MUSSEL SHELLS AS ENVIRONMENTAL TRACERS: AN EXAMPLE FROM THE LOVEDAY BASIN

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It is logical to assume that changes within, or contamination of, an environment can be inferred from analysis of the creatures that live in it. Analysis of biota can reflect many facets of an ecosystem or habitat, and can be a valuable complement to purely physical and geochemical methods. Studies have shown that molluscs, bivalves in particular, can be very useful bioindicators of pollution as metals can accumulate in both the soft tissue of the mollusc and their hard calcium carbonate shells. Indeed, in some cases the chemistry of shells can reflect the impact of anthropogenic activity upon their ecosystem (Carell *et al.* 1987). Detailed studies on molluscs began as early as the 1960s and have continued through to the present day.

This study will focus on the shell of a mussel species commonly found in the lakes and billabongs of the Murray River system, *Velesunio ambiguus*, and seek to determine whether it can be used as a biomonitor of pollution and as a means to interpret the environmental history of the mussel's habitat.

In assessing the validity of using the metal content of bivalve shells as an indicator of environmental pollution, it is necessary to have a basic understanding of the process of shell secretion and associated metal incorporation. Initially, cells in a region of the animal called the mantle secrete an organic substance, known as the periostracum, which forms an external protective coating on the shell. A layer of crystalline calcium carbonate is then deposited against this protein rich layer. As the animal grows, epithelial cells within the mantle cavity accumulate calcium and bicarbonate ions from water. These are then transported through the organism to the extrapallial fluid, which lies between the mantle and the inner shell surface. The mantle also secretes periostracum material into the extrapallial fluid, which forms the organic matrix for the nucleation of additional calcium carbonate crystals, in the form of either calcite or aragonite (Langston & Bebianno 1998, Westbroek & De Jong 1983). This carbonate material comprises the bulk of the shell. These growth cycles are seasonal, with carbonate being deposited during periods of growth, and organic material secreted during dormant periods. These can be seen in shell cross sections as lighter and dark layers respectively.

Metals such as Mg, Mn, Zn, Pb, and Cu can substitute for the Ca^{2+} ion and thus become incorporated in the calcium carbonate crystals. It can be assumed that via this process, any metals found incorporated into the calcium carbonate structure have been taken up from the environment and were actively metabolised by the organism. Thus, it must be acknowledged that an analysis of the amount of metal incorporated into a carbonate shell provides an indication of the degree of *bioavailable* metal present in the environment, and this can not necessarily be equated with total metal. Some authors have suggested that only the inner, nacreous layer of aragonite of mussels is sufficiently protected from outside influences and sources of metal contamination to be useful in indicating the amount of metals that have been actively incorporated by the organism into its shell (e.g., Bourgoin 1990, Puente *et al.* 1996). However, the significance of this needs to be assessed; in focussing only on metals that have been actively metabolised by the organism, only the amount of bioavailable metal in the environment is measured. The total amount of metal in the environment, how the organism partitions metal between its soft tissue and hard shell and how much metal it is capable of expelling from its system altogether must also be established.

Most metals are generally concentrated many times over within an organism's soft tissue, rather than the shell, and so the vast majority of studies concentrate on the soft tissue. However, some studies of the shell material have also been conducted, and many authors suggest that shells can provide a more accurate indication of environmental change and pollution; they exhibit less variability than the living organism's tissue, and they provide a historical record of metal content throughout the organism's lifetime, with this record still preserved after death (Huanxin *et al.* 2000, Yasoshima & Takano 2001, Thorn *et al*. 1995, Carriker *et al*. 1982). Some species, such as *Margaritifera margaritifera* can live for over 100 years and can provide a valuable record of environmental change over a significant period (Carrel *et al.* 1987). *Velesunio ambiguus* has been known to live for up to 30 years (Walker 1992).

Samples of *Velesunio ambiguus* were collected from the Loveday Basin, South Australia. The area was once a floodplain of the Murray River, but has been cut off from the river, and was used as a discharge basin for

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highly saline irrigation runoff waters from the 1970s to the early 2000s. The wetlands became seriously degraded over this time and the area is now being extensively studied with a view to rehabilitate the site. Sulfur cycling and hydrogeological studies are currently being carried out in the Basin, and an analysis of the biogenic carbonate record could well provide a useful insight into metal mobility and salinity variations over time. It is widely accepted that heavy metals are highly toxic to an environment when present in sufficient concentrations, and this study will begin the process of determining whether the use of the Loveday Basin as a disposal basin has affected the mobility or bioavailability of any heavy metals in the area.

In this preliminary study, a single shell was analysed for metal content, with a view to determining: a) which metals can be found in the shell; and, b) the patterns, if there are any, of inter-shell variation in metal content.

All specimens found thus far in the investigated section of the Basin were no longer living. Analysis of the shells was conducted using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). A number of transects across the shells were analyses. These transects are shown in Figure 1.

A range of elements was analysed including Mg, Fe, Mn, Cr, Ni, Cu, Pb, Zn, Co, Sr, Ba, U, and Th.

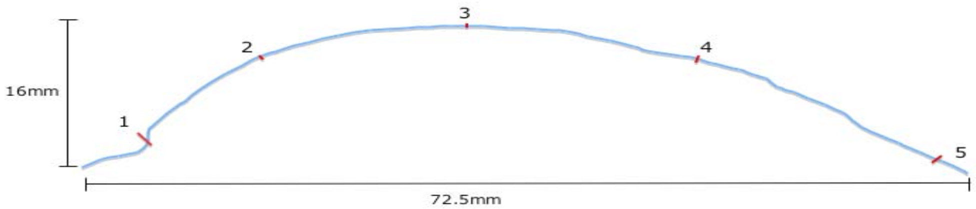

Figure 1: Outline of the shell analysed, with locations of transects 1 – 5.

PATTERNS AND CORRELATIONS BETWEEN ELEMENTS

With the exception of Mn, Sr and Mg, the concentrations of metals found in the mussel shell were very low, and it was difficult to isolate any major patterns or variations in the various metal concentrations across the transects.

However, the transect analyses do show some distinct patterns. In a number of the transects, the outermost edge section of the shell, the organic rich periostracum, exhibited metal concentrations far exceeding those throughout the rest of the transect, with some transects showing concentrations up to 16 times greater in this area. The enrichment can be explained by the fact that metals will naturally have a higher affinity with the organic material, and it is also possible for metals to adsorb onto the outermost edges of the shell. These enriched periostracum concentrations effectively dwarfed any other variation in the shell. Hence, for some transects, the periostracum area was excluded from the analysis.

Across the transects, there is a distinct variation in the concentration of Sr. Strontium readily partitions into the aragonitic lattice of the shell, and thus can be reliably related to growth rates. Troughs in Sr levels indicate periods of low growth, when the organism effectively shuts down, and produces organic material rather than carbonate. This generally occurs seasonally during periods of environmental stress such as extreme temperature (Walker 1992).

It can also be seen from Figure 2 that there is a marked correlation between Mn and Sr across the growth bands in the transects. Mn concentration can be related to the redox conditions of shell formation, such as the depth of burrowing in anoxic sediments.

However, as the Mn concentrations closely follow Sr concentrations across the transects, it is more likely that the variations are an indication of changes in salinity, possibly relating to times of increased discharge, where a flux of saline waters containing increased metal concentrations enters the system. A study of the oyster *Crassostrea virginica* found a statistically significant correlation between salinity and Mn concentrations in the shells, and an even stronger correlation with salinity when the Mn and Sr correlations were combined (Rucker & Valentine 1961).

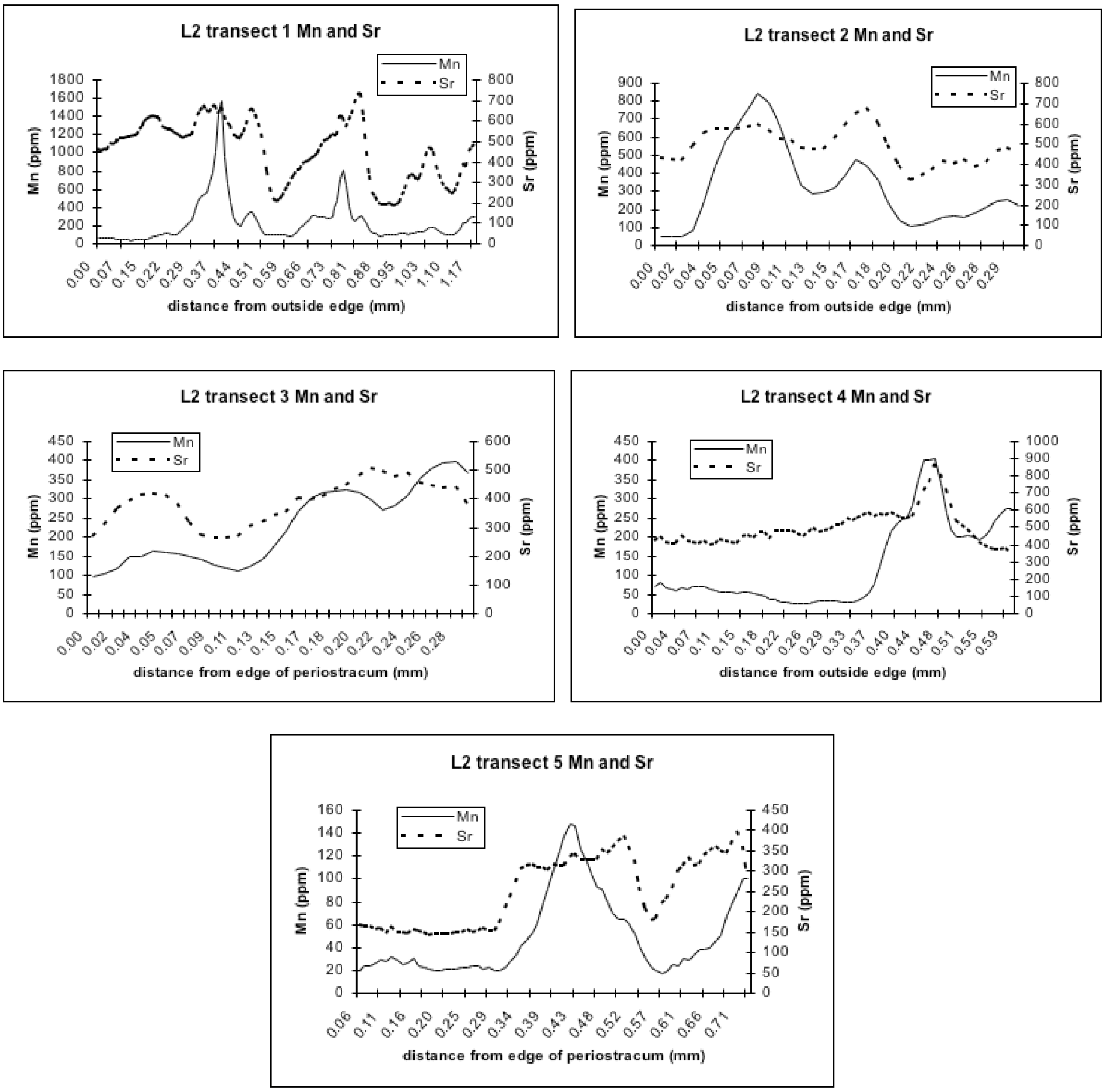

Figure 2: Concentrations of Mn and Sr across transects 1 – 5.

Mg/Ca AND Sr/Ca

Information about changes in salinity over time can be gleaned from the ratios Mg/Ca and Sr/Ca. Generally, an increase in each of the ratios correlates with an increase in the salinity of the environment. The data from shell L2 show distinct peaks in both Mg/Ca and Sr/Ca as the transects traverse through the growth bands. These are particularly noticeable in transects 1, 2 and 4, and indicate that there were periods of increased salinity throughout the shell's history (Figure 3).

These increases in salinity could be the reflection of seasonal variations, with increased salinity during summer periods as a result of increased evaporation. Alternatively, the salinity peaks could relate to times of increased saline discharge into the Basin.

The preliminary results of this study suggest that the shell of *Velesunio ambiguus* is likely to be of limited use as a biomonitor of metal contamination in the Loveday Basin. However, it could well provide other valuable information as regards environmental changes such as salinity fluctuations over time.

Further studies on other shells from the Loveday Basin will seek to corroborate and clarify these results, and will include an analysis of living mussels compared with their host waters and sediments. This will enable the establishment of the distribution coefficients of metal partitioning between the environment, soft tissue and hard shell of *Velesunio ambiguus*. Determination of the age of specimens found in the area will also help to more accurately reconstruct recent environmental history in terms of metal contamination and changes in salinity and redox conditions. Oxygen isotopes will also be studied to isolate the effects of changes in salinity as opposed to changes in temperature.

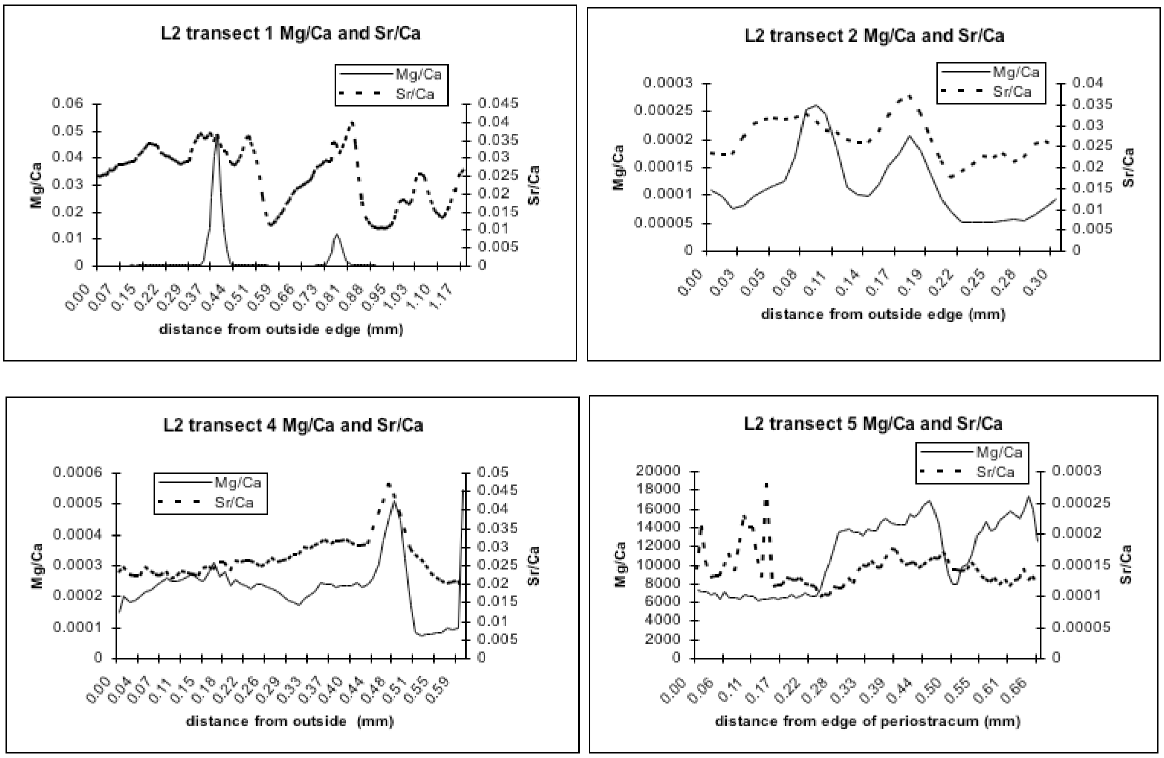

Figure 3: Mg/Ca and Sr/Ca across transects 1, 2, 4 and 5.

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