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Copper, Zinc, Lead and Cadmium Concentrations in the Mediterranean Mussel *Mytilus galloprovincialis* Lamarck, 1819 From the Sinop Coast of the Black Sea

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Abstract: The concentrations of copper, zinc, lead and cadmium in the living tissue of the Mediterranean mussel *Mytilus galloprovincialis* from the Sinop coasts of the Black Sea were measured by atomic absorption spectrophotometry for monitoring metal pollution in the coastal water. A statistically significant difference in the concentrations of all metals was observed among four sampling stations. The results were compared with previous studies and discussed.

Key Words: *Mytilus galloprovincialis, biomonitor, heavy metal*

Karadeniz'in Sinop Kıyılarından Toplanan Akdeniz Midyesi *Mytilus galloprovincialis* Lamarck, 1819'lerde Bakır, Çinko, Kurşun ve Kadmiyum Konsantrasyonları

Özet: Karadeniz'in Sinop kıyılarından toplanan *Mytilus galloprovincialis*'ların dokularında bakır, çinko, kurşun ve kadmiyum konsantrasyonları kıyısal suların metal kirliliğini belirlemek amacıyla atomik absorpsiyon spektrofotometresiyle ölçülmüştür. Elde edilen ağır metal konsantrasyonları örneklenen üç istasyon arasında istatistiksel olarak farklılık göstermiştir. Sonuçlar önceki çalışmalarla karşılaştırılmış ve tartışılmıştır.

Anahtar Sözcükler: *Mytilus galloprovincialis, biyomonitör, ağır metal*

Introduction

Metals are natural constituents of the biosphere. They occur at a wide range of concentrations and with a broad array of chemical attributes. Many are essential to biological systems such that in the absence of an essential metal an organism can neither grow nor produce (1). Apart from the major ions such as sodium, potassium, calcium and magnesium which are essential to sustain life, other metals, normally only present in trace amounts, are also required to some degree. Organisms absorb heavy metals, essential or not, from the surrounding environment with the potential to accumulate them within their bodies. All heavy metals are potential toxins at some concentration (2-5), the non-essential metals e.g. mercury, lead and cadmium are particularly toxic at relatively low concentrations (6, 7). The body concentrations of a metabolically available metal must be kept below threshold levels. It is well known that non-essential metals are very toxic to animals, so that the metal concentrations are regulated for human health and drinking water.

Great efforts have been made to determine concentrations of these metals in marine ecosystems, their speciation in natural waters and sediments, to assess their bioavailability and to develop methods for determination of their impact (8). Studies have shown that gross analyses of water and sediments for the metals cannot be used to predict or assess their environmental impact since the majority of these metals are present in the anoxic layer of sediments in mineralised forms or strongly bound to insoluble organic matter (8, 9) and thus are not directly available to biota (10).

Bivalves are commonly sessile forms, so they are directly influenced by environmental conditions. They have been used as biomonitors of environmental pollution by heavy metals (9-14). A number of properties are desirable for monitoring metal pollution of the coastal waters: (a) pollutants should be accumulated without lethal impacts to the species employed; (b) biomonitors should be sedentary, so as to be representative of the area in which they are sampled; (c) high survival rate under control conditions; (d) ease of collection; (e) sufficient tissue for contaminant analysis; (f) biomonitors should tolerate brackish water and (g) a simple correlation should exist between the contaminant content of a biomonitor and the average contaminant concentration in its ambient environment (9, 10).

Mussels are commonly employed in the monitoring of metal pollution (15-21) because they are consumed by humans and they have a broad geographical range (22, 23). They also fulfil many of the criteria listed by Phillips (9), and Phillips and Rainbow (10). In the present study, therefore, the Mediterranean mussel *Mytilus galloprovincialis* was chosen as a biomonitor of coastal metal pollution.

Materials and Methods

Mussels were collected monthly by scuba divers from four stations (Fig.1) in the upper-infra littoral zone of Sinop coasts of the Black Sea, at a depth of 1-8 m from February 1992 to January 1993.

At each station 25 mussels of 68±4 mm were collected. Zelimir and Mirjana (24) indicated that mussels grow rapidly within the first 14 months and when they reach 60 mm, growth slows. On the other hand, the size of mussels for marketing varies between 50 and 80 mm in Europe while the minimum length of the mussels for consumption is approximately 70 mm in Turkey (25).

After collection, the samples were transported to the laboratory. The animals were rinsed with clean seawater and then placed in about 20 litres of constantly aerated clean seawater for 24 hours to allow depuration (26-29). Following elimination of the gut contents the entire soft parts of the mussels were removed using stainless steel equipment. The bulked soft parts were weighed, homogenised and deep frozen until analysis. All samples were run in triplicate and all values were expressed as µg metal g^{-1} wet wt.

For the determination of zinc, copper, lead and cadmium, 5g of wet samples was placed in flasks and 10

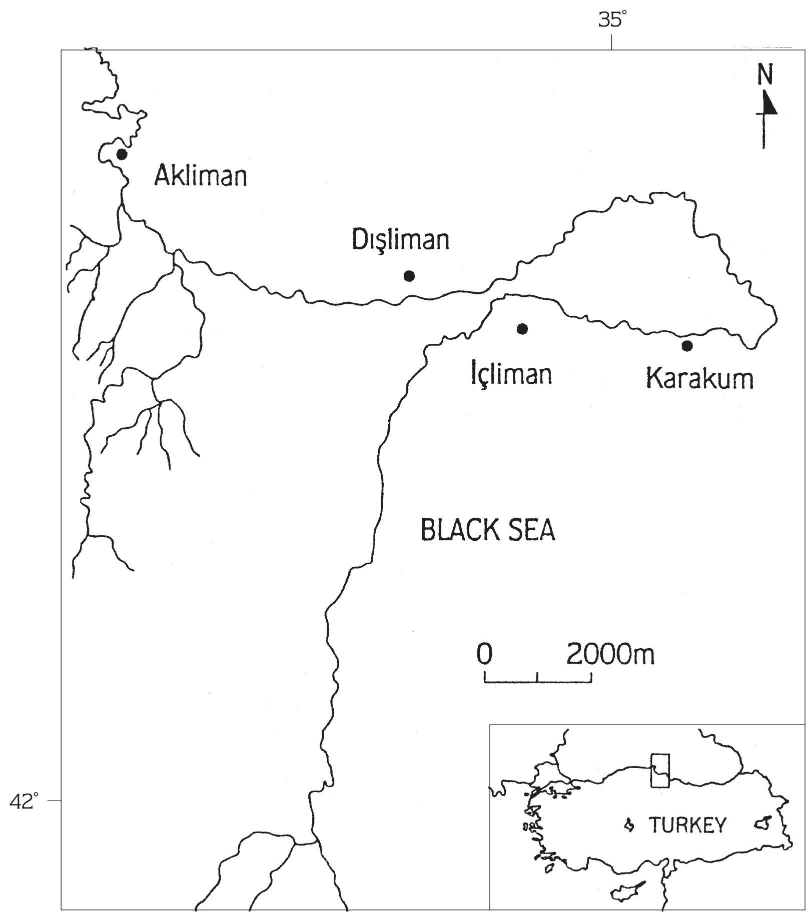


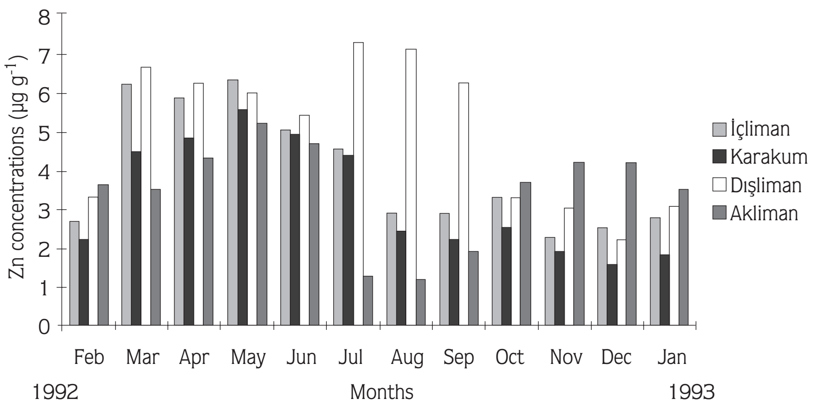
Figure 1. Sampling stations and study area.

ml of concentrated HNO_3 : $HClO_4$ (5:1) was added to each flask and the solution was evaporated to dryness on a hot plate. After allowing the flasks to cool, 10 ml of N/10 HCl (per 1g fresh wt) was added to bring the volume to 50 ml and filtered through Whatman filter paper with a pore size of 0.45µm. The samples were analysed by atomic absorption spectrophotometry (Perkin Elmer Model 2280) using the method described by Bernhard (30). The data were analysed using single classification of ANOVA (31). The concentrations of zinc, copper, lead and cadmium in mussels were compared among the four stations by the use of F values, to determine if a significant difference exists between the stations.

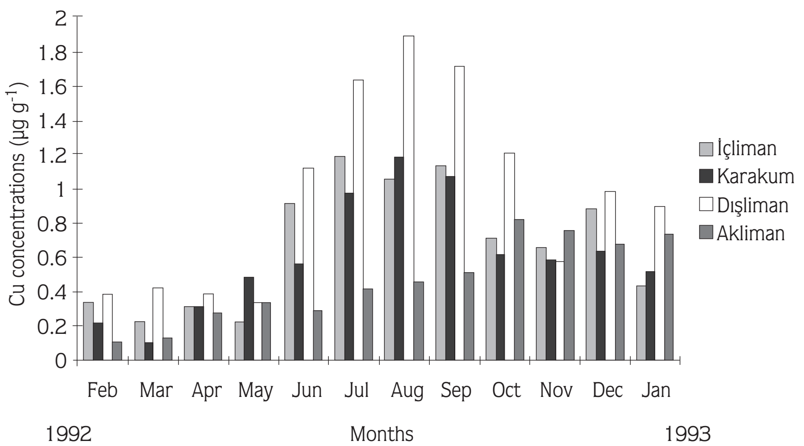
Results and Discussion

Figures 2A-2D show the concentration of heavy metals in the mussel, *Mytilus galloprovincialis*, from the Sinop coast. The results showed that the calculated F values were greater than the critical F value at the 0.05 level indicating that there was a statistically significant difference between the concentrations of the metals among the four stations (Figs. 2A-2D).

These variations between stations may be due to their different geographic locations. The highest concentration of Zn, Cu and Pb was observed in the samples from Dışliman, whereas the highest concentration of Cd was observed in those from İçliman. However, the lowest values of Cu, Pb and Cd were measured in Karakum and the lowest value of Zn was obtained in Akliman. In terms of geographical locations the highest values appeared to be associated with Dışliman and İçliman areas and this may be due to the discharge of untreated domestic wastes, harbour activities, the dumping of ship wastes and other coastal activities.

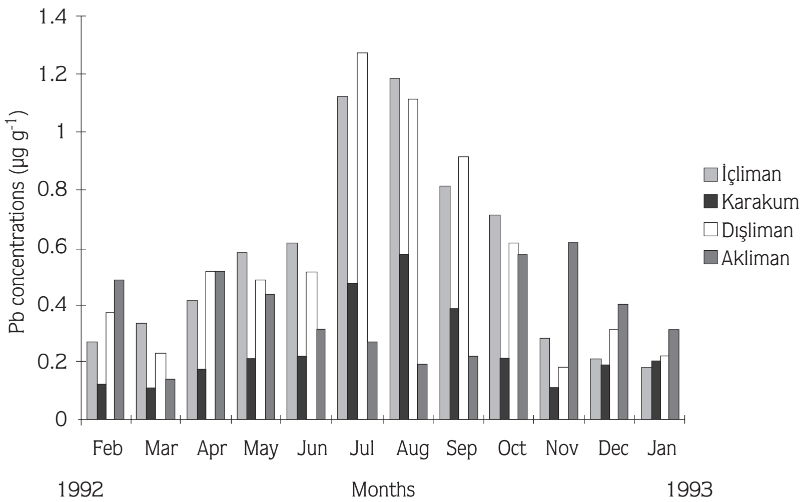


2a



2b

Figure 2. Mean concentrations (µg g-1 wet wt) of Zn (A), Cu (B), Pb (C) and Cd (D) in the Mediterranean mussel *Mytilus galloprovincialis* from the Black Sea.



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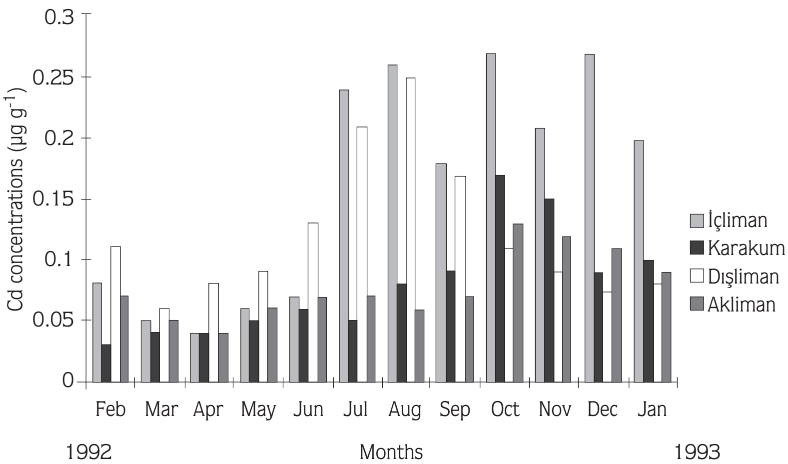

2d

Metal concentrations in the Mediterranean mussel, *Mytilus galloprovincialis*, decreased in the order: Zn>Cu>Pb>Cd (Figs. 2A-2D). Öztürk (32) found that the levels of Cd and Pb in *Mytilus galloprovincialis* from the same stations were higher than those in the present study whereas the levels of Zn and Cu were lower. Moreover, Ünsal and Beşiktepe (33) found that the concentration of Pb (2.58 µg g^{-1}) in the Mediterranean mussel Mytilus galloprovincialis from Sinop was considerably higher than those measured in the present study. Ünsal and Beşiktepe (33) pointed out that when mussels were collected in 1991 the rainfall maintained a high level and resulted in higher industrial discharge of pollutants into the sea throughout the winter and spring. They also indicated that used lead batteries were occasionally encountered on the Sinop coast. However, these authors (33) found the levels of Cu to be similar to those of the present study. Regional comparison of the results must be made with caution because of the variations in sampling procedures and methodology. For example, in Ünsal and Beşiktepe's (33) study no time was allowed for the animals to clear their guts. Moreover, in the present study the mussels of 68±4 mm in length were selected, whereas in Ünsal and Beşiktepe's (33) and Öztürk's (32) studies the mussels of 47±0.8 and 35-70 mm in length were selected, respectively. Phillips (11) observed a weight-dependant variation in concentrations of metals in *Mytilus edulis*. In the environment, smaller and lighter individuals were found to contain significantly higher concentrations of Zn, Cd, Pb and Cu than larger and heavier individuals (11). However, if growth is slow relative to the rate of accumulation of a metal, the concentration of that metal will increase with age and weight. Alternatively, if growth is rapid compared with metal accumulation, the observed concentration of the metal will decrease with age and weight, even though the overall metal content increased (10).

In the present study, the concentrations of zinc in mussels were consistently higher and also extremely variable (Fig. 2A). The highest concentrations of all metals studied were well below the permitted levels (34, 35).

To examine any monthly variations in metal concentrations at each station, F values (at the 0.05 significance level) were used. It was found that zinc, copper, lead and cadmium concentrations varied significantly from month to month at each station. Figure 2A indicates that Zn concentrations in the mussels collected during spring and early summer were high compared with other metals (Figs. 2B-2D). Some random fluctuations appear to exist throughout the rest of the year, making it difficult to locate a definite trend with any degree of certainty. Aral (25) indicated that the growth and reproduction of the Mediterranean mussel, *Mytilus galloprovincialis,* occur mostly in spring and early summer which would indicate a change in metabolic activity. Similarly, Phillips (11) observed seasonal variations in the concentrations of Zn, Cd, Pb and Cu in *Mytilus edulis* and found that concentrations of these metals were highest in late winter. Seasonal variations in metal concentrations arise from the reproductive cycle which involves the maturation of the gonads and gametes and changes in the availability of food (36). These events involve substantial changes in body weight, water content and general condition of the mussel. The loss of gametes leads to a loss in body weight. If the gametes are relatively poor in metals, spawning is associated with an increase in tissue metal concentrations. Moreover, the availability of food directly affects the growth rate of the mussel. Phillips (11) observed a weight-dependant variation in concentrations of metals in *Mytilus edulis*. In the environment, smaller and lighter individuals were found to contain significantly higher concentrations of Zn, Cd, Pb and Cu than larger and heavier individuals (11). In periods of food shortage, the growth rate slows down and as a consequence the concentrations of metal rise. It is possible that the increased concentration noted for zinc in spring and early summer reflects an increased requirement resulting from these changes in metabolic activity. However it should be noted that since the monthly sample size was insufficient to reduce the effect of individual variation, the monthly variation could reflect the wide variability among individuals rather than a change in requirement. Further monthly sampling and individual tissue analysis are required.

At İçliman, Dışliman and Karakum, the highest concentrations of copper in the mussels were observed in July and August. In the last decade, the local population in Sinop has been about 25000, increasing to 60000 in summer. Thus, untreated domestic wastes and human activity along the coastal zone increase in July and August and probably give rise to high metal concentrations.

At Akliman the concentrations of Zn, Cu, Pb and Cd in the mussels were higher in winter than those in summer (Figs. 2A-2D). This was believed to have been caused by the presence of polluted freshwater (Sırakaraağaçlar and Karasu) outfall 1.5 and 2.5 km away. This effect disappared when freshwater was less in summer.

Conclusions

The data presented here were compared with the guidelines (34, 35) for heavy metals in shellfish. From the public health point of view, the levels of the metals found in this study were generally lower than the permitted levels and those of previous studies (32, 33).

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