# Calcareous skeletons of sea urchins as indicators of heavy metals pollution. Portman Bay, Spain

C. Auernheimer · S. Chinchon

**Abstract** Portman Bay presents elevated quantities of metals and heavy metals in the sediments and rocky outcrops. The calcitic skeletons of the sea urchins that live there present elevated concentrations of Mn, Fe, Zn, and Pb (249, 273, 32, and 59 ppm) in comparison with control zones (beach of La Vila) where the concentrations for these elements are 5, 7, 8, and 2 ppm, respectively. Two species of sea urchins have been studied: *Paracentrotus lividus* and *Arbacia lixula*. The different compositions between the plates and the spines of their skeletons have also been studied.

**Key words** Sea urchins · Heavy metals · Pollution · Spain

## Introduction

Portman Bay, located on the SE Spanish coast (Fig. 1), is filled with sandy sediments with very elevated quantities of metals and heavy metals. The bay is located in a zone with rocky outcrops of mica schists, gneisses, marbles, and calcium schists impregnated by diverse metals such as Mn, Fe, Zn, and Pb. The invertebrate organisms, such as the echinoderms that live in the bay, live in an environment with an elevated quantity of these metals. These organisms concentrate the calcium and the magnesium dissolved in the water, many times over, in order to construct skeletons of magnesium calcite. The crystalline structure is formed basically of calcium and magnesium, although when chemically analyzed, notable quantities of other elements are obtained. What governs the incorporation of these elements to the crystalline structure? We think that this incorporation of minority metals is governed by crystallographic laws and that the capacity of discrimination of the physiology of the organism is either null or very low.

Due to its high concentration in heavy metals, Portman Bay is an ideal natural laboratory to demonstrate that the organisms that live there incorporate into their skeletons greater quantities of these elements than those that live in normal zones (beach of La Vila). For this reason, we have sampled and analyzed the substrate, interstitial waters, free waters and two species of echinoderms: *Paracentotus lividus* and *Arbacia lixula,* in Portman Bay (polluted point) as well as the beach of La Vila (clean point, normal or control).

The objective of this study is to demonstrate that it is only the inorganic crystallographic laws that govern the entrance of minor or anomalous elements into the calcite crystalline structures of the skeletons of marine invertebrates. The concentrations of metallic elements found by the analysis carried out on mineral skeletons of the echinoderms could serve, therefore, as indicators of contamination of the marine waters, with certain advantages over those carried out directly on waters or on soft tissues.

## Mineral skeletons as indicators of contamination

Most of the marine invertebrates build their skeletons with calcium carbonate, adopting a crystalline structure such as calcite or aragonite. The structure and composition of the skeletons of the Echinoidea have been described by Chave (1954) and Raup (1966). The skeletons of the sea urchins have a fenestrate structure and are built with magnesium calcite. All of their parts as well as the plates and spines behave like monocrystals under the polarization microscope. In the spines the *c* axis coincides with the elongation.

For several decades there have existed general works on the elementary composition of invertebrate skeletons that show the composition is not exclusively of calcium carbonate. Minor elements substitute for the calcium in the calcite or aragonite structure in accordance with the ionic radius; the small ions in the calcium crystalline structure with more ease, while the large ions substitute in the aragonite structure more easily.

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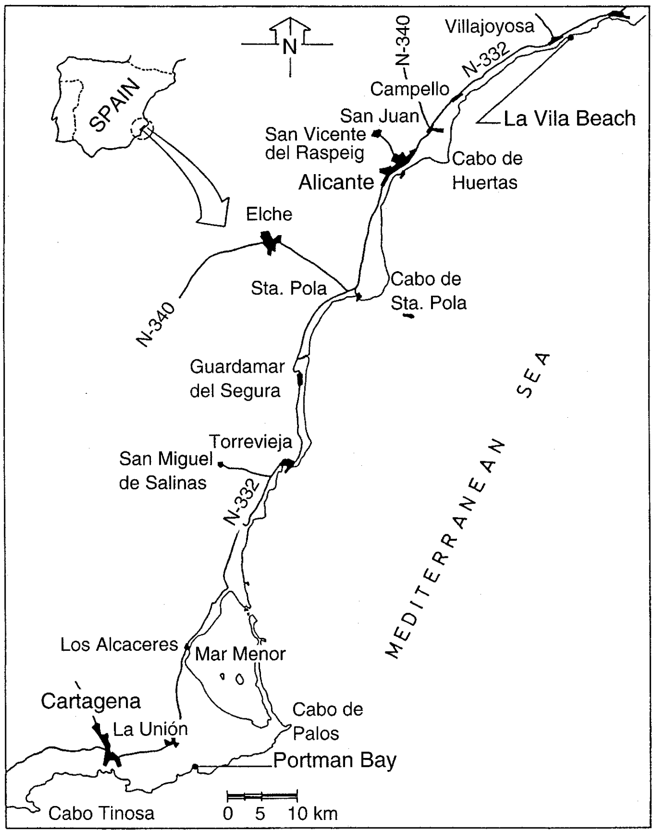


**Fig. 1**
Sampling zones locations

For some authors (Chave 1954; Lowenstam 1963) the organisms exercise some control on the incorporation of these elements into their skeletons due to the physiologic activity, that is, the organism distinguishes the calcium ion of other foreign ions, through their metabolic processes. These authors even claim that the organisms of more primitive taxa discriminate other elements besides calcium to a lesser degree, and in consequence, they present more elevated concentrations of minority elements. Dodd (1965) and Pilkey and Hower (1960) believe that the presence of minority elements in the calcite or the aragonite crystalline structure is due to environmental factors of temperature and salinity; although they do not clarify whether it is the organic or inorganic factors that govern the process.

Auernheimer and others (1984) carried out a study on bivalve species (*Cerastoderma edulis* and *Venerupis aurea*) in Mar Menor (coastal lake connected to the Mediterranean Sea) polluted by elevated concentrations of metals and heavy metals. The shells of these bivalves presented unusually high quantities of Fe, Zn, Mn, and Pb, concluding that these elements displace the calcium of the aragonite crystalline structure by isomorphic substitution. Lingard and others (1992) share the same opinion for the freshwater bivalve species of *Elliptio complanata.*

On the other hand, numerous work exists that utilize analysis of soft tissue organisms as bioindicators of contamination of waters, but very few exist that utilize the calcareous skeleton of the organism analyzed. Among them we would like to highlight the studies done by Campbell and Evans (1987), Scott (1990), Bourgoin (1990), Anderlini (1992), Guzman and Gimenez (1992), and Auernheimer and others (1995).

As for the sea urchins we have found analytic antecedents in Pilkey and Hower (1960) that relate the increase of Mg of the skeleton of the *Dendraster* to the increase of the temperature. Since we have established that the minor elements, among which are the heavy metals, substitute for the calcium in the crystalline structure isomorphically, the utilization of the analysis of contaminating elements in calcareous skeletons as bioindicators provides us with several advantages over those carried out on soft tissues. The results have less variability than those obtained from soft tissues, which have intervening factors such as age, sex, size, sexual state, and type of analyzed tissue. The samples are easier to conserve. The sample to be analyzed can be homogenized better, and it provides us with the average of contamination over a long period of time, attenuating, therefore, possible periodic contaminations, and it allows us to have historic series, since the composition of the shell remains unalterable, even though much time passes after the organism dies.

## Sampling zones

The sampling zones have been selected so that they present a great contrast in the materials that form the substrates on which the sea urchins live. Portman Bay (Mediterranean Sea), in the southeast of the Iberian Peninsula, is located in the Portman mountain range that belongs to the Béticas mountain range. This mountain range is formed by metamorphic rocks such as mica schists, calcium schists, and gneisses of the Paleozoic and Triassic eras. There is an abundance of Blenda (zinc sulfide), pyrite (iron sulfide), and galena (lead sulfide) that fill diaclases or impregnate carbonated rocks, resulting a rock of green–blue color that is called grenalite.

The entire zone had active mining from the time of the Roman Empire to 1991 when the activity ceased for lack of profitability. In the last 30 years more than 50 millon tons of crushed (sterile) rock has been dumped into the bay from the mineral washes. As a result of this process, 80% of the bay has been filled. The coastal line has advanced about 800 m, gaining 70 ha of earth from the sea. The current beach is a sandy black beach with high contents in heavy metals. It is preserved by two rocky promontories that provide a hard submarine substrate, where the two species of sea urchins studied live.

The beach of La Vila was selected as the control zone. It is located at about 110 km north of Portman Bay, in a completely different lithological context. The cliffs that skirt this small beach are formed by materials of the Eocene. They are limestones and loamy limestones without any metallic mineralization, except some occasional nodules of Fe (altered pyrite).

## Sampled species

*Paracentrotus lividus* (Lamarck) and *Arbacia lixula* (Linnaeus) are two common species of sea urchins in the Mediterranean Sea. They are sessile organisms that live on the rocks of the coast, although they are permanently covered by water (subtidal). Both species could be found on the same rocks (same habitat), but their feeding habits and ecological niches are different. *Paracentrotus* is distinguished by having some blackish brown or slightly purple colors and is sciophyllous (it lives in penumbra). At a depth of 0 to 10 m, it is found in the fissures of the rocks and covers its body partially with pieces of shells or pieces of the Phanerogamae *Posidonia oceanica.* It feeds on fleshy algae. *Arbacia* is an intense black color and lives on the surfaces of the rocks nearest to the sea surface, since it is photophile. It is found between 0 and 5 m of depth and feeds on incrustating calcareous algae such as *Lithophyllum.*

## Method

The sampling was carried out by taking two species of sea urchins; of the gathered samples, 10 of each species of equal size were selected. In both sampling stations, samples are distributed in an extension of underwater rocks of one Ha at similar depth between 1 to 2 meters. In the same manner, we took rock samples on which colonies of sea urchins live, as well as beach sand, surface water, and interstitial water. For the submarine sampling, we used the usual equipment for underwater fishing and simple gear.
Once the samples of sea urchins were selected, they were exposed to the sun for several weeks, then placed in individual containers with hydrogen peroxide for 10–12 days so as to destroy the organic material completely. When the skeletons were completely clean the various parts of the shell were separates: plates, spines, and Aristotle's lantern.
The plates and the spines of each specimen were crushed for separating; 1 g of each of the two skeletal parts was weighed. This material was dissolved with nitric acid. The solution was raised with ultrapure distilled water (up to 25 m). The different elements were analyzed with ICP; the patterns used were carried out with standard comercial brand solutions, which are recognized internationally.
The analyses of sand and rock were carried out in a similar way, although the nitric acid utilized was hot. The cations of the waters were analyzed directly in the ICP. The analyzed metallic elements were Mn, Fe, Zn, and Pb, and the earth alkali elements Mg and Sr were analyzed. The chlorides and the sulfates of the waters were determined using an anionic chromatograph.

## Results and discussion

### Substrate composition of Portman and La Vila

The comparison between the concentrations of metallic elements (Table 1) demonstrates large differences between the Portman Bay sampling station and the station at La Vila for the analysis carried out in the rocks of the submarine rocky strand. In Portman Bay the concentrations were 9989 ppm Mn, 97 725 ppm Fe, 6356 ppm Zn, and 57 797 ppm Pb. In La Vila they were 181 ppm Mn, 5101 ppm Fe, 22 ppm Zn, 16 ppm Pb. The quantities of magnesium are comparable in both stations; however, strontium showed more elevated quantities in La Vila than in Portman.
The results of the analysis carried out for the beach silts correspond to the results for the rocks; they are of the same order of magnitud, and they maintain the differences between the two stations. The two stations present very similar general environmental parameters. The tem-

**Table 1**
Element concentrations (ppm) in water and substrate of Portman Bay and La Vila Beach

| | Mn | Fe | Zn | Pb | Mg | Sr |
|---|---|---|---|---|---|---|
| Portman Bay | | | | | | |
| Free water | 0.080 | 0.031 | 0.118 | 0.037 | 772 | 7.14 |
| Interstitial water | 1.171 | 0.095 | 1.113 | 0.194 | 834 | 7.46 |
| Beach sediments | 5391 | 132 375 | 5950 | 1802 | 5650 | 11.00 |
| Underwater rocks | 9989 | 97 725 | 6356 | 57 797 | 13 225 | 4.25 |
| La Vila Beach | | | | | | |
| Free water | 0.008 | 0 | 0.102 | 0.017 | 854 | 7.21 |
| Interstitial water | 0.010 | 0 | 0.112 | 0.002 | 851 | 7.37 |
| Beach sediments | 70 | 1290 | 12.50 | 15.00 | 4238 | 427.50 |
| Underwater rocks | 181 | 5101 | 22.00 | 16.50 | 12 350 | 846.50 |

perature in both varies between 18 and 24 °C according to the season. The concentration of chlorides and sulfates are practically the same in both stations. The waters of Portman present a concentration of 24.32 $g\,l^{-1}$ and 2.7 $g\,l^{-1}$, respectively, the waters of La Vila contain 24.39 $g\,l^{-1}$ and 2.7 $g\,l^{-1}$.

### Water composition of Portman and La Vila

The analysis carried out for the metals in the waters reflects to a lesser degree the differences found in the rocky and sandy substrates of the two sampling stations.
The interstitial waters of the beach silts of Portman have 1.7 ppm Mn, 0.09 ppm Fe, 1.11 ppm Zn, and 0.19 ppm Pb, whereas the interstitial waters of La Vila have 0.01 ppm Mn, no detectable Fe, 0.11 ppm Zn, and 0.01 ppm Pb. Mg and the Sr are found in practically equal quantities.
In the free (or surface) waters the differences between the two stations are reduced still more and the concentrations are so low that they are at the limit of reliability for the analytical techniques that are usually used. For this reason, conclusions drawn based on results obtained from studies done solely on marine waters could be questionable.
What is the cause of such small differences found in waters that are so near substrates with metallic compositions that are so different? In the first place, only a small part of the rock is dissolved; in the second place, the current, the tides, and the marine surf disperse and homogenize the dissolved elements. So then we know that, logically, we are in a zone of waters contaminated by metals, but the demonstration through analytical results could be technically difficult and the conclusions could be questionable. Therefore, it is convenient to use bioindicators, which act as concentrators of dissolved chemical elements (among which are the metals) in the seawater.

### Analytic results of sea urchins

The utilization of the analysis of the calcareous skeletons of the *Paracentrotus* and *Arbacia* sea urchins as indicators of contamination has given good results. Tables 2 and 3 show the concentrations of the elements analyzed for the plates and the spines of the shells in the Portman and La Vila sampling points. The discussion to analyze the differences of concentration between the two species of studied sea urchins (*Paracentrotus* and *Arbacia*) in the two sampling stations (Portman and La Vila) has been organized in four parts.

### Composition of skeleton versus composition of sea-water

The calcareous skeletons of the sea urchins concentrate the metallic elements of the seawater from tens to thousands of times. The manganese of the plates of *Paracentrotus* at Portman Bay is concentrated up to 3112 times, the iron 8800 times, the lead 1616 times, and the zinc 278

**Table 2**
Comparison of element contents (ppm) of *Paracentrotus lividus* in Portman Bay and La Vila Beach

| | Mn | Fe | Zn | Pb | Mg | Sr |
|---|---|---|---|---|---|---|
| Portman Bay (polluted sampling site) | | | | | | |
| *Paracentrotus* | | | | | | |
| Plates ($n=10$) | | | | | | |
| Average | 249.00 | 273.20 | 32.87 | 59.80 | 18995 | 1755 |
| SD | 46.06 | 128.86 | 6.78 | 5.87 | 539 | 73 |
| Max value | 304.72 | 473.07 | 40.92 | 71.57 | 19825 | 1825 |
| Min value | 145.57 | 101.57 | 19.32 | 54.47 | 18125 | 1600 |
| Spines ($n=10$) | | | | | | |
| Average | 11.07 | 83.21 | 20.30 | 21.00 | 7665 | 1500 |
| SD | 1.72 | 32.29 | 4.46 | 3.66 | 436 | 88 |
| Max value | 14.35 | 147.10 | 31.20 | 24.92 | 8225 | 1700 |
| Min value | 7.90 | 23.75 | 15.67 | 11.75 | 6850 | 1400 |
| La Vila Beach (control sampling site) | | | | | | |
| *Paracentrotus* | | | | | | |
| Plates ($n=10$) | | | | | | |
| Average | 5.40 | 7.32 | 8.62 | 2.20 | 17605 | 1502 |
| SD | 0.85 | 4.03 | 1.62 | 0.22 | 1098 | 141 |
| Max value | 6.22 | 18.45 | 11.87 | 2.45 | 19150 | 1675 |
| Min value | 4.32 | 2.85 | 7.25 | 1.80 | 16050 | 1300 |
| Spines ($n=10$) | | | | | | |
| Average | 0.56 | 3.02 | 6.94 | 2.20 | 6675 | 1210 |
| SD | 0.10 | 1.34 | 0.31 | 0.23 | 452 | 53 |
| Max value | 0.75 | 5.35 | 7.40 | 2.62 | 7350 | 1300 |
| Min value | 0.45 | 1.32 | 6.50 | 1.92 | 6125 | 1150 |

**Table 3**
Comparison of element contents (ppm) of *Arbacia lixula* in Portman Bay and La Vila

| | Mn | Fe | Zn | Pb | Mg | Sr |
|---|---|---|---|---|---|---|
| Portman Bay (polluted sampling site) | | | | | | |
| *Arbacia* | | | | | | |
| Plates ($n = 10$) | | | | | | |
| Average | 81.92 | 119.7 | 24.35 | 59.13 | 17 355 | 1612 |
| SD | 20.02 | 81.77 | 4.44 | 13.18 | 513 | 32 |
| Max value | 115.15 | 283.72 | 30.42 | 69.20 | 18 250 | 1675 |
| Min value | 52.75 | 33.22 | 17.95 | 51.85 | 16 325 | 1575 |
| Spines ($n = 10$) | | | | | | |
| Average | 10.72 | 69.04 | 17.56 | 22.39 | 10 995 | 1277 |
| SD | 2.52 | 53.71 | 3.47 | 3.18 | 598 | 81 |
| Max value | 13.40 | 220.27 | 26.27 | 28.22 | 11 900 | 1400 |
| Min value | 8.15 | 11.32 | 12.85 | 19.42 | 9750 | 1125 |
| La Vila Beach (control sampling site) | | | | | | |
| *Arbacia* | | | | | | |
| Plates ($n = 10$) | | | | | | |
| Average | 4.89 | 7.78 | 11.84 | 2.60 | 17 068 | 1496 |
| SD | 2.13 | 2.46 | 2.87 | 0.15 | 888 | 123 |
| Max value | 9.32 | 12.20 | 18.90 | 2.87 | 18 600 | 1650 |
| Min value | 2.27 | 3.47 | 9.30 | 2.42 | 15 950 | 1325 |
| Spines ($n = 10$) | | | | | | |
| Average | 0.70 | 4.15 | 9.89 | 2.98 | 11 681 | 1362 |
| SD | 0.09 | 1.18 | 0.99 | 0.50 | 879 | 133 |
| Max value | 0.85 | 6.35 | 12.02 | 4.02 | 13 050 | 1550 |
| Min value | 0.57 | 1.85 | 9.20 | 2.25 | 10 675 | 1225 |

times. *Arbacia* behaves in a similar manner. The spines of both species present a high capacity of concentration; however, these indexes are lower to the shells.

### Composition of Portman versus La Vila sea urchin skeletons

The skeletons of the two species of sea urchins at the Portman station demonstrate a high concentration of heavy metals both in the plates and in the spines. The differences with La Vila are important and constant. The plates of *Paracentrotus* of Portman Bay present 249 ppm Mn; 273 ppm Fe; 32.8 ppm Zn, and 59.8 ppm Pb that contrast with the values obtained in La Vila of 5.4, 7.3, 8.6, and 2,2, respectively. We could find similar outstanding differences in *Arbacia.* The spines of both sea urchins are also good indicators, concentrating the elements with differences similar to those between the two sampling stations. However, the absolute concentration of some elements is less than that found in the plates. The reasons for these differences will be explained in the following section.

### Plates versus spines

The concentrations of Mn, Fe, Zn, and Pb in the plates of *Paracentrotus* and *Arbacia* in Portman Bay as well as in La Vila are much greater than the concentrations of those same elements in the spines. So, for example, the manganese has a concentration in the *Paracentrotus* of Portman Bay of 249 ppm in the plates and 11 in the spines. The same species in La Vila contains 5.4 ppm in the plates and 0.56 in the spines. Similar differences were found for *Arbacia* in the two sampling stations.

What is the reason for a single organism to concentrate different quantities of metallic elements in distinct parts of its mineral skeleton? In order to find a reason, we should first study the behavior of the earth alkali elements Mg and Sr. The concentrations of Mg in the plates of the two sea urchins of the two sampling stations are very similar – about 17 500 ppm, as are the concentrations of Sr, with values around 1600 ppm. If we contrast, in the same species, plates against plates and spines against spines, we find in both stations the same concentrations for magnesium and strontium. The notable differences are established when we compare the content of these elements between the plates and the spines. The plates contain, clearly, more magnesium and, although in lesser quantity, strontium. In all the cases, the differences are significant and constant. *Paracentrotus* of Portman Bay has 18 995 ppm Mg and 1755 ppm Sr in the spines. Similar differences could be established with *Paracentrotus* in La Vila and *Arbacia* in both sampling stations.

We think that these clear differences are structural. Plates and spines must have two different types of calcite magnesian crystalline structures (presently under research). The crystalline structure of the plates and spines are formed with determined quantities of Ca, Mg, and Sr, which are always the same but different for the plates and spines. They are two different calcite magnesian crystalline structures. The crystalline structure of the plates would be more tolerant to isomorphic phenomena (substitution of elements of the structure) for the analyzed metals and, in consequence, these would be presented in greater concentration in the plates than in the spines.

### Paracentrotus versus Arbacia

From the data in the tables, it can be deduced that *Paracentrotus* concentrates more metallic elements than *Arbacia*. In Portman Bay where the quantity of pollutant elements in the skeleton of the sea urchins allows better comparisons, the concentrations of Mn, Fe, Zn, and Pb of *Paracentrotus* are greater in the plates and in the spines than those concentrations in *Arbacia*. These differences are not very large, although they are statistically consistent. They stand out above all in the manganese and iron of the plates.
What is the reason for these differences? Different crystalline structures or different ecological niche? Is it a question of isomorphism, or a question of distinct feeding habits? Probably the differences – which are not very notable – are due to slight differences in habitat (different, although near ecological niches) and feeding habits. *Paracentrotus* is found at a greater depth in the sea than *Arbacia*, the composition in the water column probably indicates greater concentrations of elements near the bottom than at the surface. Feeding is also different. Different algae (*Paracentrotus* feeds on fleshy algae and *Arbacia* on incrustated calcareous algae) could act as preconcentrators of minor elements in a differential manner so as to facilitate different quantities of minor elements to the two sea urchin species.

## Conclusions

– The Portman Bay (SE of Spain) present in underwater rocks and in beach sediments unusually high concentrations of metals (Mn, Fe, Zn, and Pb). The calcareous skeletons of *Paracentrotus* and *Arbacia* also present very elevated quantities of those elements.
– The calcareous skeletons of the sea urchins act as concentrators of dissolved minor polluting elements in the seawater, permitting easier analysis and more reliable measurements than those carried out directly on the water or on soft tissues.
– The minor elements, including heavy metals, are incorporated into the calcite magnesian crystalline structure through isomorphism. For this reason, the skeletons of the echinoderms are stable bioindicators of the heavy metal contamination in the sea.
– The quantity of metallic elements varies in a notable way, according to the species of sea urchin and above all according to the part of the sea urchin studied: plates or spines. This suggests that the basic calcite magnesian crystalline structure is different in the distinct skeletal parts of the echinoderms.
– The greater or lesser tolerance of each distinct calcite magnesian crystalline structure permits a greater or lesser incorporation of minor elements (metals and heavy metals in the skeleton).
– The studies done on the amount of minor elements (including heavy metals) in mineral skeletons of organisms should be done on the same species and also on the same skeletal part of that species, so that the results are reliable and comparable.

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