THE IMPACT OF THE ATHENS’ DOMESTIC WASTES TREATMENT ON METAL BIOAVAILABILITY IN THE MARINE ENVIRONMENT OF SARONIKOS GULF (CENTRAL AEGEAN SEA, GREECE)

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ABSTRACT

Saronikos gulf -the gulf in front of Athens- suffers from an important water quality decline due to anthropogenic activities (municipal and industrial wastes as well as naval activities). The Athens’ wastes are treated since 1996. The aim of the present paper is to investigate the changes of metal concentrations in coastal marine environment due to the wastes treatment and the description of metallic temporal trends in Saronikos gulf by the means of metal accumulation in bioindicators (natural populations of mussels *Mytilus galloprovincialis*). The knowledge of changes is useful in order to reveal the effectiveness of the measures taken for the protection of the marine environment. are used as bioindicators.

Mussels were collected from four stations along the coasts of Saronikos Gulf, seasonally during the period 1986-2006 and scarcely till 2011. Samples were analysed for Cu, Cr, Cr, Ni, Zn, Fe, Mn and occasionally for Pb and Hg by atomic absorption spectrophotometry.

Results showed a decreasing metal gradient towards the open sea. A similar pattern in temporal evolution of metal bioaccumulation in mussels from the different stations was recorded for most metals. The pattern comprises several temporal variations. It was found that the operation of the wastes treatment unit caused a temporal reduction in metal bioavailability, followed by increase as the quantity of wastes increased too.

1. INTRODUCTION

Trends of marine pollution are of major interest for decision makers and Governments, since they represent the effectiveness of the measures taken. Saronikos gulf -the gulf in front of Athens- is among the Greek marine areas needing monitoring because it suffers by an important water quality decline due to anthropogenic activities. The main pollution sources implicate municipal and industrial wastes as well as naval activities. The biggest port of Greece, Piraeus, and the largest industrial zone of Elefsis bay, hosting almost 50% of the industrial activity of Greece, operate in the coastal area of Saronikos. The short
renewal time of the surface waters (reaching 2-3 months) limits the extent of pollution of Saronikos gulf (Frilingos & Barbetseas 1990).

The Athens’ wastes treatment unit, located in Psittalia island (northern Saronikos gulf), operating since 1996 resulted to the significant reduction of organic charge and the amelioration of the trophic state of Saronikos’ waters (Pagou et al. 2011). Although the treatment unit is not especially designed to eliminate metals, their particulate form is partially retained during the phase of sedimentation.

The aim of the present paper is to describe temporal trends of metals in the coastal environment of Saronikos gulf by the means of metal accumulation in marine organisms in order to reveal the effectiveness of the Athens’ wastes treatment and consequently the measures taken for the protection of this marine environment.

The bioaccumulation of contaminants by the tissues and organs of marine organisms has been extensively studied throughout the world and led to the adoption of the bio-indicator concept for the environmental quality assessment (Langston and Spence, 1995). Mussels are recognized as pollution bioindicator organisms because they accumulate pollutants in their tissues at elevated levels in relation to pollutant biological availability in the marine environment (Phillips. 1976). Moreover, this ability has led to the adoption of the international “Mussel Watch” program under the CIESM frame and IAEA collaboration and several national programs on Mussel Watch in the marine environment have been carried out (Goldberg et al., 1983; Jernelov, 1996; Claisse, 1989).

2. METHODOLOGY

Mussels *Mytilus galloprovincialis* are abundant in several coastal areas of Saronikos gulf. They were collected from four stations (Fig 1) seasonally during the period 1986-2006 and scarcely till 2011.
During each sampling occasion five to six replicates of composite samples consisting of the soft parts of 20 specimens of similar size, were prepared. After freeze-drying with a CHRISt GAMMA 1-20 lyophilisator, about one g of dried tissue was digested with 10 ml of HNO3 in a microwave-device (CEM MDS 2100). After digestion the sample was diluted with distilled water to 20 ml. A Varian Spectr AA 20 Plus flame Atomic Absorption Spectrophotometer was used for the determination of Cu, Cr, Ni, Zn, Fe and Mn concentrations. The accuracy and precision of the analytical methodology was tested with reference materials.

The statistical treatment of the data, including summary statistics, one-way ANOVA and regression analysis was performed using the STATGRAPHICS software package.

3. RESULTS AND DISCUSSION

Totally 1537 samples of mussels from Saronikos gulf were analysed during the period 1985-2011. Summary statistics are given in Table 1 expressed in μg/g dry weight.

With some exceptions, Saronikos Gulf’s mussels are generally characterised as moderately contaminated by metals (Catsiki 2005). Among the studied metals mainly Ni seems to be abundant in mussels. However data are similar to those cited by the Report of the European Environmental Agency for the Mediterranean (Catsiki et al, 1999).

<table>
<thead>
<tr>
<th>Cd</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Zn</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>890</td>
<td>1517</td>
<td>1370</td>
<td>1515</td>
<td>1480</td>
<td>1152</td>
</tr>
<tr>
<td>Average</td>
<td>0.96</td>
<td>6.61</td>
<td>4.20</td>
<td>4.51</td>
<td>150.61</td>
<td>216.39</td>
</tr>
<tr>
<td>Median</td>
<td>0.81</td>
<td>6.18</td>
<td>3.53</td>
<td>3.88</td>
<td>119.22</td>
<td>161.82</td>
</tr>
<tr>
<td>SD</td>
<td>0.66</td>
<td>2.88</td>
<td>2.99</td>
<td>3.05</td>
<td>101.20</td>
<td>172.23</td>
</tr>
<tr>
<td>Min</td>
<td>0.02</td>
<td>0.39</td>
<td>0.02</td>
<td>0.10</td>
<td>13.36</td>
<td>29.56</td>
</tr>
<tr>
<td>Max</td>
<td>5.15</td>
<td>24.8</td>
<td>20.87</td>
<td>29.23</td>
<td>1010.0</td>
<td>1609.8</td>
</tr>
</tbody>
</table>

Metal levels in mussels varied according to the sampling station. Results showed a decreasing metal gradient towards the open sea; Elefsis’ bay mussels being the more contaminated (Bei et al 1998). In addition the sampling season has a statistically significant effect on metal bioaccumulation. Mussels collected during the cold period of the year and especially during December (when their gonads were well developed) presented the higher concentrations (P<0.05). This fact is mainly related to the biological cycle of the mussels and only secondary to environmental parameters.

The metallic temporal evolution in mussel samples present important fluctuations related to biological factors (i.g increase during the cold periods of
the year) and environmental ones, (i.e. abundance of phytoplankton, seawater temperature and quality etc). We noticed a simultaneous decrease or increase of metallic levels in the mussels from all the sampling stations (Fig. 2) which suggests that the changes in the bio-available quantities of metals follow the same pattern in the entire Saronikos gulf. Similar observations, concerning the extension of quality changes in Saronikos gulf, have been obtained by the author for the macroalgae Ulva lactuca (Catsiki & Papanastassiou 1993). Consequently the investigation of temporal evolution of metals in this paper will not take into account the sampling station of the mussels.

Fig.2: Similarity in Cu temporal evolution in mussels collected at the 4 sampling stations of Saronikos gulf (stations C3, C8A, C8B & C10)

A specific statistical treatment of the data, as the LWC (Locally Weighted Regression) smoothing technique reduces the fluctuations because it does not take into account the temporally limited changes, even if they are much important. The plots of median smoother consider only the changes that have duration of at least six months - since the sampling in Saronikos gulf was seasonal. As a result it archives to smooth the fluctuations and to give the clearer image of the evolution of metal bioavailability (Fig. 3).

The pattern comprises several temporal variations. For most studied metals levels maintained relatively constant during the period 1985-89, followed by an increasing period till 1993 for Cr & Mn and till 1997 for Zn. During 1997, with the exception of Cr, metals either reach their higher levels (Cu, Fe, Zn), or they have a secondary pick (Ni, Cd, Mn). The year 1997 coincides with the first year of operation of the wastes treatment unit, time probably necessary for a first sign of the effectiveness of the Athens’ wastes treatment. However the period 1993-94 marks also changes in anthropogenic activities, since important industries ceased to function.
Especially Cr presents its minimal levels during 1997, fact showing that all metals are not interrelated and their origin is variable. After 1997 the concentrations temporally return to their previous levels of 1985 and either continued to decrease or start to increase again.

Regression analysis reveals trends during the 25-years duration of the monitoring of the bioavailable metals in mussels (Fig.4).

Regression analysis showed that Cu, Cd, Ni and Mn levels present a statistically significant decrease in relation to 1985. On the contrary Fe & Zn (metals especially related with domestic sewages) have a statistically significant increase, while for Cr the observed fluctuations mask the overall trend.

Although the operation of the sewages treatment and the reduction of industrial activity in the area had obviously result to the observed decrease trends, we can not neglect the significant gradual augmentation of the quantity of...
(treated) sewages released into Saronikos gulf, that are probably the cause of the observed increase trends.

Fig. 4: Regression analysis of bioaccumulated metal levels in mussels for the period 1985-2011

4. CONCLUSIONS

In conclusion the operation of the wastes treatment unit caused a temporal reduction in metal bioavailability, followed by increase as the quantity of wastes increased too. The observed increasing trends of Fe and Zn yield on robust data and should be taken into consideration by the decision makers since the actual sewage treatment only indirectly removes metals.

Finally although metals do not represent a serious risk for the Hellenic coastal marine environment, given their toxicity and their secondary effects on humans and marine life, it is imperative to monitor their levels and extend their study in all marine areas with anthropogenic activities.
REFERENCES


