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Historical Changes of the Anthropogenic Impact in a coastal Lagoon: Pb isotopes and trace metals on Mussel's fleshes and shells

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SUMMARY. The mussels are good recorders of the metal level variations in the environment by their ability to concentrate and accumulate metals from seawater. We have analysed the lead concentrations in five locations in a coastal lagoon surrounded by natural and anthropogenic sources. Moreover to determine the lead inputs sources we have analysed the Pb isotopic compositions during two seasons and compare them to different sources present in the watershed. As the shells can also be used as a recorder of environmental changes, we compare the isotopic compositions in recent and ancient shells (1-6 th centuries), showing an anthropogenic impact since the Roman Empire.

1. INTRODUCTION

Mollusks are known to concentrate metals in a very strong manner and equilibrate rapidly with their environment since Goldberg (1) has tried to use them as global indicators. They filter waters and accumulate metals 10^3 to 10^4 times above water levels. So they are used in many programs of coastal survey (NOAA, French Mussel Watch,...) as bioindicators.
The lead concentrations in the fleshes allow us to determine spatial and temporal variations in the environment but they are influenced by biological factors such as weight. In order to understand the becoming of the pollutant substances inputs, we have also analysed the Pb isotopic compositions of the mussel fleshes, tracing by their intermediary the water movements in the lagoon.

But the trace metal metals assimilated by the animal are also accumulated in the shell to considerable extent. According to several authors (Sturesson (2); Bourgoin, et al. (3)), the chemical composition of shells then could be a record of its environmental metal levels, and moreover could be used to compare present environment with those of the past (Pitts and Wallace (4)). The shell, instead of fleshes would be a medium-term record. The second aim of the study is to compare the lead concentrations in ancient and recent shells in order to evaluate the antropogenic impact and to compare their isotopic compositions to different sources identified on the watershed.

2. LOCATION OF THE STUDY AND METHOD

The Thau coastal lagoon (70 Km^2) is located in the South of France near Montpellier. This lagoon was chosen because of the various sources of both natural and anthropogenic inputs. The surrounding rocks are principally Jurassic limestones and Miocene marls. The Sète industrial harbour presents a high density of industries: cement and fertilizer factories, car and boat workshops, and so forth.. An important highway crosses the Thau watershed. Several water treatment plants are located in the watershed and their outputs reach the lagoon.

Mussel spat from the sea, was introduced in june 95 in five locations of the lagoon: in the Sète harbour, at the Véne exutory draining the main water treatment plants, in the lagoon center, near the city Marseillan and in the sea (Figure 1). Ten animals (*Mytilus galloprovincialis*) were sampled in May 96 and Oct 96 to minimize the intra-population variability. The ancient shells (1st century to 6th century ad) came from a rubbish tip of a Roman villa in Loupian. Lead castings (1*6 cm) dated of the sames ages as the shells were also analysed.

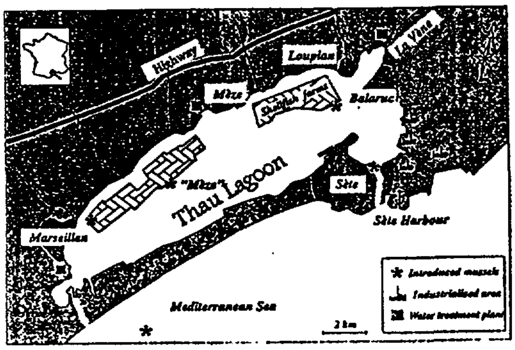

Fig 1: Map of the sampling locations

All chemical preparation was done in a clean room (class 100). Shells were leached with acids to remove external contamination. Blanks were under 100 pg and are negligible.

3. MUSSEL'S FLESHES

Concentrations

The lead concentrations vary between 0.5 ppm and 2.3 ppm dry weight. The higher concentrations are localised in Mèze, the point representing the lagoon center. These spatial and temporal variations may be due to a combination of biological cycles (spawning, growth, ...) and variable source inputs (vineyard treatment products, ...). As it is difficult to determine the variation part due to biological influence we have analysed the lead isotopic compositions to determine the main sources in the watershed.

Pb isotopes

The results of the isotopic compositions measurements in fleshes are plotted in a $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagram (Figure 2). Are reported here different endmembers: 1- Jurassic Limestone (Petelet, et al. (5)), 2- Tertiary sediments (Monna, et al. (6)), 3- road: water from highway (Luck and Ben Othman (7)), 4- water treatment plants (Luck and Ben Othman (7)). The flesh representative points are localised between these 2 principal endmembers: the anthropogenic one (water treatment plants, and road) and the natural one (Miocene marls and Jurassic limestone).

We observe nice alignments in May 96 and October 96 explained by a simple mixing model between 2 endmembers. The position of the representative points between those endmembers simply represents the different proportions of the sources inputs. The first one is constant, corresponding to the Marseillan location: this could be explained by its location near the coast (near the road and the water treatment plants inputs) and also at the opposite side of the main seawater entries. The other one varies towards more radiogenic values. We clearly see the seawater entries in the lagoon. The influence of the different endmembers is connected to the wind direction and the convective cells formed in the lagoon (Rosello-Tournoud (8)).

We can easily distinguish the lagoon samples with $^{206}Pb/^{204}Pb$ ratios 18.03-18.35 and the sea samples which are more radiogenic. The sea samples move towards the natural endmember and show a smaller anthropogenic impact than in the lagoon.

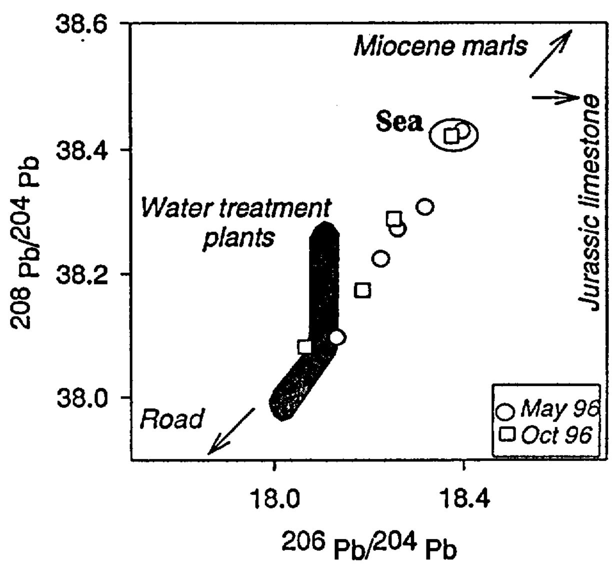

Fig 2: $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ in mussel's fleshes during different seasons.

4. MUSSEL'S SHELLS

Concentrations

We compare shells of the same size to avoid variations due to this variable. The ancient shells show a similar range of concentrations to recent ones: between 0.4 -1.1 ppm for ancient shells and 0.4 -1.7 for recent ones. We have two explanations: Mussel gathering during the Roman Empire took place by the shore of the lagoon explaining the relatively high concentrations observed, the edge being more polluted than the lagoon center; lead was intensively used in Roman society for cooking and as material, and its dispersion in the environment was important as it is shown by Hong et al. (9).

Pb isotopes in recent shells

The Pb isotopic compositions of recent and ancient shells show three well clustered domains (figure 3). Data are plotted in a $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}$ Pb diagram, with the same endmembers used for the fleshes, and the Sète harbour, determined by on both shell and flesh analyses of mussels collected in the harbour.

An alignment is observed for the recent shells between two principal endmembers: a radiogenic endmember represented by tertiary sediments and a less radiogenic one reflecting the anthropogenic activities (principally the road and the Sète harbour inputs). In particular the lagoon shells plot between the road and the Sète harbour endmembers indicating a rather high proportion of gasoline (road) lead.

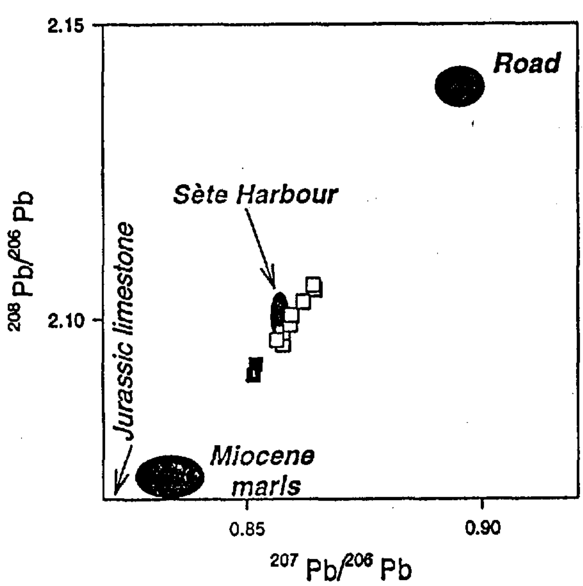

Fig 3: ^{208} Pb/^{204} Pb vs ^{206} Pb/^{204} Pb in ancient shells (white triangle), recent lagoon shells (black triangle), and sea shells (grey triangle) compared to different endmembers: tertiary sediments, jurassic limestones, Sète harbour and road.

The sea shells are slightly more radiogenic and less influenced by the road endmember compared to the lagoon shells, but nevertheless they reveal a clear anthropogenic impact in their isotopic signature (they plot close to the harbour domain).

Pb isotopes in ancient shells

For archaeological applications the diagrams usually used are ^{208} Pb/^{206} Pb versus ^{207} Pb /^{206} Pb diagram (Figure 4).

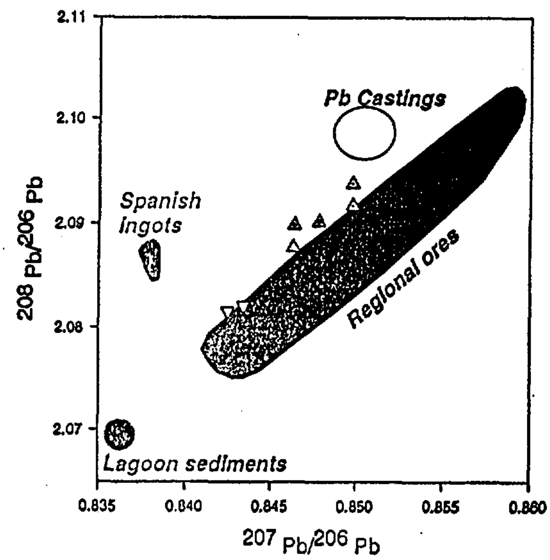

Fig 4: ^{208} Pb/ ^{206} Pb vs ^{207} Pb/^{206} Pb in ancient shells (1st century: white triangle head down; 4th century: triangle with cross; 5th century: triangle with point, 6th century: white triangle head up) compared to lead castings, Spanish lead ingots, mining districts and pre-industrial sediments.

The lead sources were different during the Roman Empire than nowadays so we compared with different endmembers: Lead castings, and natural leads. The isotopic ratios of the lead castings found in Loupian represent the lead commonly used by the population. We also plotted the isotopic composition of the ancient sediments from the lagoon (Fillion, et al. (10)) and of the regional ores (Brevart, et al. (11); Le Guen, et al. (12)).

The ancient shells show an alignement betwwen two endmembers: the Loupian castings and the pre-industrial sediments indicating a simple mixing. The respective proportions of the endmembers change with the age of the shells. The first century shells plot near the sediment endmember, then the 4th century shells shift towards the castings endmember and the 6th century plot again near the sediment endmember. We suggest two different explanations: The anthropic impact on the shells follows the population development on the lagoon shore: increase durind the 3-4 th century with the peak of Roman civilization and a decrease corresponding to a reduced development of the area after the Roman Empire decline. But it could also be connected to a change in the habits: lead was not intensively used after the 5th century. All the explanations show a decrease of the lead inputs in the lagoon. These results agree with other archeological studies.

5. CONCLUSION

This article shows how lead isotopes can be applied to living organisms in order to trace anthropogenic impact. We have shown that mussels fleshes may record the mean water movements using lead isotopes as tracers. The lagoon mussels are under two main endmembers influence: the water treatment plants and the sea. We have also shown that we can use shells to compare the different pollution sources in recent and past environments. It is shown on a local scale that human activities have already influenced the environment during the Roman Empire.

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