusks (bivalves and gastropods) are the cornerstone of this study. In most recent researches, there are several contributions towards the geochemical analysis using invertebrate shells (Hamed *et al.,* 2014). Near-shore human activities may result in marine organisms being exposed to high concentrations of metals (Esslemont, 2000; El-Sorogy, 2008; Oladoja *et al.,* 2015). Most studies on the concentration of major and trace elements in marine organisms are focused on the soft part (tissues), while there are very few studies on the hard shells. Walsh *et al.,* (1995) concluded that gastropods are useful for monitoring the contaminants in the marine environment. The present work aims to: 1) classify the collected molluskan species; 2) determine the concentrations of major and trace elements in the recent mollusks along the Mediterranean coast from Abu Traba to Al Kuwifia; and 3) determine the sources of pollution in the study area and proposing the adequate solutions. The studied samples are collected from five localities (Abu Traba, Tocra, Daryanah, Sidi Khalifa and Al Kuwifia, Fig. 1).

2. Materials and Methods

Mollusks shells are collected from the five visited beaches localities in October 2015. The number of the collected specimens is judged on basis of their abundance, the rare species and the fragile shells are packed with care. The surveyed localities are easily reachable by car. On each station, sediments are briefly described and general type of beach indicated with illustrations, selected samples (mostly shells) are cleaned, labeled, packed in plastic bags. Identification of the collected shells is based on the description of Leal, (1995), whereas the shell classification to species level wad achieved according to Abbott, (1974). Chemical analysis of the shells was carried out using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique in the laboratory of Nuclear Materials Authority of Egypt. The enrichment factor (EF) is calculated using the equation of Ergin *et al.,* (1991).

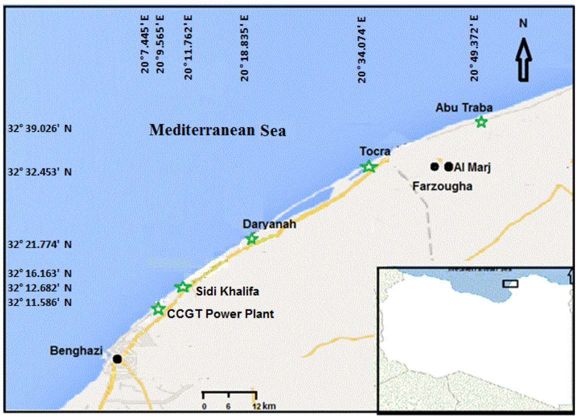

Fig. 1 Index map of NE Libya showing the location of the studied stations (modified after Google maps.com).

3. Results and Discussion

3.1. Taxonomy

The identification and classification of the collected shells were carried out at the Department of Earth Sciences of Benghazi University and illustrated in (Table 1).

3.1.1. The Analyzed Shells (Species)

The collected molluskan shells (Fig. 2) are classified and analyzed geochemically. However, additional molluskan shells such as *Chlamys* sp., *Lima lima*, *Mytilus* sp., *Spondylus* sp., *Conus* sp., *Natica* sp. and *Dentalium* sp. together with Annelida "*Serpula* sp." and Tracheophyta *Posidonia oceanica* are notanalyzed due to samples are not enough to produce suitable powder for geochemical analysis purposes.

Table 1

Summary chart shows the taxonomy of the reported species (after Abbott, 1974)

KINGDOM	PHYLUM	CLASS	ORDER	FAMILY	GENUS	SPECIES
Animalia	**Mollusca**	Pelecypoda	Arcoida	Arcidae	Arca	zebra
					Barbatia	barbata
			Veneroida	Cardiidae	Cerastoderma (Cardium)	glacum
				Donacidae	Donax	variabilis
				Mactridae	Mactra	stultorum
				Veneridae	Venus	sp.
			Pectinida	Pectinidae	Chlamys	sp.
			Limoida	Limidae	Lima	lima
			Lucinoida	Lucinidae	Lucinoma	borealis
			Mytiloida	Mytilidae	Mytilus	sp.
			Pectinoida	Spondylidae	Spondylus	sp.
		Gastropoda	Neotaenioglossa	Cerithiidae	Cerithium	sp. A
						sp. B
			Neogastropoda	Conidae	Conus	sp.
				Nassariidae	Nassarius	sp.
			Vetigastropoda	Trochidae	Monodonta	turbinata
			Littorinimorpha	Naticidae	Natica	Natica sp.
			Archaeogastropoda	Patellidae	Patella	vulgata
		Scaphopoda	Dentaliida	Dentaliidae	Dentalium	sp.
		Cephalopoda	Sepiida	Sepiidae	Sepia	officinalis
	Annelida	Polychaeta	Canalipalpata	Serpulidae	Serpula	sp.
Plantae	**Tracheophyta**	Liliopsida	Najadales	Posidoniacea	Posidonia	oceanica

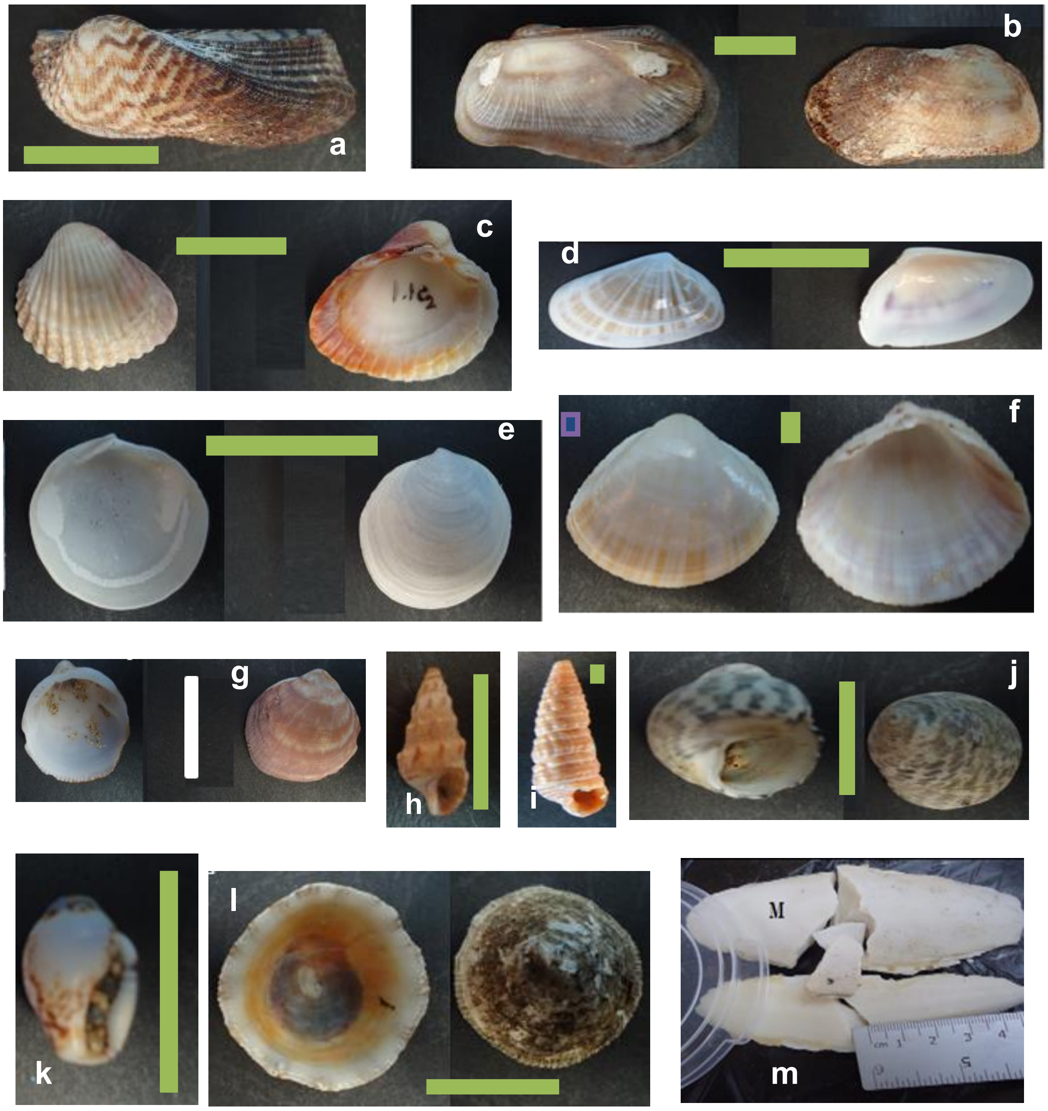

Fig. 2. a) *Arca zebra*; b) *Barbatia barbata*; c) *Cerastoderma (Cardium) glacum*; d) *Donax variabilis*; e) *Lucinoma (L) borealis*; f) *Mactra stultorum*; g) *Venus* sp.; h) *Cerithium* sp. A.; i) *Cerithium* sp. B.; j) *Monodonta turbinata*; k) *Nassarius* sp.; l) *Patella vulgata*; m) *Sepia officinalis*.

3.2. Environmental Geochemistry

Thirteen taxa (seven Pelecypods, five Gastropods and one Cephalopod) were selected for geochemical study (Tables 2-4). The identified species have a wide geographical distribution along the Mediterranean coast (Abott, 1974). The sources of these elements could be natural or anthropogenic; the natural sources include chemical weathering, while the most important sources of anthropogenic metals in the studied shells include petroleum pollution (Fig. 3), desalination, sewage disposal and paints. Tables (2-4) show that all the studied species contain lower concentrations of major and trace elements (except for Sr, As, Pb and Se) than the upper continental crust as estimated by Taylor and McLennan (1985).

Fig. 3. Petroleum Pollution at Al Kuwifia site

3.2.1. Major Elements

There is an urgent need for information on the behavior of phosphorus (P) in coastal areas to understand the impact of human activities on the coastal environment (Suzumural and Kamatani, 1995). All studied species have a reciprocal distribution towards P (Fig. 4). On the other hand, the distribution of Fe and Mg is very heterogeneous (Figs. 5-6). This heterogeneity may be controlled by the flow of the wadis to the Mediterranean coast. The shells of *Cerastoderma (Cardium) glacum, Venus* sp., *Patella vulgata*, *Arca zebra*, *Donax variabilis*, *Barbaria barbata*, *Lucinema (Lucina) borealis* and *Mactra stultorum* contain more Mg (>0.21%) than those of *Cerithium* sp. A, *Cerithium* sp. B, *Monodonta turbinata*, *Nassenaria* sp. and *Sepia officinalis* (<0.12%). The content of Fe in the studied *Patella vulgata* is higher than the shell of *Patella aspera* (0.004%) as estimated by (Cravo *et al.,* 2002), while the content of Fe in the studied *Monodonta turbinata* is approximately similar to the same species in the Iskenderun Bay, North-Eastern Mediterranean Sea (0.21%) as estimated by Duysak and Ersoy (2014).

Table 2.

Chemical analysis data of the studied species (major elements in wt%, trace elements in ppm) at Abu Traba and Tocra

Location	Abu Traba					Tukra		
Species	*Cerastoderma glacum (Cardium)*	*Cerithium sp. A*	*Cerithium sp. B*	*Cerastoderma glacum (Cardium)*	*Venus sp.*	*Patella vulgata*	*Monodonta turbinata*	*Nassenaria sp.*
Fe	0.01	0.11	0.15	0.03	0.04	0.06	0.21	0.10
Mg	0.24	0.03	0.02	0.27	0.23	0.30	0.11	0.05
P	0.003	0.004	0.003	0.002	0.002	0.004	0.004	0.003
Sr	1262	1536	1528	1220	1238	1308	1727	1617
Ba	14.50	1.40	1.71	13.22	12.53	29.71	4.60	1.82
Cu	3.11	0.64	0.57	3.29	4.00	1.26	0.30	0.27
Zn	7.91	0.92	0.88	7.67	6.55	2.30	0.46	0.40
Pb	350.51	0.93	1.26	238.20	179.32	18.18	0.63	0.20
Ni	4.52	6.60	5.91	4.44	3.61	1.11	0.94	2.21
As	2.88	2.43	1.98	2.56	3.13	1.09	1.12	1.19
Se	1.40	0.10	0.19	1.91	1.62	0.20	0.17	0.10
Th	6.47	1.60	1.48	5.60	5.23	0.70	0.30	0.49
U	0.10	2.70	2.43	0.19	0.17	0.10	0.13	0.47

Table 3

Chemical analysis data of the studied species (major elements in wt %, trace elements in ppm) in Daryanah and Sidi Khalifa

Location	Daryana					Sidi Khalifa				
Species	*Venus sp.*	*Arca zebra*	*Donax variabilis*	*Barbaria barbata*	*Lucinema borealis (Lucina)*	*Donax variabilis*	*Mactra stultorum*	*Sepia officinalis*	*Barbaria barbata*	*Arca zebra*
Fe	0.02	0.07	0.06	0.05	0.03	0.06	0.01	0.04	0.07	0.07
Mg	0.25	0.35	0.39	0.36	0.22	0.35	0.24	0.02	0.36	0.33
P	0.003	0.004	0.003	0.003	0.003	0.002	0.002	0.001	0.003	0.003
Sr	1211	1135	1151	1190	1222	1186	1257	1009	1117	1143
Ba	10.92	23.70	21.22	24.09	11.11	22.07	12.54	0.83	23.12	20.94
Cu	1.35	0.84	0.76	0.63	1.44	0.53	1.60	0.27	0.72	0.58
Zn	2.90	1.88	1.40	1.62	2.41	1.24	2.33	0.55	1.51	1.36
Pb	11.72	25.56	30.53	29.87	13.19	22.27	18.17	0.39	31.00	28.22
Ni	3.09	3.35	2.31	2.20	2.87	2.21	2.55	0.80	1.98	1.66
As	1.30	1.59	1.70	1.63	1.21	1.47	1.23	1.00	1.44	1.60
Se	0.55	0.39	0.25	0.24	0.48	0.33	0.49	0.09	0.23	0.25
Th	2.30	3.22	3.00	3.14	2.42	3.77	2.11	0.11	3.53	3.08
U	0.11	0.18	0.10	0.10	0.16	0.10	0.15	0.10	0.10	0.11

Table 4

Chemical analysis data of the studied species (major elements in wt%, trace elements in ppm) at Al Kuwifia

Location	Al Kuwifia		
Species	*Sepia officinalis*	*Cerastoderma glacum (Cardium)*	*Barbaria barbata*
Fe	0.03	0.02	0.06
Mg	0.02	0.25	0.39
P	0.002	0.003	0.003
Sr	1025	1219	1133
Ba	0.77	13.00	22.12
Cu	0.23	1.56	3.33
Zn	0.64	8.00	6.67
Pb	0.33	870.30	517.55
Ni	0.62	5.73	4.41
As	1.10	2.94	2.75
Se	0.09	1.57	1.66
Th	0.16	10.00	8.81
U	0.10	0.19	0.18

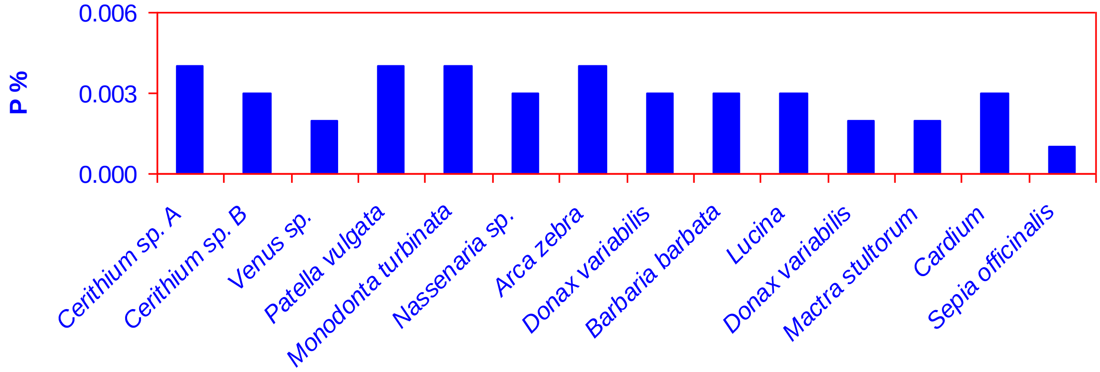

Fig. 4. Concentrations of phosphorus in the studied species

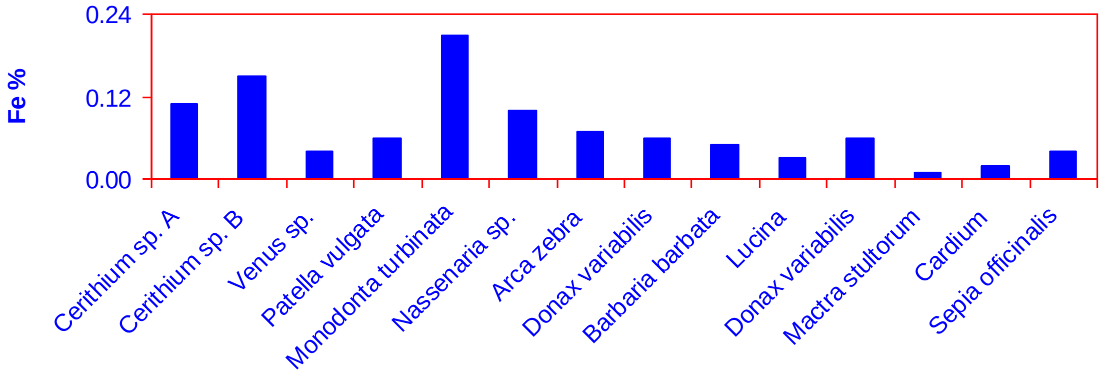

Fig. 5. Concentrations of iron in the studied species

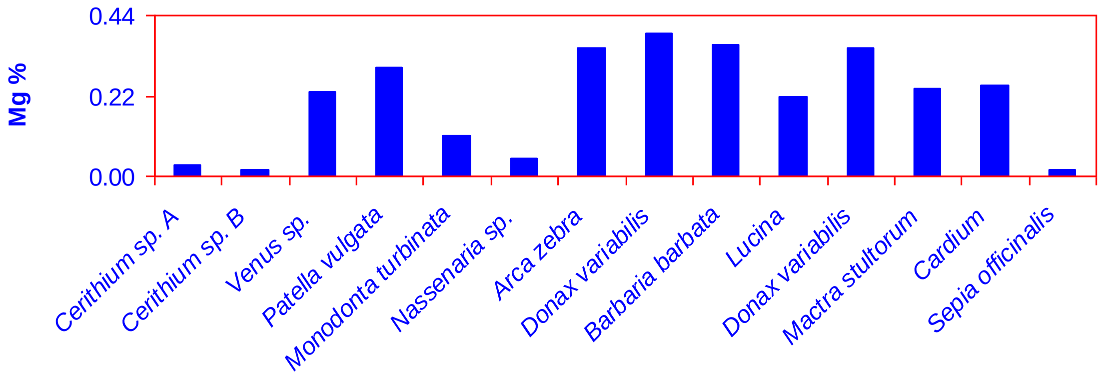

Fig. 6. Concentrations of magnesium in the studied species

3.2.2. Trace Elements

Like the phosphor, all the studied shells have a communal behavior of Strontium (Sr) (Fig. 7), but *Cerithium* sp. A, *Cerithium* sp. B, *Monodonta turbinata* and *Nassenaria* sp. have a higher level of concentration (1536, 1528, 1727 and 1617ppm, respectively). The maximum concentration of Ba is recorded in *Patella vulgata* (29.71 ppm) while the minimum concentration is recorded in *Sepia officinalis* (0.83 ppm, Fig. 8). The maximum and minimum contents of Zn are recorded in *Cerastoderma (Cardium) glacum* and *Nassenaria* sp., respectively (Fig. 9). The shells of *Cerastoderma (Cardium) glacum, Venus* sp., *Patella vulgata*, *Lucinema (Lucina) borealis* and *Mactra stultorum* are better accumulators for Cu than the other species (Fig. 10). The concentration of Pb in *Cerastoderma (Cardium) glacum* at Al Kuwifia is more than 109 times than the crustal average 8 ppm, mentioned by McLennan and Taylor, 1985 (Fig. 11).

The content of Ni ranges from 0.8 to 6.6 ppm (Fig. 12). The studied species have a similar ability for uptake of As (Fig. 13). The concentration of Se in *Cerastoderma (Cardium) glacum* at Abu Traba (1.91 ppm, Fig. 14) is 24 times higher than the upper continental crust (0.05 ppm, by Taylor and McLennan, 1985). Thorium (Th) varies between 0.11 and 10 ppm (Fig. 15). Moreover, Fig. 16 shows that *Cerithium* sp. A and *Cerithium* sp. B can be used as a good indicator of U pollution in the coastal marine environment. According to Faure (1992), the Th/U ratio is 3/1 and 1/1700 in the endogenic rocks and oceanic water, respectively. Table 5 shows that some species are stick to beach rocks and sediments, while the others are immersed by seawater. According to Duysak and Ersoy (2014), the contents of Cu, Zn and Ni in *Monodonta turbinata* in the Iskenderun Bay are 3.3, 1.2 and 2.6 ppm, respectively. These values are higher than those in the studied *Monodonta turbinata*.

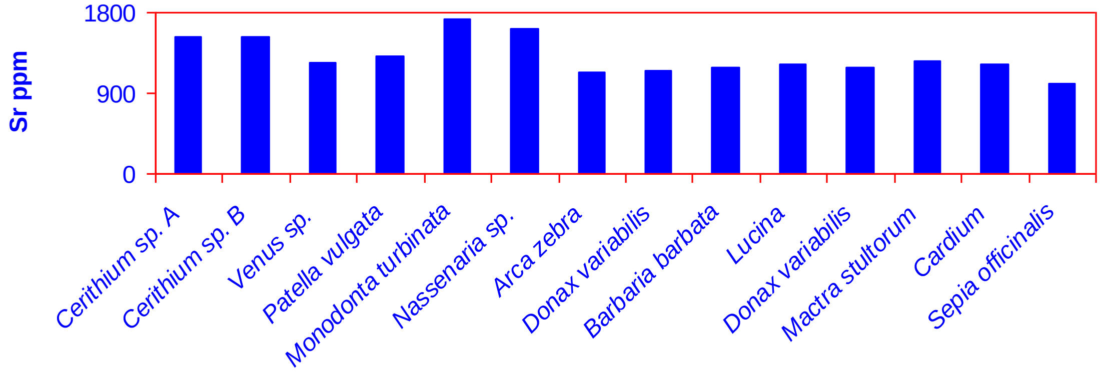

Fig. 7. Concentrations of strontium in the studied species

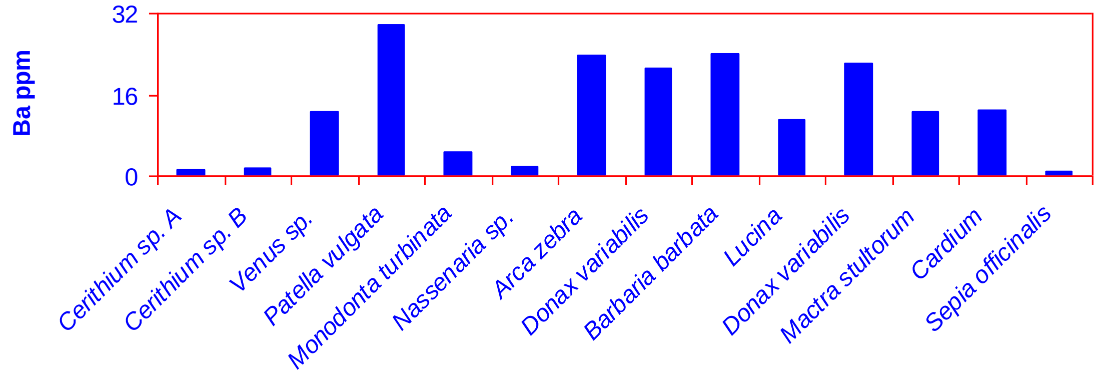

Fig. 8. Concentrations of barium in the studied species

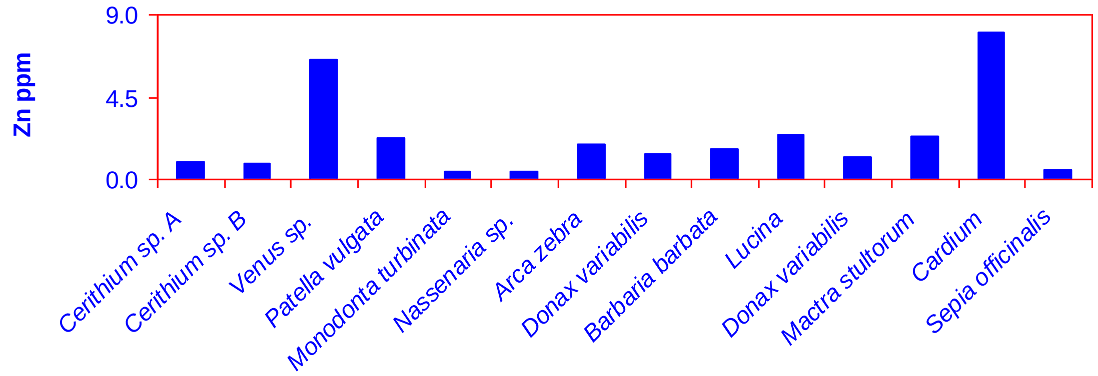

Fig. 9. Concentrations of zinc in the studied species

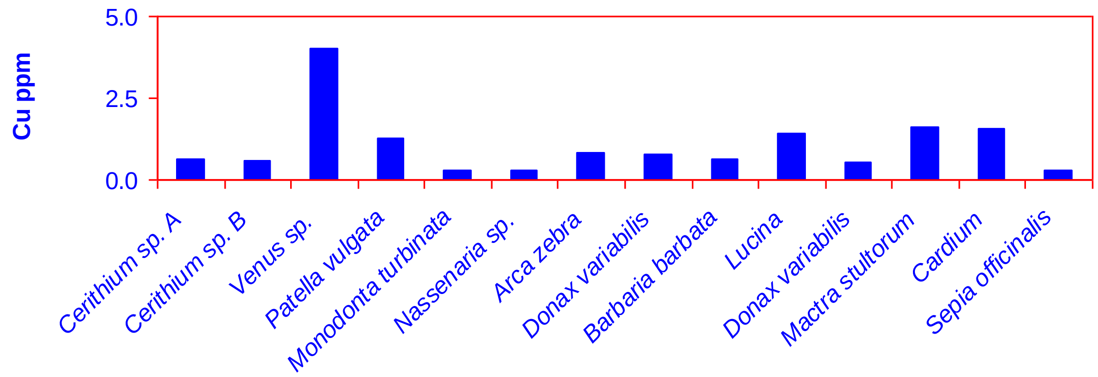

Fig. 10. Concentrations of copper in the studied species

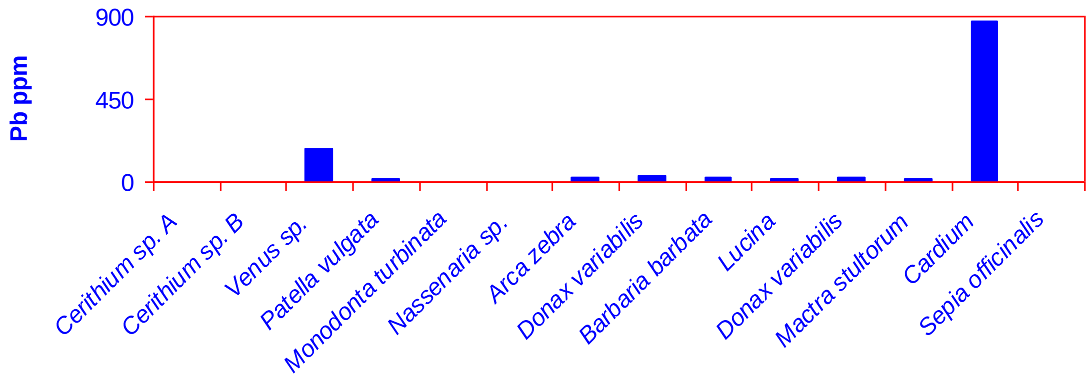

Fig. 11. Concentrations of lead in the studied species

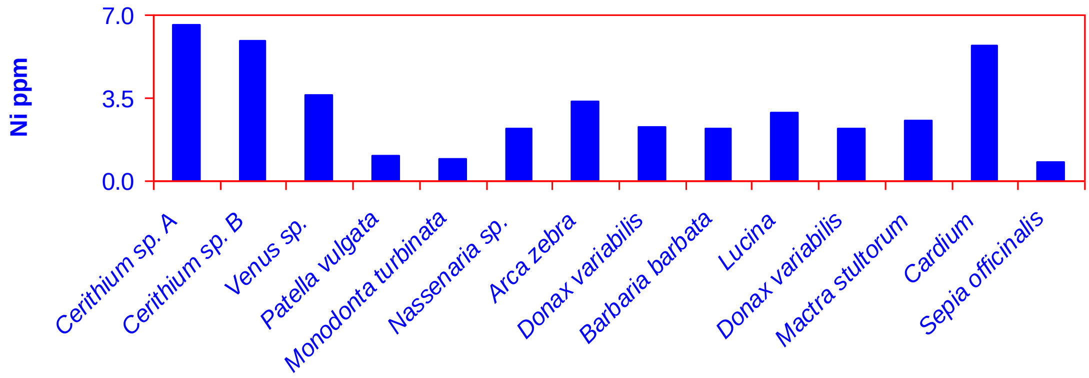

Fig. 12. Concentrations of nickel in the studied species

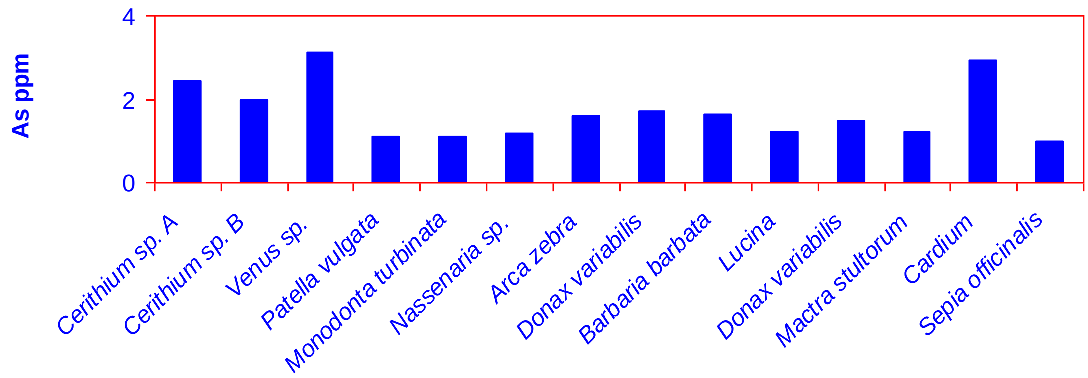

Fig. 13. Concentrations of arsenic in the studied species

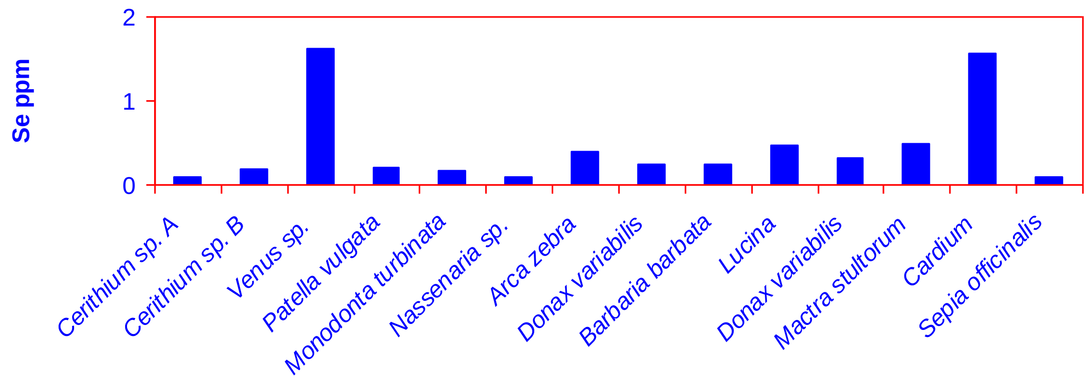

Fig. 14. Concentrations of selenium in the studied species

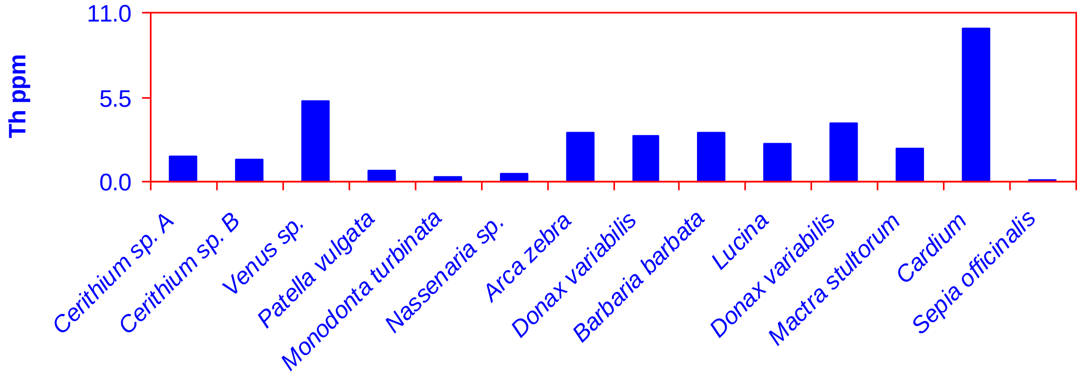

Fig. 15. Concentrations of thorium in the studied species

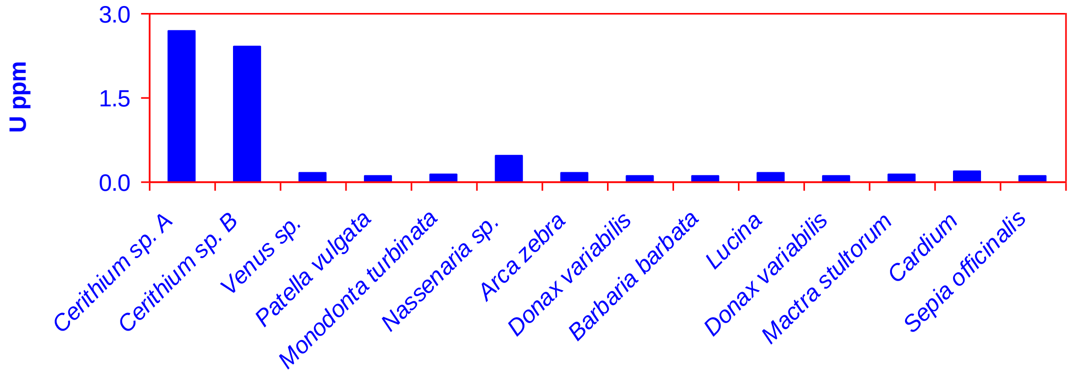

Fig. 16. Concentrations of uranium in the studied species

Table 5

Th/U ratio in the studied species

Species	Th/U
Cerastoderma glacum (Cardium)	64.70
Cerithium sp.A	0.59
Cerithium sp.B	0.61
Venus sp.	30.76
Patella vulgata	7.00
Monodonta turbinata	2.31
Nassenaria sp.	1.04
Arca zebra	17.89
Donax variabilis	30.00
Barbaria barbata	31.40
Lucinema borealis (Lucina)	15.13
Mactra stultorum	14.07
Sepia officinalis	1.10

3.2.3. Enrichment Factor

According to Ergin *et al.,* (1991) the Enrichment Factor (EF) is calculated as

$$EF = \frac{(X/Fe)_{sample}}{(X/Fe)_{upper\ continental\ crust}}$$

Where, X is the metal concentration. Metal concentrations of average continental crust (Taylor and McLennan, 1985) are used as for calculation of EF. According to Grousset *et al.,* (1995), a low value of EF (≤2) indicates a lithogenic origin for the metal while the value is greater (EF>2) in the case of the anthropogenic origin. Most of the analyzed metals are mainly of anthropogenic origin (EF>2, Table 6).

Table 6

Enrichment Factor in the studied species

Species	Enrichment Factor											
	EF Mg	EF P	EF Sr	EF Ba	EF Cu	EF Zn	EF Pb	EF Ni	EF As	EF Se	EF Th	EF U
Cerastoderma glacum (Cardium)	27.91	11.83	1664.39	18.46	7.39	35.49	38508.85	19.37	1043.70	11147.40	1014.29	74.12
Cerithium sp.A	0.61	2.87	381.31	0.36	0.55	0.74	7.48	4.06	156.85	129.10	29.51	191.51
Cerithium sp.B	0.30	1.58	278.17	0.32	0.36	0.52	7.43	2.66	93.72	179.87	20.02	126.40
Venus sp.	12.84	3.94	845.17	8.90	9.47	14.53	3967.26	6.10	555.58	5751.21	265.24	33.16
Patella vulgata	11.16	5.26	595.30	14.06	1.99	3.40	268.14	1.25	128.98	473.35	23.67	13.00
Monodonta turbinata	1.17	1.50	224.57	0.62	0.14	0.19	2.65	0.30	37.87	114.96	2.90	4.83
Nassenaria sp.	1.12	2.37	441.56	0.52	0.26	0.35	1.77	1.49	84.49	142.01	9.94	36.67
Arca zebra	11.16	4.51	442.77	9.62	1.14	2.38	323.14	3.24	161.27	791.17	93.31	20.06
Donax variabilis	14.51	3.94	523.85	10.04	1.20	2.07	450.29	2.60	201.17	591.69	101.43	13.00
Barbaria barbata	16.08	4.73	649.92	13.68	1.19	2.87	528.67	2.97	231.46	681.62	127.39	15.60
Lucinema borealis (Lucina)	16.37	7.89	1112.32	10.52	4.55	7.13	389.09	6.47	286.37	2272.08	163.64	41.61
Mactra stultorum	53.58	15.78	3432.55	35.61	15.15	20.67	1607.96	17.24	873.30	6958.25	428.03	117.03
Sepia officinalis	1.12	1.97	688.83	0.59	0.64	1.22	8.63	1.35	177.50	319.51	5.58	19.51

4. Conclusions

The chemical analysis of the studied shells include a group of environment-sensitive elements such as Fe, Mg, P, Sr, Ba, Cu, Zn, Pb, Ni, As, Se, Th and U. The analysis indicated that *Cerastoderma (Cardium) glacum* and *Venus* sp. are fine collectors for Zn, Pb and Th, while *Cerithium* sp. A and *Cerithium* sp. B are good accumulators for U. All species are excellent accumulators for As and Se, while they have almost the same sensitivity for Fe, Mg, P and Sr. The Enrichment Factor (EF>2) indicates that the human activities are the main source of the analyzed metals. The pollution levels for Pb, As and Se are considered to be serious and should be treated with sufficient care, especially in Abu Traba and Al Kuwifia sites.

5. Recommendations

1-Extensive reconnaissance on most populated parts of Libya-coast using mollusks in detecting the polluted areas.

2- Test chemical analysis (heavy metals) on the living tissues of the mollusks to give comparative study with shells.

3- Further examination of dietary influence on shell dynamics for multiple species of bivalves exhibiting different shell microstructural properties and life histories is necessary to determine species-specific influences and commonalities among similar species. Experimental design should allow for uniform growth and analysis of shell fractions separately in conjunction with ontogenetic examinations.

4- Fracture analysis on subsamples of shells with known diet is necessary to determine the effects diet can have on the strength of the shell.

5- Microstructural analyses on fractured shells are needed to determine differences based on elemental chemistry and dietary influences. This will further increase knowledge as to the influence organic matter has on the microstructure and elemental composition of the mineral partition.

6- Increased experimentation with local species of bivalves to catalogue potential signatures that can then be examined in the field. Upon these determinations, the use of shell for the ecological association will be possible given the ability to differentiate between the signatures and natural variability.

References

Abbott, R. T. (1974) American Seashells. 2. ed. Van Nostrand, Chicago, 663p

Cravo, A., Foster, P., Bebianno, M.J. (2002) 'Minor and trace elements in the shell of Patella aspera (Roding, 1798)', *Environ. Int.*, 28, pp. 295-302.

Duysak, O., Ersoy, B. (2014) 'A Biomonitoring Study: Heavy Metals in Monodonta turbinate (Mollusca: Gastropoda) From Iskenderun Bay, North-Eastern Mediterranean', *Pakistan J. Zool.*, 46(5), pp. 1317-1322.

El-Sorogy, A.S. (2008) 'Contributions to the Pleistocene coral reefs of the Red Sea coast, Egypt', *Arab Gulf J. Sci. Res.*, 26 (1-2), pp. 63-85.

Ergin, M.; Saydam, C.; Basturk, O.; Erdem, E. and Yoruk, R. (1991) 'Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the northeastern Sea of Marmara', *Chem. Geo.*, 91, pp. 269-285.

Esslemont, G. (2000) 'Development and comparison of methods for measuring heavy metal concentration in coral tissues', *Mar. Chem.*, 69, pp. 69-74.

Faure, G. (1992) Principles and Applications of Inorganic Geochemistry. Macmillan Pub. Co., New York, 626p.

Grousset, F.E., Quetel, Q.E., Thomas, B., Donard, O.F.X., Lambert, C.E., Guillard, F., Monaco, A. (1995) 'Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea', *Mar. Chem.*, 48, pp. 291-310.

Hamed, S. S., Radwan, E. H. and Saad, G. A. (2014) 'Impact of Selected Environmental Pollutants on the Ultrastructure of the Gills in Pinctada radiata from Coastal Zones', *Egypt. Open Journal of Ecology*, 4, pp. 907-917.

Leal, J. H. (1995) Bailey-Matthews Shell Museum, Bivalves, Florida, USA, 419p.

Oladoja, N.A., Adelagun, R.O.A., Ahmad, A.L., Ololade, I.A. (2015) 'Phosphorus recovery from aquaculture wastewater using thermally treated gastropod shell', *Process Safety and Environmental Protection*, 98, pp. 296-308.

Suzumural, M., Kamatani, A. (1995) 'Origin and distribution of inositol hexaphosphate in estuarine and coastal sediments', *Limnol. Oceanogr*, 40(7), pp. 1254-1261.

Taylor, S.R., McLennan, S.M. (1985) The Continental Crust: its composition and evolution. Blackwell Scientific Publishers, Oxford.

Walsh, K.; Dunstan, R.H. and Murdoch, R.N. (1995) 'Differential bioaccumulation of heavy-metals and organopollutants in the soft tissue and shell of the marine gastropod (abstract), Austrocochlea constricta', *Arch. Environ. Contam. Toxicol.*, 28 (1), pp. 35-39.