

Tamar Feldstein · Yoel Kashman · Avigdor Abelson ·  
Lev Fishelson · Ofer Mokady · Vladimir Bresler ·  
Yigal Erel

## Marine molluscs in environmental monitoring

### III. Trace metals and organic pollutants in animal tissue and sediments

Received: 24 September 2002 / Revised: 30 May 2003 / Accepted: 12 June 2003 / Published online: 25 July 2003  
© Springer-Verlag and AWI 2003

**Abstract** Concentrations of trace elements and organic pollutants were determined in marine sediments and molluscs from the Mediterranean and Red Sea coasts of Israel. Two bivalve species (*Donax trunculus*, *Pterea aegyptia*), two gastropod species (*Patella caerulea*, *Cellana rota*) and sediments were sampled at polluted and relatively clean, reference, sites. Along the Mediterranean coast of Israel, sediments and molluscs from Haifa Bay stations were enriched with both organic and trace element contaminants. In the Red Sea, differences between the polluted and reference sites were less pronounced. Bio-concentration factors indicate a significant concentration of Zn, As, Cd, Sn and Pb in animal tissue relative to the concentrations of these elements in the sediments. In contrast, Ce, La and U were not concentrated in molluscs. The trace element results indicate a saturation of the detoxification mechanisms in molluscs from polluted sites. The concentrations of organic pollutants at the same sites are at the lower range of values recorded in other studies. However, synergistic

effects between these compounds and between them and metals can lead to acute toxicity.

**Keywords** Chemical monitoring · Marine pollution · Heavy metals · Trace elements · Bio-concentration

#### Introduction

More than half the world's population lives within 60 km of the shoreline, and this could rise to three-quarters by the year 2020. Adverse anthropogenic effects on the coastal environment include eutrophication, heavy metals, organic and microbial pollution and oil spills (Kingston 1992; Costello and Read 1994; Muir et al. 1999; Boudouresque and Verlaque 2002). Consequently, levels of contaminants in the marine environment are increasing continuously. In order to establish adequate coastal management programmes it is important to characterise the environment of concern chemically.

The extent of contamination can be assessed by measuring pollutant concentrations in water, sediments and organic tissue samples. Although easier to process, water samples are difficult to interpret since the water is constantly flowing, transporting pollutants from one place to another while diluting them, often to concentrations below detection limits. A typical dilution factor of 2,500 within 1 km has been observed for hydrocarbons, with factors up to 10,000 and 20,000 for benzene and toluene, respectively (Holdway and Heggie 2000). In the case of phenols, concentrations drop between 25–50 times within 20 m of the point of discharge (Kvestak and Ahel 1994). Sediment samples, on the other hand, integrate chemicals over time and over the water column via precipitation, and organisms often concentrate pollutants in their tissues (bio-concentration; Bresler and Fishelson 1994; Baumard et al. 1998), facilitating the detection of specific substances. Due to their economic and ecological importance, as well as sedentary life, molluscs have assumed a major role in monitoring contaminants worldwide (Lauenstein 1995; Baumard et al. 1998; Boening 1999).

Communicated by: H. von Westernhagen, A. Diamant

T. Feldstein · A. Abelson · O. Mokady (✉) · V. Bresler  
The Institute for Nature Conservation Research,  
The George S. Wise Faculty of Life Sciences,  
Tel Aviv University,  
Tel Aviv, Israel  
e-mail: mokady@post.tau.ac.il  
Fax: +972-3-6407304

Y. Kashman  
School of Chemistry,  
Tel Aviv University,  
Tel Aviv, Israel

L. Fishelson  
Department of Zoology, Faculty of Life Sciences,  
Tel Aviv University,  
Tel Aviv, Israel

Y. Erel  
Institute of Earth Sciences,  
The Hebrew University of Jerusalem,  
Jerusalem, Israel

**Table 1** Protocol for selective sequential dissolution procedure, following Han and Banin (1997)

No.	Component	Reagents	pH	Temperature (°C)	Time	Agitation	Note
1	EXC	1 M HN <sub>4</sub> NO <sub>3</sub>	7	25	30 min	Continual	
2	Carb	1 M NaOAc-(Hac)	5	25	6 h	Continual	
3	ERO	0.04 M NH <sub>2</sub> OH·HCl in 25% HAc	2	25	30 min	Continual	
4	OM	30% H <sub>2</sub> O <sub>2</sub> and 0.01 M HNO <sub>3</sub> (1:1)	2	80	3 h	Intermittent	Water bath
5	RO	0.04 M NH <sub>2</sub> OH·HCl in 25% HAc	2	90	3 h	Intermittent	Water bath

They are abundant, sedentary and easy to collect, which makes them ideal for biomonitoring (see also Bresler et al. 2003a).

The Haifa Bay (Mediterranean, Israel) is a heavily industrialised area, with a power plant, refineries and chemical industry. The industrial waste is treated to some extent, and then dumped into the sea directly or via the Kishon and Na'aman rivers. Numerous studies have shown that this bay is contaminated with organic pollutants and trace metals (e.g. Bresler and Fishelson 1994; Fishelson et al. 1999; Tom et al. 1999). Cleaning efforts in recent years are beginning to show positive results (Herut et al. 1996). In southern Israel, the city of Eilat lies at the tip of the Gulf of Aquaba (Red-Sea). A decade ago, fish farm cages were introduced into this oligotrophic sea. These cages are the issue of a public debate regarding their impact on the environment. In general, eutrophication from the cages and the city sewage is the main concern in this area since it is hazardous to the adjacent coral reefs. However, accidental oil spills have also occurred in the past (Loya and Rinkevich 1979).

The aim of this study was to assess the state of trace element and organic compound contamination in molluscs and sediments at a number of marine coastal sites. These data provide the background for the biomonitoring part of the German-Israeli MARS 2 project (Bresler et al. 2003a, 2003b).

## Methods

### Specimens and collection sites

A total of 23 samples of molluscs and sediments were collected and analysed for their trace element concentrations. Another 54 samples were screened and analysed for organic pollutant concentrations.

The Mediterranean molluscs *Patella caerulea* and *Donax trunculus*, and the Red Sea molluscs *Pteria aegyptia* and *Cellana rota* were sampled from apparently polluted [Shemen beach (SH), Frutarom (FR) and Ardag (ARD)] and reference sites [Ma'agan Mikha'el (MM), Caesarea (CS) and the Marine Biology Laboratory (MBL)] detailed by Bresler et al. (1999, 2003a). In addition, the sediment dwelling bivalve *Circe* sp. was sampled in the Red Sea at Ardag and the Dekel beach, which is located between ARD and MBL (for a map of the various sites see Bresler et al. 2003a). To remove any possible size effect on bioaccumulation, care was taken to collect animals of similar body size (Herut et al. 1999).

For metal analysis, superficial sediments (top 10 cm) were collected with a polypropylene 50 ml centrifuge tube. Sediments for organic pollutant analysis were collected either in glass jars or in polyethylene bags.

### Analysis of organic pollutants

Samples of sediments and molluscs were kept frozen (−20°C) until lyophilised and weighed. About 500 g dry sediments or 2 g dry tissue were extracted twice with ethyl-acetate:methanol (95:5) as follows. Samples were first sonicated for 30 min and then extracted overnight at room temperature. On the following day, the extracts were evaporated on a rotor evaporator. Sediment extracts were cleaned of debris on a short flash silica column with ethyl-acetate:methanol (95:5). To eliminate sterols extracted from molluscs, tissue extracts were chromatographed on a silica column eluted with distilled petroleum-ether. Clean extracts were then evaporated and lyophilised until analysis. Samples were screened for organic pollutants in a GC-MS (Finnigan Polaris) by an EPA certified laboratory, following an EPA protocol (EPA 525.2).

### Analysis of trace elements

Samples of sediments and molluscs were kept frozen (−20°C) until dried in an oven (70°C). 1 g sample was extracted using the selective sequential dissolution (SSD) protocol (Han and Banin 1997; Teutsch et al. 2001). The procedure included five successive steps (Table 1). After each step, the suspension was centrifuged, the supernatant decanted and the residue from each step washed with the same solution before treatment with the next solution. 25 ml extraction solution were used in each step. The 'EXC' and 'RO' steps were omitted for the dissolution of organic tissue since it is mainly composed of organic matter and, following the 'OM' stage, all the solids were dissolved. The precision of the SSD procedure was tested by digesting a soil sample (SHO-2-1, previously calibrated against international standards) with each batch of digested samples (Teutsch et al. 2001). In addition, three samples were analysed in duplicate. A blank sample was also processed with each batch, to control for reagent-contributed contamination. Before analysis by ICP-MS (Perkin-Elmer Elan 6000) samples were diluted 15-fold in double distilled water and internal standards (Rh and Re) were added to each sample for quantitative analysis of Cu, Zn, As, Cd, Sn, La, Ce, Pb and U. Due to background problems, levels of Cu in the sediment are not presented. Precision values (%) for each of the metals were as follows: Cu=16, Zn=11, As=22, Cd=10, Sn= 62, La=17, Ce= 19, Pb=12 and U=1. Except for Sn, all values are similar or lower than the average of tens of samples processed in our lab. Precision values for duplicate samples were even lower.

## Results and discussion

### Organic pollutants

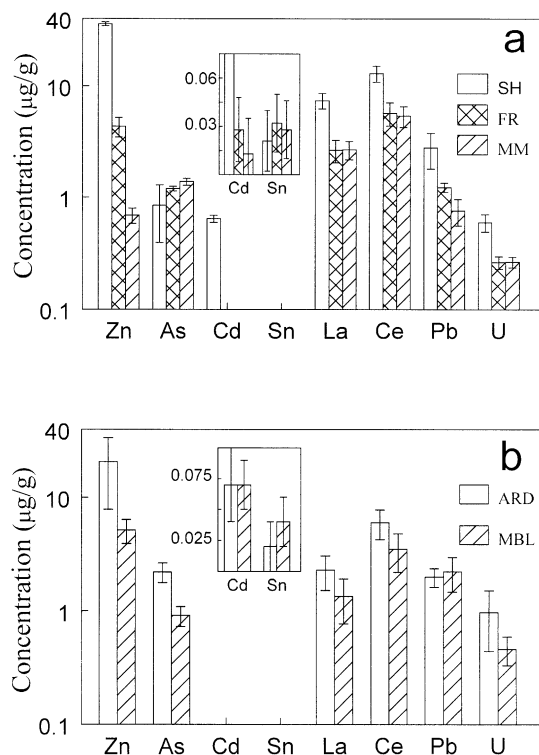
Twenty-three organic pollutant compounds were detected in sediments from the Mediterranean Sea. Of them, 18 were detected in Shemen beach (SH), 15 in Frutarom beach (FR) and only 5 in Ma'agan Mikha'el (MM) (Table 2). All the 18 compounds that were detected in SH were present there in higher concentrations than at the other two sites. Four of the five substances detected in MM were at lower concentrations than at FR.

**Table 2** Concentration of organic pollutants (ng/g dry weight) extracted from marine sediments (Sed.) and molluscs' tissue as measured by GC-MS. *N* number of samples. *n* if >0 is the number of samples (out of *N*) were a certain substance was detected. Blank cells are equal to 0

Site Sample	MM Sed.	FR Sed.	SH Sed.	CS Patella	SH Patella	MM Donax	FR Donax	MBL Sed.	ARD Sed.	MBL Cellana	ARD Cellana	MBL Pieria	ARD Pieria
<i>N</i>	3	5	3	5	7	4	4	1	4	5	4	3	6
2(4H)-Benzo(furanone-5,6,7,7a-tetrahydro-4,4,7a-trimethyl)				30.93 45.47 2	44.52 86.53 2					266.42 250.75 3	31.26 62.53 1	4.47 7.74 1	1.39 2.17 2
Anthracene	Average SD <i>n</i> if>0	0.88 1.96 1						2.34 0.00 1	0.84 0.92 3	0.76 1.71 1			
Benzo(a)anthracene	Average SD <i>n</i> if>0	0.22 0.49 1	0.93 1.62 1	0.92 2.05 1	5.71 11.34 2		0.29 0.57 1		0.50 0.30 4	1.45 3.25 1		1.21 2.09 1	0.77 1.89 1
Benzo(a)pyrene	Average SD <i>n</i> if>0		4.31 4.60 3						0.06 0.11 1	1.83 4.08 1			
Benzo(b)fluoranthene	Average SD <i>n</i> if>0	0.03 0.04 2	8.73 11.82 3				0.10 0.20 1	0.13 0.00 1	0.13 0.17 2				0.77 1.89 1
Benzo(ghi)perylene	Average SD <i>n</i> if>0	0.01 0.03 1	3.90 5.81 3										
Benzo(k)fluoranthene	Average SD <i>n</i> if>0	0.01 0.02 1									3.05 6.10 1		
Benzy(biphenyl)	Average SD <i>n</i> if>0	0.05 0.11 2			71.14 179.08 2	0.34 0.40 2	4.06 8.12 1						0.68 1.65 1
Biphenyl	Average SD <i>n</i> if>0	0.03 0.05 1						0.12 0.00 1	0.08 0.09 2				
Chrysene	Average SD <i>n</i> if>0	0.18 0.40 1	10.76 17.15 2				0.20 0.41 1		0.28 0.39 2	5.22 7.17 2			
Methylpyrene	Average SD <i>n</i> if>0	0.01 0.02 2	9.65 15.47 2		4.60 12.10 1				0.02 0.04 1	1.05 2.35 1			
p-Benzoquinone-2,6-diterbutyl	Average SD <i>n</i> if>0								0.05 0.10 1				
Parsol (MCX)	Average SD <i>n</i> if>0								0.26 0.53 1				
Phenanthrene	Average SD <i>n</i> if>0	0.07 0.12 1	4.88 5.91 3	41.64 57.03 2	101.43 109.15 5	0.49 0.62 2	1.08 0.75 3	2.98 0.00 1	1.19 0.70 4	2.37 3.38 2	92.19 104.68 3		12.94 18.45 4
Phenol-diterbutyl-methyl	Average SD <i>n</i> if>0								0.14 0.28 1				

Table 2 (continued)

Site Sample N	MM Sed. 3	FR Sed. 5	SH Sed. 3	CS Patella 5	SH Patella 7	MM Donax 4	FR Donax 4	MBL Sed. 1	ARD Sed. 4	MBL Cellana 5	ARD Cellana 4	MBL Pieria 3	ARD Pieria 6
Phenol-tertbutyl-methoxy	Average SD n if>0								0.15 0.30 1				
Phenylene diisothiocyanates	Average SD n if>0								1.47 2.95 1				
Pyrene	Average SD n if>0	0.28 0.48 4	5.67 7.60 3	6.00 8.94 2	37.14 41.52 6	0.16 0.19 2	0.44 0.35 3	0.13 0.00 1	0.39 0.26 4	7.03 8.03 3	2.93 3.42 2	1.21 2.09 1	0.89 1.40 2
Tetramethylphenanthrene	Average SD n if>0		2.45 3.64 2										
Trimethylphenanthrene	Average SD n if>0	0.03 0.05 2	11.29 18.30 2		39.37 89.06 2		0.89 1.23 2		0.17 0.21 2	9.27 20.74 1		3.95 6.84 1	0.60 1.48 1
Trimethyltetrahydrobenzofuranone	Average SD n if>0		58.10 113.57 2							54.53 121.94 1			
Diisopropylnaphthalenes	Average SD n if>0				24.17 63.95 1				0.1 0.2 1				
Dimethylanthracene	Average SD n if>0	0.004 0.010 1		1.85 3.51 2	49.20 87.91 3	0.33 0.40 2	0.68 0.81 2			3.46 7.73 1	3.91 7.82 1		1.89 2.42 3
Dimethylnaphthothiophene	Average SD n if>0		0.596 1.033 1		2.733 7.232 1				0.025 0.05 1	0.831 1.859 1			
Dimethylphenanthrene	Average SD n if>0	0.01 0.02 1	11.70 20.27 1		4.07 10.77 1		0.26 0.40 2			1.57 3.50 1	4.78 5.89 2		0.09 0.21 1
Dimethylpyrene	Average SD n if>0		4.15 7.18 1										
Fluotanthene	Average SD n if>0	0.03 0.03 3	3.54 4.17 3	3.00 4.12 2	7.66 11.45 4	0.21 0.24 2	0.24 0.29 2	0.06 0.00 1	0.30 0.33 3	1.13 2.17 2	3.20 6.39 1		0.64 1.24 2
Indenol(1,2,3-ed)pyrene	Average SD n if>0		3.52 4.95 3										
Methylanthracene	Average SD n if>0		3.28 5.68 1	11.52 15.98 2	39.94 40.88 5	0.19 0.38 1	0.50 0.60 2			3.53 7.90 1	22.55 26.73 2	3.38 5.85 1	2.62 3.95 3
Methylbenzothiophene	Average SD n if>0		3.23 5.59 1										
Methylphenanthrene	Average SD n if>0	5.42 9.38 1		8.15 18.22 1	47.70 42.14 5	0.31 0.39 2	0.56 0.65 2		0.04 0.09 1	2.75 6.15 1	35.55 42.16 2	1.25 2.16 1	5.34 7.88 3

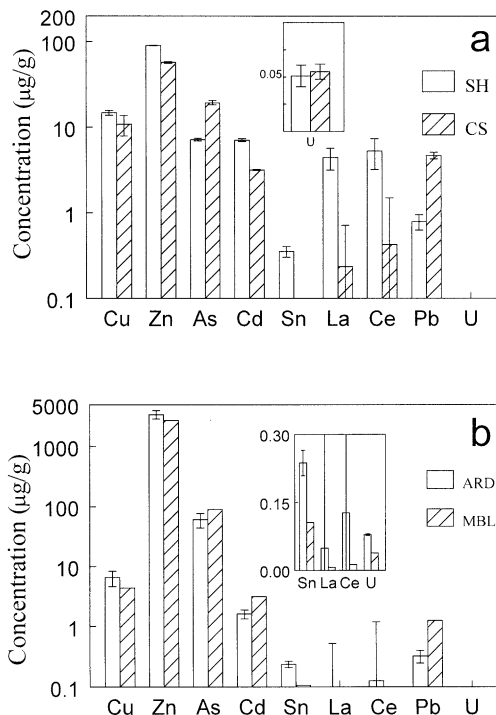


**Fig. 1a, b** Concentration of heavy metals ( $\mu\text{g/g}$  dry weight) extracted from marine sediments as measured by ICP-MS (logarithmic scale). Error bars indicate absolute deviation from the mean. **a** Mediterranean: SH ( $n=2$ ); FR ( $n=2$ ); MM ( $n=2$ ). **b** Red-Sea: ARD ( $n=4$ ); MBL ( $n=3$ )

In sediments from the Red Sea, concentrations of organic pollutants were higher in Ardag (ARD) relative to the marine biology laboratory (MBL) for 15 of the 19 compounds detected (Table 2). Phenanthrene and anthracene, which were more abundant in MBL, are among the more soluble low-molecular polycyclic aromatic hydrocarbons (PAHs).

The levels of organic pollutants in mollusc tissues revealed trends similar to the sediments in the Mediterranean. *Patella caerulea* from SH and *D. trunculus* from FR contained a larger number of organic pollutants at higher concentrations than the reference sites at Caesarea (CS) and MM, respectively. However, in molluscs from the Red Sea, samples from the clean site (MBL) contained higher concentrations of some PAHs than those from ARD (Table 2)

High concentrations of pollutants in SH sediments and *P. caerulea*, with a high standard deviation, may reflect the fact that one of the sampling sessions took place 1 month after a minor oil spill in Haifa bay. However, Glegg et al. (1999) argued that the decrease in PAH concentrations in the body of *Patella vulgata* following an oil spill was very quick (about 70% within the first month), and even higher concentrations of PAHs have been found in native *Patella ulyssiponensis* in the Canary Islands (Pena-Mendez and Garcia-Montelongo 1998).



**Fig. 2a, b** Concentration of heavy metals ( $\mu\text{g/g}$  dry weight) extracted from molluscs' tissue (logarithmic scale). Error bars indicate absolute deviation from the mean. **a** *Patella caerulea*: SH ( $n=3$ ); MM ( $n=2$ ). **b** *Pteria aegyptia*: ARD ( $n=2$ ); MBL ( $n=1$ )

Therefore, this result possibly reflects the general situation in Haifa Bay and not an outstanding event.

Except for SH sediments, the concentrations of all organic pollutants are within the same order of magnitude in Mediterranean and Red Sea sediments and animals. The concentration of the pollutants in the organic tissue is an order of magnitude greater than in the sediment, and they are comparable with concentrations reported in the literature (Lauenstein 1995; Baumard et al. 1998). In *P. caerulea* from SH and *C. rota* from ARD the concentration of phenanthrene reaches the typical maximum value recorded for shellfish (100 ng/g dry weight; QUASI-MEME 2002). In addition, although most of the other organic compounds are found in both the Mediterranean and the Red Sea sediments in relatively low concentrations, the long list of pollutants is alarming.

#### Trace elements

Heavy metal concentrations were within the same order of magnitude in the Mediterranean and the Red Sea sediments (Fig. 1) except for Cd. The concentrations of Zn and Pb in the sediments recorded in this study are similar to the ones reported for the Syrian coast (Mediterranean, north of Israel), while As was an order of magnitude lower than in Syria (Othman et al. 2000). Much higher concentrations of Zn and As were found in *Pteria aegyptia* compared to *Patella caerulea* (Fig. 2).

**Table 3** Bio-Concentration Factor of heavy metals in mollusc's tissue: the ratio between metal content in the molluscs and the concentration in sediments in their vicinity. Names of polluted sites are in italics. For map location, see Fig. 1, Bresler et al. (2003)

Element	Mediterranean Sea		Red Sea		
	<i>Shemen</i>	Caesarea – Ma'agan Mikha'el	<i>Ardag</i>	MBL	
	<i>P. caerulea</i>	<i>P. caerulea</i>	<i>P. aegyptia</i>	<i>Circe</i> sp.	<i>P. aegyptia</i>
Zn	2.6	9.4	170	2.5	1820
As	8	25	28	24	580
Cd	17	53	22	4	70
Sn	14	ND	9.5	14	24
La	0.46	0.15	0.02	0.07	0.01
Ce	0.32	0.11	0.02	0.09	0.01
Pb	0.34	1.7	0.16	0.34	5
U	0.10	0.15	0.08	0.19	0.17

Anatomical differences may partially explain these differences. Whereas *Patella caerulea* is mostly composed of a muscular leg, the gills and digestive gland account for most of the body mass of *Pteria aegyptia*. Feeding habits are also markedly different: *Patella caerulea* grazes on turf algae while *Pteria aegyptia* filters particles from the water. In this context, it is interesting to compare the concentrations measured in *Pteria aegyptia* with the ones measured in the con-familial *Pinctada martensii* (Pteriidae Gray, 1847) collected from the Syrian coast (Abosamara et al. 1989). Whereas Cd and Cu showed similar concentrations in both animals, Pb was ten times higher and Zn was much lower in *P. martensii*.

While some measurements show the expected pattern between the sites, others are worth a closer examination. For example, in the Mediterranean sites, concentrations of five of the eight metals measured (Zn, Cd, La, Ce, U) were higher in SH sediments. Concentrations of Pb and As were the same at SH and MM, whereas Sn concentration was slightly higher at MM. Similarly, in the tissue of *Patella caerulea*, concentrations of most metals were higher from SH except for As and Pb that showed the opposite trend. Previous measurements of Cu, Zn and Cd in *Patella caerulea* from SH and MM have indicated similar values (Herut et al. 1999). In the Red Sea, ARD sediments contained more heavy metals, except for La and Sn. *Pteria aegyptia* from ARD contained higher concentrations of Cu, Zn, Sn, La, Ce and U, but less Cd, As and Pb.

In order to explain these results, we calculated the bio-concentration factor (BCF) for each metal (Bresler and Fishelson 1994; Baumard et al. 1998; Environmental Health Criteria 224 2001). Assuming that the concentration of metals in the sediments characterises a site, we divided the concentration measured in molluscs' tissue by the concentration in the sediment of their surroundings and the result is the factor by which the mollusc concentrates a certain metal from its surrounding, referred to as BCF (Table 3). A potential caveat, which should be kept in mind while applying the BCF approach to compare sites, is that the relative accumulation of trace elements in sediments may vary between metals and sites, especially since the sediment composition varies between sites. However, this was our best approximation for characterising the environment with respect to metals

(Cheggour et al. 2001; Hung et al. 2001; Soto-Jimenez et al. 2001). Baumard et al. (1998) argue that there is a fair correlation between concentration of pollutants in mussel tissue and in sediments if the pollutants are not dissolved in water, but adsorbed on particulates. According to the BCF values (Table 3), we can easily divide the trace elements into two groups. The first group comprises Zn, Cd, As and Sn, which are concentrated in the biological tissue and all have a higher BCF at the clean sites than at the polluted sites. Lead (Pb) behaves like group 1 in the clean sites, concentrated in the biological tissue, and has a higher BCF at the clean sites than at the polluted. However, at the polluted sites, Pb concentration in the tissue is depleted (BCF value lower than 1). Group 2 comprises La, Ce and U which are depleted in the biological tissue. La and Ce, unlike U, have higher BCF values at the contaminated sites.

Tissue enrichment in group 1 metals can be explained by the chemical behaviour of these elements. Zn and Cd belong to class B metals, which are often present in +II valency. They tend to form metal ligand complexes (notably with S) and are mainly sequestered by soluble, low molecular weight proteins (e.g. metallothionein, glutathione) in the cytosol. They can also be diverted into insoluble forms (e.g. lipofuchsin) in lysosomes and related vesicle-bound granules (Langston et al. 1998). Pb(II) is often detoxified through the same pathways as class B metals in biological tissues. A different mechanism acts on Sn and As, which form organic complexes. Tin (Sn) is often introduced to the marine environment in the organic complex of tributyl-tin (TBT) which facilitates its entry across biological membranes. Chemically similar to phosphate, As is absorbed by algae via the same route as P. Therefore, in photic zones, methylated As compounds are present as a result of algae and phytoplankton methylating capabilities. Anoxic bacterial decomposition of algae produces an As derivative, converted in turn to arsenobetain, which is present in many marine animals (Edmonds and Francesconi 1998). This unique metabolism can account for the fact that As is highly concentrated in molluscs.

Trace elements from the second group, La(III), Ce(III,IV) and U(IV, VI), are chemically different from group 1 and probably react differently within cells. In marine research, Ce is mainly used to investigate

paleoredox conditions since its oxidised (IV) form, unlike other rare-earth elements, is absorbed by Mn, Fe-oxyhydroxides or organic particulates. As a consequence, the remaining solution tends to exhibit a negative Ce anomaly (Holser 1997; Moffet 1990). Other researchers point out that Ce is recycled from planktonic debris to a lesser extent than Zn and Cd, and thus is transported faster to the sediment by sinking phytoplankton aggregates (Lee and Fisher 1992). These data are in accordance with our observation that Ce was not concentrated by the molluscs, relative to the sediments. Uranium is investigated mainly in marine microbial mats. Under anaerobic conditions, U(VI) serves as an electron acceptor in bacterial hydrogen metabolism and is converted to U(IV), which is much less soluble than U(VI) (the dominant U species in oxygenated marine water; Lovely et al. 1993). In spite of the above, it is possible that fish would be better monitors for Ce, La and U pollution. For example, it has been demonstrated that fish hard tissues concentrate U in an efficient manner (Matsuba et al. 2000), and Ce and La have even been used to tag juvenile coho-salmon (Ennevor 1994).

The fact that Pb is only concentrated in the reference sites may indicate that Zn, Cd and Pb are sequestered in the cell via the same detoxification mechanism. In the polluted sites, the concentrations of Zn and Cu are an order of a magnitude higher than Cd and Pb. Therefore, the detoxification mechanism is saturated by these metals while Pb is not being concentrated by the cells. In the reference sites, on the other hand, the concentration of Pb is half of that of Zn, and it can compete with it on binding sites in the cells. Therefore, Pb is concentrated only in the relatively clean sites. Furthermore, Cd concentration in the Red Sea is higher in molluscs from the clean MBL site. The occurrence of 'saturation' is further supported by the fact that the BCFs are higher for the reference sites than for the polluted sites. As concentration was higher in molluscs from clean sites in both the Mediterranean and the Red Sea. This may be explained by the heavy burden of trace elements at the polluted sites, which occupy all the available binding sites within the molluscs' tissue, while at the clean sites (MM and MBL) they can still absorb metals at lower concentration. In addition, tissue samples from CS did not contain Sn, though it was present in the sediments. This can be accounted for by the low biotransformation rate of Sn. While As undergoes methylation by a vast range of organisms (Environmental Health Criteria 224 2001) evidence for biomethylation of Sn exists only in micro-organisms (White et al. 1999), and methylation of Sn is slower than that of Hg and Pb (Hadjispyrou et al. 1998). Metals from the second group (La, Ce, U) were not concentrated at all, and further work is needed to indicate potential explanations for this observation.

Generally speaking, the SH site was polluted to a greater extent than any of the other sites. Concentrations of organic and trace element contaminants were higher at SH in both sediments and gastropods. BCF values for divalent ions suggest trace element saturation of molluscs. The FR site was contaminated in organic pollutants

relative to the reference site at MM, a fact that was also demonstrated via accumulation in *D. trunculus* tissue. However, the two sites did not differ in their trace element concentrations. In the Red Sea, contamination near ARD was slightly higher than at MBL. High concentrations of Zn in ARD sediments probably accounts for the differences in BCF in *Pteria aegyptia*.

Though concentrations of organic pollutants were very similar to the typical minimum (QUASIMEME 2002), synergistic effects between these compounds and between them and metals can lead to acute toxicity (Sabaliūnas et al. 2000; Viarengo et al. 2000). However, these effects can only be monitored biologically, hence the importance of biomonitoring and biomarkers on top of direct, chemical analysis of environmental quality.

**Acknowledgements** The authors wish to thank the German GKSS and Israeli MOST for the generous support of this research, performed within the framework of the German Israeli Cooperation in Marine Sciences (MARS 2 project). Thanks are also due to the Marine Biology Laboratory at the H. Steinitz Interuniversity Marine Institute, Elat, for hospitality and use of diving facilities. The experiments performed in this research conform with current laws and regulations of the state of Israel.

## References

- Abosamara F, Nahhas R, Zabalaw N (1989) Trace metals and petroleum hydrocarbons in Syrian coastal waters and selected biota species. In: Albaigera J (ed) Marine pollution. Hemisphere, pp185–199
- Baumard P, Budzinski H, Garrigues P (1998) Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean Sea. *Environ Toxicol Chem* 17:765–776
- Boening DW (1999) An evaluation of bivalves as biomonitors of heavy metals pollution in marine waters. *Environ Monit Assess* 55:459–470
- Boudouresque CF, Verlaque M (2002) Biological pollution in the Mediterranean Sea: invasive versus introduced macrophytes. *Mar Pollut Bull* 44:32–38
- Bresler V, Fishelson L (1994) Microfluorimetric study of bioaccumulation of benzo(a)pyrene and marker xenobiotics in the bivalve *Donax trunculus* from clean and polluted sites along the Mediterranean shore of Israel. *Dis Aquat Org* 19:193–202
- Bresler V, Bissinger V, Abelson A, Dizer H, Sturm A, Kratke R, Fishelson L, Hansen PD (1999) Marine molluscs and fish as biomarkers of pollution stress in littoral regions of the Red Sea, Mediterranean Sea and North Sea. *Helgol Mar Res* 53:219–243
- Bresler V, Abelson A, Fishelson L, Feldstein T, Rosenfeld M, Mokady O (2003a) Marine molluscs in environmental monitoring. I. Cellular and molecular responses. *Helgol Mar Res* (in press)
- Bresler V, Mokady O, Fishelson L, Feldstein T, Abelson A (2003b) Marine molluscs in environmental monitoring. II. Experimental exposure to selected pollutants. *Helgol Mar Res* (in press)
- Cheggour M, Chafik A, Langston WJ, Burt GR, Benbrahim S, Texier H (2001) Metals in sediments and the edible cockle *Cerastoderma edule* from two Moroccan Atlantic lagoons: Moulay Bou Selham and Sidi Moussa. *Environ Pollut* 115:149–160
- Costello M, Read P (1994) Toxicity of sewage sludge to marine organisms: a review. *Mar Environ Res* 37:23–46
- Edmonds JS, Francesconi KA (1998) Arsenic metabolism in aquatic ecosystems. In: Langston WJ, Bebianno MJ (eds) Metal metabolism in aquatic environments. Chapman & Hall, London, pp159–183

- Ennevor BC (1994) Mass marking coho salmon, *Oncorhynchus kisutch*, fry with lanthanum and cerium. Fish Bull 92:471–473
- Environmental Health Criteria 224 (2001) Arsenic and arsenic compounds. International programme on chemical safety, World Health Organization
- Fishelson L, Bresler V, Manelis R, Zuk-Rimon Z, Dotan A, Hornung H, Yawetz A (1999) Toxicological aspects associated with the ecology of *Donax trunculus* (Bivalvia, Mollusca) in a polluted environment. Sci Total Environ 226:121–131
- Glegg GA, Hickman L, Rowland SJ (1999) Contamination of limpets (*Patella vulgata*) following the Sea Empress oil spill. Mar Pollut Bull 38:119–125
- Hadjispyrou SA, Anagnostopoulos A, Nicholson K (1998) Correlation of the methylating capacity of river and marine sediments to their organic sediment index. Environ Geochem Health 20:19–27
- Han FX, Banin A (1997) Long-term transformations and redistribution of potentially toxic heavy metals in arid-zone soils incubated: I. under saturated conditions. Water Air Soil Pollut 95:399–423
- Herut B, Hornung H, Kress N, Cohen Y (1996) Environmental relaxation in response to reduced contaminant input: the case of mercury pollution in Haifa Bay, Israel. Mar Pollut Bull 32:366–373
- Herut B, Kress N, Shefer E (1999) Trace element levels in molluscs from clean and polluted coastal marine sites in the Mediterranean, Red and North seas. Helgol Mar Res 53:154–162
- Holdway D, Heggie DT (2000) Direct hydrocarbon detection of produced formation water discharge on the Northwest Shelf, Australia. Estuar Coast Shelf Sci 50:387–402
- Holser WT (1997) Evaluation of the application of rare-earth elements to paleoceanography. Paleogeogr Paleoclimatol Paleocool 132:309–323
- Hung TC, Meng PJ, Han BC, Chuang A, Huang CC (2001) Trace metals in different species of mollusca, water and sediments from Taiwan coastal area. Chemosphere 44:833–841
- Kingston PF (1992) Impact of offshore oil production installations on the benthos of the North Sea. ICES J Mar Sci 49:45–53
- Kvestak R, Ahel M (1994) Occurrence of toxic metabolites from nonionic surfactants in the Krka river estuary. Ecotoxicol Environ Safety 28:25–34
- Langston WJ, Bebbiano MJ, Burt GR (1998) Metal binding strategies in molluscs. In: Langston WJ, Bebbiano MJ (eds) Metal metabolism in aquatic environments. Chapman & Hall, London, pp219–283
- Lauenstein GG (1995) Comparison of organic contaminants found in mussels and oysters from a current mussel watch project with those from archived mollusc samples of the 1970s. Mar Pollut Bull 30:826–833
- Lee B-G, Fisher NS (1992) Degradation and elemental release rates from phytoplankton debris and their geochemical implications. Limnol Oceanogr 37:1345–1360
- Lovley DR, Roden EE, Phillips EJP, Woodward JC (1993) Enzymatic iron and uranium reduction by sulfate-reducing bacteria. Mar Geol 113:41–53
- Loya Y, Rinkevich B (1979) Abortion effects in corals induced by oil pollution. MEPS 1:77–80
- Matsuba M, Ishii T, Nakahara M (2000) The concentration of uranium in marine organisms (in Japanese, English abstract). Radioisotopes 49:346–353
- Moffet JW (1990) Microbial mediated cerium oxidation in sea water. Nature 345:421–423
- Muir D, Braune B, DeMarch B, Norstrom R, Wagemann R, Lockhart L, Hargrave B, Bright D, Addison R, Payne J, Reimer K (1999) Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: a review. Sci Total Environ 230:83–144
- Othman I, Al-Masri MS, Al-Rayyes AH (2000) Sedimentation rates and pollution history of the eastern Mediterranean Sea: Syrian coast. Sci Total Environ 148:27–35
- Pena-Mendez EM, Garcia-Montelongo F (1998) Hydrocarbon contamination in the Canary islands. II. Intertidal limpet *Patella ulyssiponensis aspera*. Bull Environ Contam Toxicol 61:72–79
- QUASIMEME (2002) QUASIMEME laboratory performance studies. <http://www.quasimeme.marlab.ac.uk>. Cited 16 June 2002
- Sabaliūnas D, Lazutka JR, Sabaliūnienė I (2000) Acute toxicity and genotoxicity of aquatic hydrophobic pollutants sampled with semipermeable membrane devices. Environ Pollut 109:251–265
- Soto-Jimenez M, Paez-Osuna F, Morales-Hernandez F (2001) Selected trace metals in oysters (*Crassostrea iridescens*) and sediments from the discharge zone of the submarine sewage outfall in Mazatlan Bay (southeast Gulf of California): chemical fractions and bioaccumulation factors. Environ Pollut 114:357–370
- Teutsch N, Erel Y, Halicz L, Banin A (2001) The distribution of natural and anthropogenic lead in Mediterranean soils. Geochim Cosmochim Acta 65:2853–2864
- Tom M, Jakubov E, Rinkevich B, Herut B (1999) Monitoring of hepatic metallothionein mRNA levels in the fish *Lithognathus mormyrus* – evaluation of transition metal pollution in a Mediterranean coast. Mar Pollut Bull 38:503–508
- Viarengo A, Maro A, Marchi B, Burlando B (2000) Single and combined effects of heavy metals and hormones on lysosomes of haemolymph cells from the mussel *Mytilus galloprovincialis*. Mar Biol 137:907–912
- White JS, Tobin JM, Cooney JJ (1999) Organotin compounds and their interactions with microorganisms. Can J Microbiol 45:541–554