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LEAD POLLUTION IN BIVALVE SHELLS. MAR MENOR, SPAIN

BY

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ABSTRACT

Lead pollution in bivalve shells. Mar Menor, Spain. - Mar Menor is a coastal lagoon situated in the SE of Spain (Mediterranean Sea) with high concentrations of Pb, especially in the south.

The shells of the *Cerastoderma edule* and *Venerupis aurea* bivalves demonstrate a significant difference in Pb concentrations amongst the shellfish living in the south (100 and 47ppm), and those living in the north with relatively cleaner water (14 and 7 ppm). Nevertheless, both of these sampling points have greater concentrations of Pb than other points in the Mediterranean, which have been taken as "controls" for comparison (3 and 3 ppm).

The calcareous exoskeletons of these organisms are good indicators of the presence of minor elements in the waters.

Key-words: Lead pollution. Bivalve shells. Mediterranean Sea. Spain.

INTRODUCTION

Mar Menor receives an in flow of water from the south by means of several watercourses which drain a mining zone where sphalerite, pyrite and galena are extracted. For this reason, the sediments which are dragged are rich in Zn, Fe and Pb, as well as in other associated metallic elements.

In 1984 AUERNHEIMER *et al.*, the concentrations of Fe, Mn and Zn were analyzed in the shells of the *Cerastoderma edule* and *Venerupis aurea* in eight sampling points of Mar Menor. The concentrations of these heavy metals were much greater in the southern points than in the northern points.

In this project can be seen the results of the Pb analysis carried out at the same stations for the same bivalves, thus, completing the study of the main contaminating heavy metals of the area.

This study, which is included within a wider study of the Mediterranean coast, also contains the analytic results obtained from stations which we consider "controls", such as Pinet Beach and Santa Pola Salt Marshes, situated at about 100 km. north of Mar Menor.

The shells of the bivalves concentrates many of the ions dissolved in the sea water at various degrees of magnitude. This characteristic permits us to use them as bio-

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indicators of contamination, which has its advantages over the direct analysis of sea water or over the analysis of the organisms soft tissues.

The studies carried out on soft tissues present great variations according to annual season, age or sex of the sample (BOURGOIN, 1990). In addition, the soft tissues are very sensitive to momentary contamination and there are great differences in the concentrations of the tissues amongst the organisms.

The analysis carried out on the shells are very stable and they provide us with the average concentrations of heavy metals of at least one full year. They can also be attributed with the characteristic of having "memory", being that the concentration of heavy metals can be seen after the organisms have died and the soft tissues have disappeared.

The shells of the bivalves are formed by a crystalline structure of calcium carbonate and of organic material. The organisms take in sea water with major and minor elements forming the pallial fluid, upon which the organic matrix and the crystalline structure are formed. In general terms, the heavy metals can be found in both parts. LINGARD & BOURGOIN (1992) shows that the heavy metals are mostly found in the crystalline structure.

The differences in concentration of minor elements from one specie to another are due to: the distinct mineralogical natures of the shells, either aragonite or calcite (DODD 1965), or the environmental differences in salinity, temperature and pressure (CHAVE 1954; PILKEY & HOWER 1960; LERMAN 1965; BLATT *et al.* 1980) and in a significant way by the concentration of the elements in the marine environment, which substitute the calcium in the crystalline structure by isomorphism (AUERNHEIMER *et al.*, 1984).

SAMPLING SITES, ENVIRONMENTAL CHARACTERISTICS

Mar Menor

Mar Menor is a coastal lagoon of approximately 170 km^2 and an average depth of about 7 meters, situated in the SE of the Iberian Peninsula, separated from the Mediterranean Sea by a sand bar which is 20 km long and from 200 to 300 meters wide. It is joined to the sea by way of a series of narrow inlets through which it gives and takes water, but in small quantities.

In the south it receives fresh water from three watercourses: rambla del Beal, rambla de Ponce and la rambla de la Carrasquilla. These three watercourses carry water from Paleozoic and Triassic grounds from Sierra de Portman and La Unión plain. Both of these zones have been the objects of intense mining activity, where minerals (sphalerite, pyrite and galena) have been extracted since the time of the Roman Empire until three years ago, when mining was ceased because of insufficient income.

SIMONNEAU (1973) found Pb concentrations up to 15900 ppm in alluvial deposits of the ramblas. The map of Pb iso-concentrations in sediments of Mar Menor varies with values greater than 2000 ppm in the south (S-Beal, Los Nietos) and values lower than 200 ppm in the north (Lo Pagan) and east (Los Urrutias).

We have found, also, the highest values in S Beal sampling point (4040 ppm), and the lowest values in Lo Pagán (32.5 ppm) and Los Urrutias (17.5 ppm) sampling points.

The temperature of the water in Mar Menor varies very little from point to point. In the summer it can go up to 28° or at times even higher.

In the free water (surface water) there is very little variation in pH from point to point, from 8.3 pH in Lo Pagán to 8.21 pH in S Beal.

The conductivity value is 69.6 ms in Lo Pagán station, due to the high concentration of chlorides 24.39 g/l and sulphates 3.5 g/l. In S Beal station the conductivity value is 71.1 ms. with 25.24 g/l of chlorides and 3.4 of sulphates. The remaining stations have similar values of conductivity, chlorides and sulphates.

The amount of Pb in the free waters is similar. It is 0.019 ppm in Lo Pagán and 0.021 ppm in S Beal.

The intersitial waters have higher concentrations of chlorides and sulphates and, in turn, of conductivity than the free waters. These values are 34.88 g/l of chlorides, 6.30 g/l of sulphates and 96.7 ms of conductivity in Lo Pagán. In S Beal the values are 38.28 g/l of chlorides, 6.8 g/l of sulphates and 99.7 ms of conductivity. The pH is lower than that of the surface water, 7.62 and 6.99 in Lo Pagán and S Beal, respectively.

The Pb content is significantly higher in S Beal, where it is 1.16 ppm, than in Lo Pagán, where it is only 0.032.

Santa Pola Salt Marshes

The salt marshes of Santa Pola are found over a coastal plain in the province of Alicante at about 38 km north of Mar Menor. They are used for extracting salt (NaCl) from the Mediterranean waters, by means of evaporation. The water is introduced by inlets which inundate large pools or "heaters" where the salt is collected. The substrate of the zone is formed by quaternary silty-clay, which comes from the erosion of calcareous, Miocene, Eocene and cretaceous mountains.

In the pool beaters normal marine life is carried out (PERTHUISOT *et al.*, 1983), typical of shallow waters where there are great quantities of bivalves, amongst which is the *Cerastoderma edule*. The pH, the chloride and the sulphate values range from normal values for this part of the Mediterranean 8.2, 22 g/l and 2.9 g/l, respectively, to values up to 7.97, 78 g/l and 15.2 g/l. The conductivity varies from 60 ms to 165 ms. The Pb content of the waters is 0.008 ppm and 27.5 for the substrate.

Pinet Beach

Pinet beach is situated 36 km north of Mar Menor. It is a sandy beach with an open sea. The sand is mainly formed of carbonates. At little depth there lives a rich bentonic fauna of bivalves, gastropods etc., which are caught and sold quite intensely. Amongst these bivalves is found the species *Venerupis aurea*.

The pH, chloride and sulphate values in the free waters are 8.21, 22.12 g/l and 2.90 g/l, respectively. The conductivity is 60.5 ms. The content of Pb is 0.009 ppm.

The interstitial waters have values of 8.01; 21 g/l, 2.90 g/l and 59.4 ms for pH, chlorides, sulphates and conductivity, respectively. The content of Pb is 0.019 ppm. The beach sand has 17.5 ppm of Pb.

In summary, Mar Menor presents us with homogeneous characteristics of pH, salinity and temperature. The salinity is somewhat higher than the average Mediterranean content. The Pb concentration of the substrate of S Beal is very high. Lo Pagán has much lower values, but higher than those of the control stations of Pinet and Santa Pola. These values are reflected in the interstitial waters and also in the free waters.

Table 1 shows a comparison of the physicochemical characteristics of the sampling stations.

TABLE 1

Sampling sites, physico-chemical parameters

Sampling sites	Santa Pola Salt Marsh	Pinet Beach	Mar Menor Lo Pagán	Mar Menor Beal (South)
pH free water	8.2 – 7.92	8.21	8.31	8.2
pH interstitial water	–	8.01	7.62	6.99
Conductivity f.w (ms)	60 – 165.3	60.5	69.6	71.
Conductivity i.w (ms)	–	59.4	96.7	99.7
Sulphates f.w.(g/l)	5 – 21.00	2.90	4.50	3.25
Sulphates i.w.(g/l)	–	2.90	7.93	6.93
Chlorides f.w.(g/l)	22 – 78.56	22.12	24.39	25.24
Chlorides i.w.(g/l)	–	21.65	34.88	38.28
Pb f.w. (ppm)	0.008	0.009	0.019	0.021
Pb i.w (ppm)	–	0.019	0.032	1.16
Pb substrate (ppm)	27.5	17.5	32.5	4050

METHODOLOGY, SAMPLING AND ANALYSIS

The sampling has been carried out in two phases. In the first phase samples were taken of *Cerastoderma* in eight sampling points of Mar Menor. Approximately a dozen valves of each point were ground, mixed and analyzed for their Pb content. The objective for this phase was to establish the average contamination at each sampling point. The results, which are shown in Table 2, indicate a maximum of contamination at S Beal and minimums at Lo Pagán and Los Urrutias. In the second phase we have

TABLE 2

Pb concentration (ppm) of *Cerastoderma edule* shells in Mar Menor sampling sites.

Mar Menor SAMPLING SITES	Pb (ppm) in *Cerastoderma* shells
Lo Pagán	13.75
Santiago de la Rivera	30.50
Los Narejos	37.65
Los Urrutias	7.25
Beal (N)	49.00
Beal (S)	93.00
Los Nietos	53.00
Punta Seca	31.87

selected two sampling points which represent the maximum and minimum contamination of Mar Menor. S Beal and Lo Pagán. In each of these points we have prepared and analyzed 10 samples of *Cerastoderma* and another 10 of *Venerupis*.

Keeping in mind that Mar Menor, in general, is contaminated by heavy metals, we have taken control sampling points in other places of the Mediterranean coast for comparison. These points are Pinet beach, where we have collected, prepared and analyzed 10 samples of *Venerupis*, and Santa Pola salt marshes which have provided us with 10 samples of *Cerastoderma*. In all cases, the samples of the four series of sampling were prepared and analyzed one by one.

The samples of bivalves were of the same size. The soft tissue was extracted from all of them, and the shells were dried in the sun for a few days. After this, they were treated with hydrogen peroxide for two or three days in order to eliminate residues of organic material. The samples were washed with (ultrapure) distilled-water, dried anda gram of each of them was dissolved in 10ml of nitric acid. The resulting solution was filtered and it was raised to 25 ml with distilled water. The Pb was analyzed with ICP.

RESULTS AND DISCUSSION

Lead Content of the Shells

The results of the analysis carried out in the eight stations of Mar Menor for *Cerastoderma* shells are shown on Table 2 and fig. 1 and they represent the average Pb content for each sampling station.

The Pb content varies from a minimum value of 13.75 ppm to a maximum value of 93 ppm. The highest values come from the shells of southern Mar Menor in the stations of: N Beal, S Beal and Los Nietos. The lowest value corresponds to Lo Pagán and Los Urrutias stations.

The results of the Pb contamination in *Venerupis* and *Cerastoderma* shells from the second phase of the study and also Pb contents in water and substrate are shown in tables 2 and 3 and figures 2, 3 and 4. The results pertain to four sampling points: S Beal

TABLE 3

Pb concentration (ppm) in *Cerastoderma* and *Venerupis* shells. Series of ten samples for each sampling site. Average and Standard Deviation.

CERASTODERMA EDULE			*VENERUPIS AUREA*		
Santa Pola Salt Marsh	Mar Menor Lo Pagán	Mar Menor Beal South	Pinet Beach	Mar Menor Lo Pagán	Mar Menor Beal South
4.67	38.02	218.42	4.02	14.47	74.35
4.62	22.92	168.95	3.85	11.45	57.80
4.15	21.17	130.57	3.67	7.05	54.15
4.10	16.12	127.57	3.49	6.82	49.12
3.75	12.52	83.77	3.44	6.55	46.70
2.90	10.12	71.10	3.34	6.42	42.76
2.75	8.07	68.10	3.28	6.15	41.85
2.72	6.17	55.80	3.22	5.27	41.32
2.62	5.22	53.77	3.12	4.12	33.90
2.50	4.12	35.00	2.49	4.07	29.57
av. 3.46	14.45	100.80	3.39	7.23	47.15
s.d. 0.81	9.99	55.48	0.40	3.10	12.13

(*Venerupis* and *Cerastoderma*), Lo Pagán (*Venerupis* and *Cerastoderma*), both of which are in Mar Menor, Pinet beach (control point for *Venerupis*) and Santa Pola salt marshes (control point for *Cerastoderma*).

In the sampling point of Lo Pagán the Pb values of *Cerastoderma* vary from 4.12 to 38.02 ppm. The arithmetical average is 14.45 ppm and the standard deviation is 9.99 ppm.

In the S Beal station the Pb content varies from 35.00 to 218.42 ppm. The average is 100.80 (55.48).

Both of these stations present us with notably higher values than the Santa Pola station, which serves us as a reference in the case of *Cerastoderma* shells. In this station the values vary between 2.50 and 4.67 ppm with an average of 3.46 (0.81).

For the *Venerupis aurea* species the values found in Lo Pagán vary from 4.07 to 14.47 ppm with an average of 7.23 (3.10). In the S Beal station the Pb content of the shells varies between 29.57 and 74.35. The average is 47.15 (12.13).

The samples analyzed in Pinet beach demonstrate much lower Pb values, varying between 2.49 and 4.02 ppm. The average and the standard deviation are 3.39 and 0.40, respectively.

The comparison between the Pb content in *Cerastoderma edule* and *Venerupis aurea* show us that the shells of Mar Menor have a high content of Pb, with significant differences between Beal station, where water with contaminated sediment penetrates, and Lo Pagán station, which is the furthest from the source of contamination.

Furthermore, both stations have more Pb contamination than the reference stations. There are also differences between *Cerastoderma* and *Venerupis*. The first species has double the amount of Pb, in the Beal station as well as in Lo Pagán.

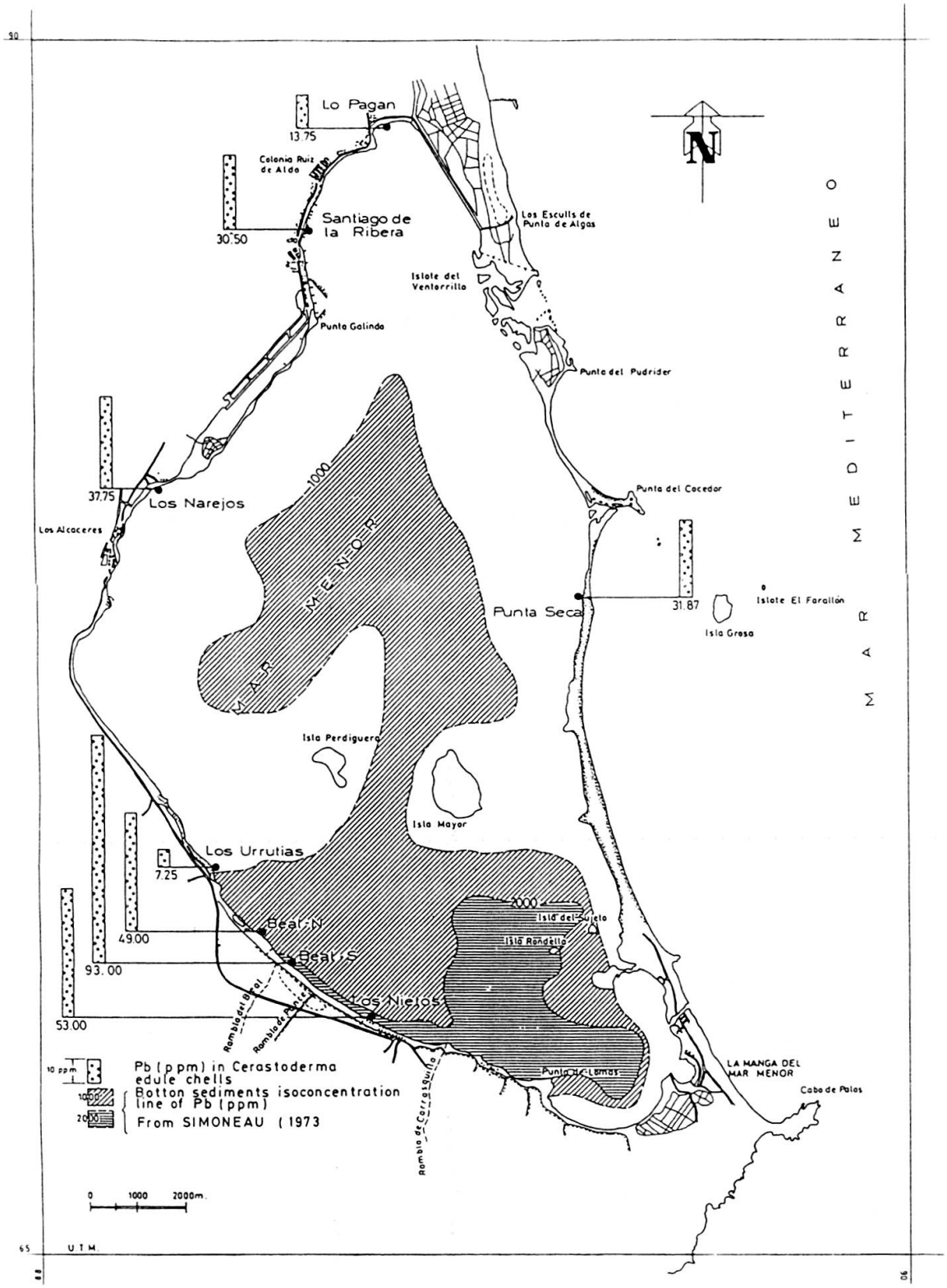

FIG. 1.

Pb in *Cerastoderma edule* shells. Botton sediments isoconcentration line of Pb.

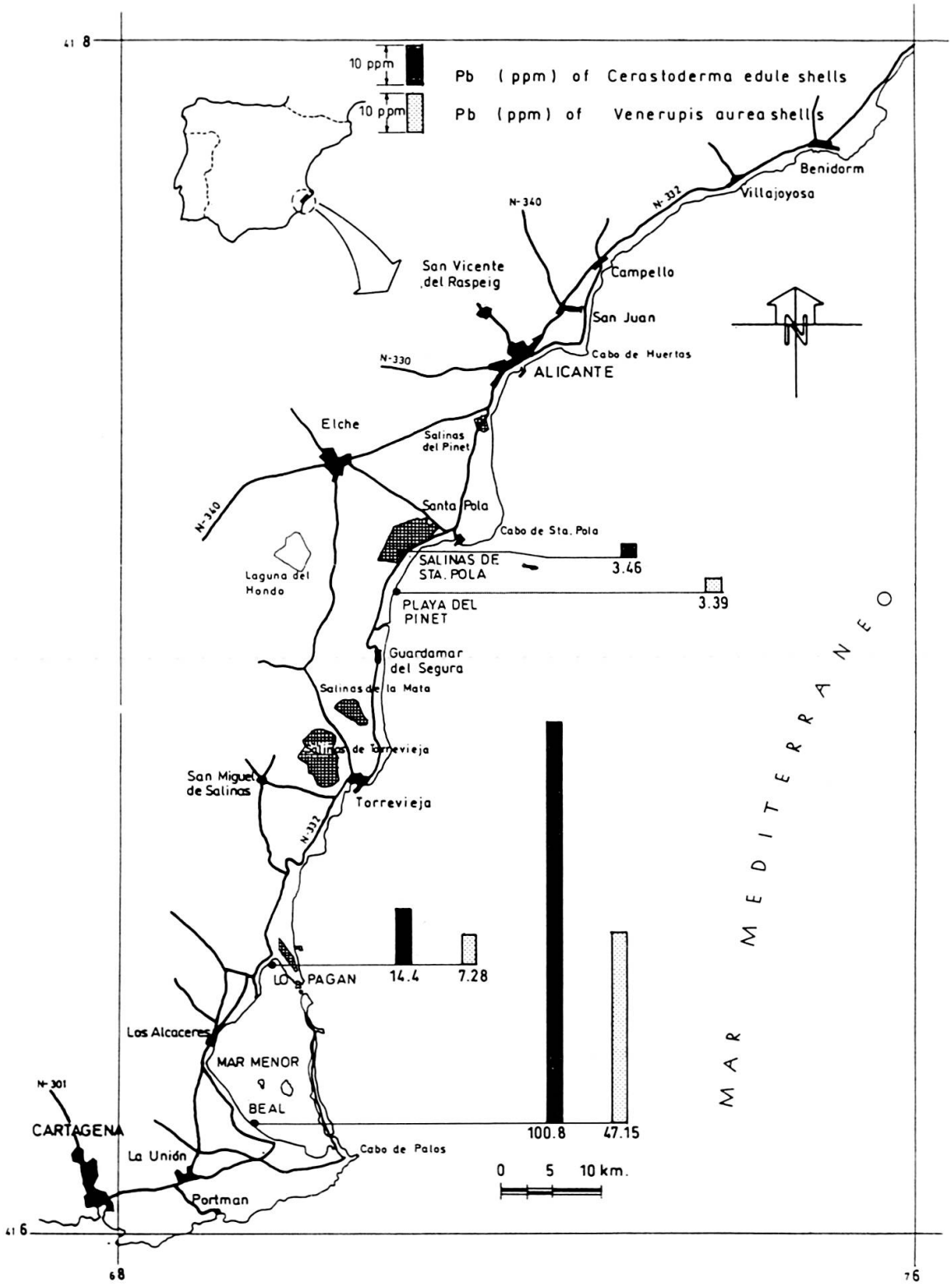

FIG. 2.

Pb in *Cerastoderma* and *Venerupis* shells.

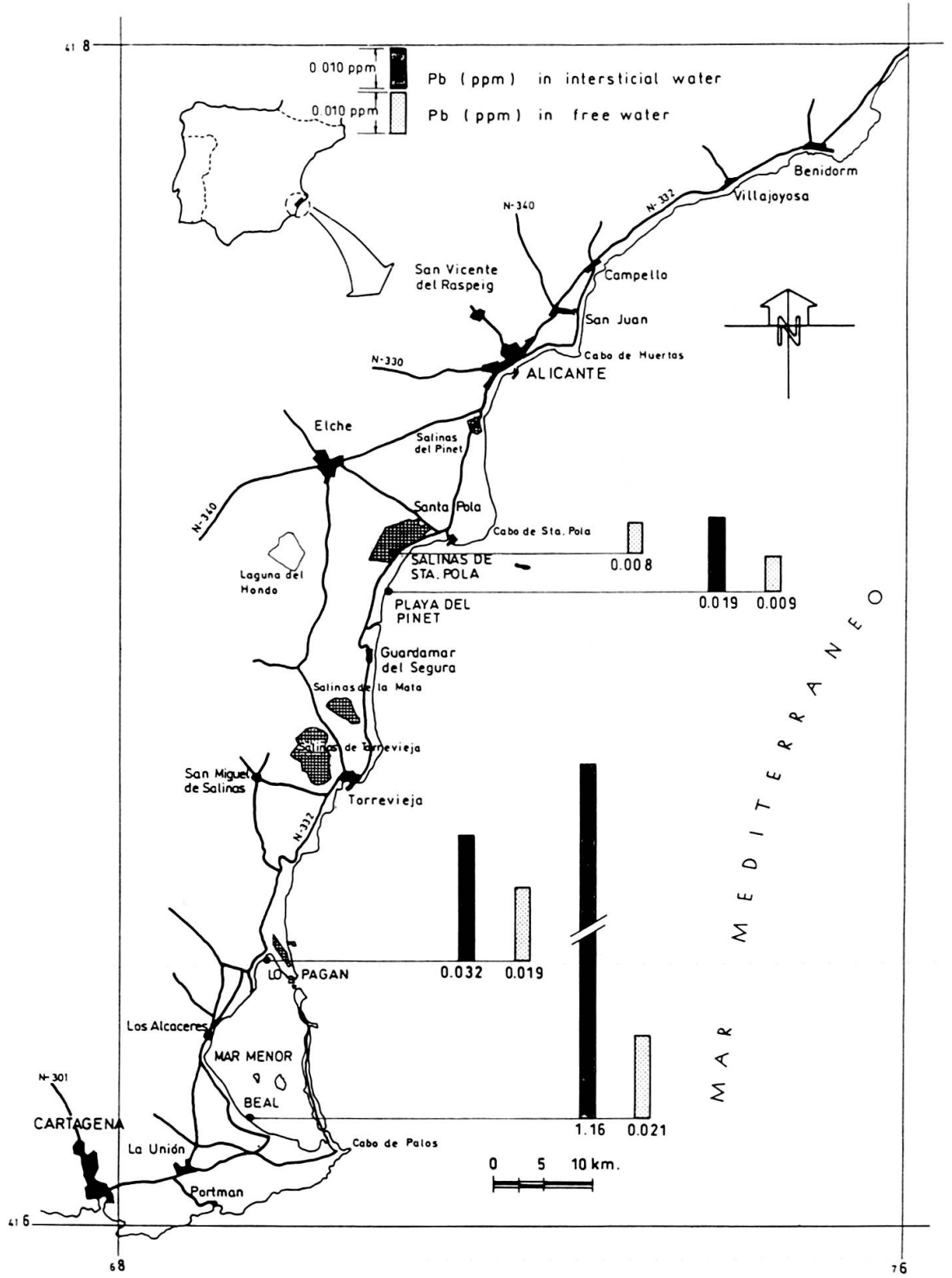

FIG. 3.

Pb in free and interstitial water.

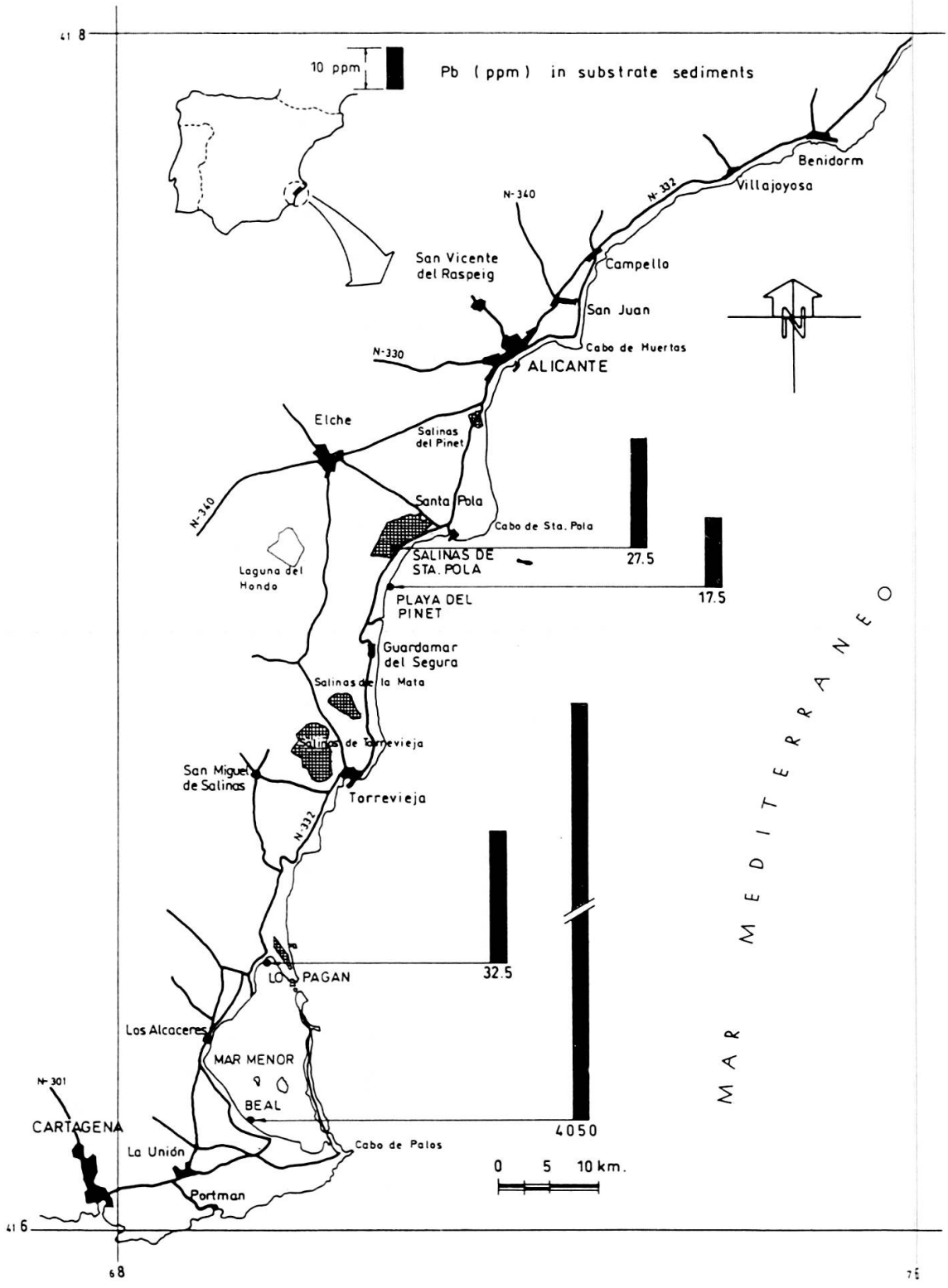

FIG. 4.

Pb in substrate sediments.

These values correspond very well with the substrate Pb values. The maximum Pb concentration, 4050 ppm, is produced in Mar Menor, Rambla of S Beal, and the minimums in Pinet beach, 22.5 ppm, and in Santa Pola, 17.5. Lo Pagán (Mar Menor) sampling point has an intermediate concentration, 32.5 ppm.

The concentrations of the superficial and interstitial waters present small differences between each other, and even between stations, except in the Beal station with 1.16 ppm. Such low values are not reliable because they are at the limit of the ICP detection, although they reflect the substrate composition.

In summary, we can say that the Pb concentrations obtained from the *Cerastoderma edulis* and *Venerupis aurea* correspond well to the Pb concentrations of the silty or sandy substrates where they live, and also with the Pb found in the water. Since the shells act as Pb concentrators, they permit a better and more reliable measurement of Pb contamination than the analysis carried out directly on the waters, where the low concentrations in minor elements make analysis difficult to carry out and uncertain conclusions to be drawn on marine contamination.

CONCLUSIONS

The shells of the bivalves, which were analyzed, reflect a Pb content which corresponds to the sediment content and the interstitial waters. This content is high in the zones with highly contaminated sediments and interstitial waters (Beal), lower in the lesser contaminated (Lo Pagán) and very low in the zones considered being uncontaminated or controls (Pinet and Santa Pola).

The quantity of Pb depends on the chemical or crystallographical norms. The organism's physiology does not discriminate the capture of elements.

The presence of these elements in the crystalline structure of the shell, converts them into good indicators of contamination. The results of this analysis are more reliable than those carried out directly on the water, where the minor elements are seen to be excessively diluted, and often under the analytical capacity of the technique used. The shells act as long lasting stores of the contaminating heavy metals. Moreover, they homogenize the eventual contaminations. Thus, the analysis of shells provides us with more advantages than the analysis of soft tissues.

RÉSUMÉ

Mer Menor est un lagon côtier du littoral méditerranéen de l'Espagne, entre Alicante et Cartagena.

Les coquilles des Bivalves *Cerastoderma edule* et *Venerupis aurea* présentent des teneurs en Pb très élevées dans la partie sud (100 et 47 ppm) par rapport à celles de la partie nord (14 et 7 ppm).

De même, les concentrations de Pb dans les échantillons de Mar Menor sont nettement supérieures à celles que l'on trouve dans d'autres sites du littoral méditerranéen.

Les coquilles de *Cerastoderma edule* et de *Venerupis aurea* constituent d'excellents bioindicateurs de pollution dans les eaux marines.

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