Behavior and trends for Zn in Saronikos Gulf

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Abstract. The study of Zn in the water column of Saronikos Gulf in Greece during a two year period between 2008 and 2010 added data to the available time series of metal data for this marine area since 1985. The Saronikos Gulf, is directly influenced by the Athens metropolitan area. The operation of the Wastewater Treatment Plant of Athens situated on the small island of Psitalia, in 1995, was considered to be the turning point in the efforts of de-pollution of the gulf. Major sources of pollution for the gulf include also the port of Piraeus, with intensive navigation and shipping activities and the significant industrial activity occurring along the coast of Attica. This study of dissolved and particulate Zn gave results consistent with previous studies of the area such as the prevalence of the dissolved form of Zn and the most affected areas being the smaller most enclosed Gulf of Elefsina and Psitalia Island near the wastewater outfall. However, the concentrations of Zn were below toxic levels for marine aquatic organisms. Furthermore, a clear decrease in the Eastern part of the gulf was exhibited as well as a more subtle decrease in the gulf of Elefsina. The levels of Zn in Saronikos Gulf were found comparable to those of other Greek coastal areas.

Key words: Zinc, Saronikos gulf, Greece, marine pollution

Introduction

Heavy metals are natural components of the Earth's crust. There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be toxic for various organisms. Increased urbanization and industrialization are responsible for elevated levels of metals in the waterways. They are usually present in increased concentrations in industrial and municipal waste and urban runoff, thus posing a threat to aquatic life. Toxicity levels depend on the type of metal, its biological role, and the type of organisms that are exposed to it. The heavy metals linked most often to human activities are lead, mercury, cadmium, copper, zinc and chromium. Some of them are micronutrients for organisms but can also be toxic in larger doses.

Zn is widely used in various industrial activities and it is ubiquitous in mechanical apparatus as well as in the household since it is contained in human hygiene products (lotions and shampoos) (Cox 1995, Alloway & Ayres 1997). Zn is a micronutrient for humans utilized by specific enzymes (Cox 1995). According to the USEPA, concentrations of dissolved Zn above 90μg/L can be harmful for marine water organisms at a short term exposure (USEPA 2009).

The Saronikos Gulf, with an area of 2600 km^2 and a maximum depth of approximately 400 m, is directly influenced by the Athens metropolitan area with more than 4 million inhabitants. The operation of the Wastewater Treatment Plant of Athens situated on the small island of Psitalia, in 1995, was considered to be the turning point in the efforts of de-pollution of the gulf. Major sources of pollution for the gulf include also the port of Piraeus, the largest port of Greece, with intensive navigation and shipping activities and the significant industrial activity occurring along the coast of Attica.

Saronikos Gulf can be divided in 4 sections according to geomorphological differences, hydrological characteristics and depth (Fig. 1): (a) the Elefsis Gulf, a shallow embayment (maximum depth 33 m) stratified during summer receiving considerable pollution loads due to intense industrial activities; (b) the eastern part

characterized by water circulation providing adequate renewal of water masses; (c) the western part which is deeper (maximum depth 400 m); (d) the Psitalia area, which includes the outlets of the sewage treatment plant. A strong seasonal thermocline appears during summer between ~30– 60 m in the main Saronikos Gulf, excluding the Gulf of Elefsis, where the thermocline appears at 15 m. The circulation in the Saronikos Gulf has been reported to depend strongly on the local winds and is particularly significant in view of transfer of pollutants originating from the sewage treatment plant outflow at 65 m in the northeastern part. The prevailing currents inside the gulf are from the northeast to the southwest and continue anti-cyclonically in the deeper layer of the west sub-basin.

Due to its proximity to the capital of Greece and its importance from an environmental point of view, it is the most studied marine area of Greece and there is an extensive time series of trace metal pollution data beginning in the mid 80's (Scoullos et al 2007).

Materials and Methods

During the period 2008-2009 eight sampling cruises were carried out with the research vessel "Aigaio" of the Hellenic Centre for Marine Research (HCMR), in a grid of nine sampling stations (Figure 1). A total of 30 samples were collected per cruise. Seawater samples were collected with polyethylene Go-Flo bottles mounted on a rosette in conjunction with a CTD probe. After their collection, seawater samples were transferred immediately to the laboratory where they were filtered through preweighed Millipore membrane filters (0.45 μm pore size) under a laminar flow hood for the collection of suspended particulate matter (SPM). The filtered samples were acidified to pH 2 with supra pure HNO_3 and stored in refrigerator until analysis.

Fig. 1. Study area and sampling stations

Dissolved trace metals were preconcentrated on Chelex-100 resin columns (Scoullos et al 2007). After removal of alkalis with ammonium acetate, the metals were eluted from the resin with HNO_3 2N.

The filters were treated with conc. HNO_3 in covered PTFE beakers for the determination of the total metal content (modified Walsh 1996, Scoullos et al 2007). Blank filters were analysed at each sampling for the determination and subtraction of possible contaminations. Concentrations of dissolved and particulate Zn were determined by Flame Atomic Absorption Spectrophotometry (FAAS), with a Varian SpectrAA 200 Flame A.A.S.

Results and Discussion

The ranges of dissolved and particulate Zn as well as the median value of each sampling are presented in the box-plots of Figures 2 and 3. Dissolved Zn ranged from 3.2 to 7.7 μg/L and particulate Zn ranged from 0.30 to 0.63 μg/L. Dissolved Zn prevailed over the particulate form with the percentages of dissolved metal ranging from 77 to 99%. The highest values of dissolved Zn for all samplings were detected at April, May and December 2009.

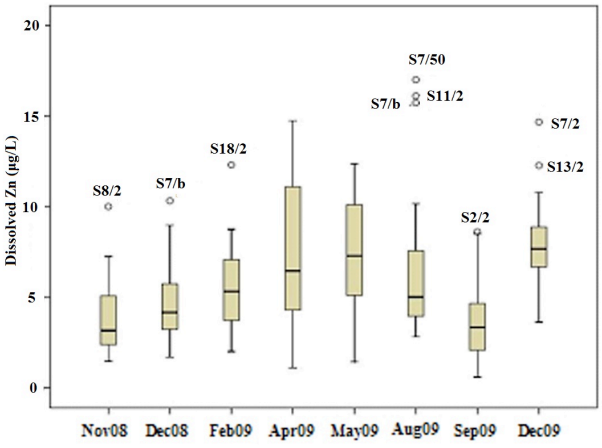

Fig. 2. Box-plot of dissolved Zn

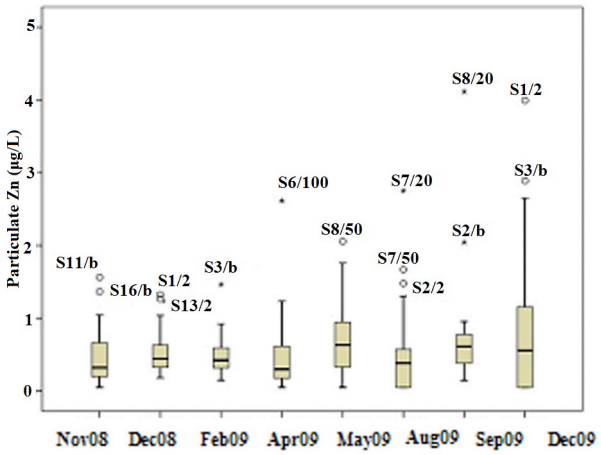

Fig. 3. Box-plot of Particulate Z

Indicative surface distributions of dissolved and particulate Zn are presented in Figures 4 and 5. The highest values of dissolved Zn for all samplings were

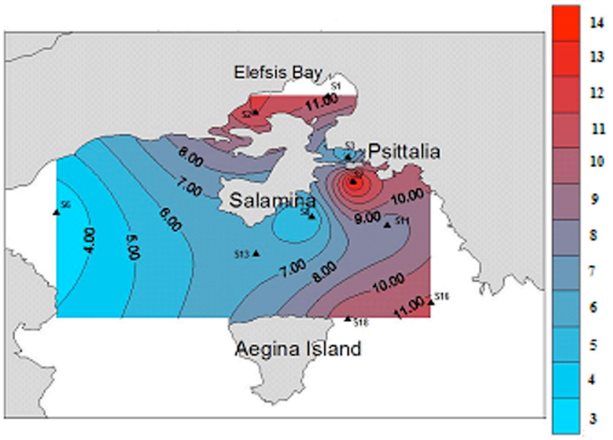

Fig. 4. Surface distribution of dissolved Zn in µg/l (April 2009)

detected at the area around the Psittalia Island. Relatively high concentrations of dissolved Zn were also detected in the Gulf of Elefsis. Therefore the Gulf of Elefsis and Psitalia Island can be considered as hot spots for dissolved Zn. The same applied for particulate Zn.

Since each of the stations was sampled at 4 depths (2-20-50 m and bottom) an attempt was made to evaluate if there was any difference in the levels of dissolved and particulate Zn between the various depths. Statistical comparisons using the SPSS 16.0 software showed no difference between the 4 depths.

For Saronikos Gulf there are available trace metal data since the mid 80's. In all the years the gulf of Elefsis was the most enriched part for dissolved Zn. During 2008-2009 there was a slight increase in the concentration of dissolved Zn in all sub areas in comparison to the period of 1995-2004, but compared to the period before the operation of the waste water treatment plant, Zn levels have shown a clear decrease (Figure 6).

Total Zn concentrations in seawater have been collected from studies of other Greek coastal areas carried out by members of the Laboratory of Environmental Chemistry (Paraskevopoulou, 2009). Total Zn levels in seawater from these studies were 0.67-14.7 µg/L (mean 2.3 µg/L) in Northwest Saronikos, 0.9-62.0 µg/L in Korinthiakos gulf, 5.0-19.1 µg/L (mean 10.8 µg/L) in Oropos gulf and 1.7-53.9 µg/L in Maliakos gulf. The wide range of Zn levels in these coastal areas is attributed to the presence of very different sources i.e. industrial activities, river discharges, agricultural diffused sources etc.

Conclusions

The study of dissolved and particulate Zn in Saronikos Gulf for the years 2008-2009 gave results consistent with previous studies of the area.

The dissolved form of Zn prevailed. The areas of Elefsis gulf and Psitalia Island presented the highest levels of Zn indicating the influence of coastal polluting industrial and harbor activities in the first sub-area and

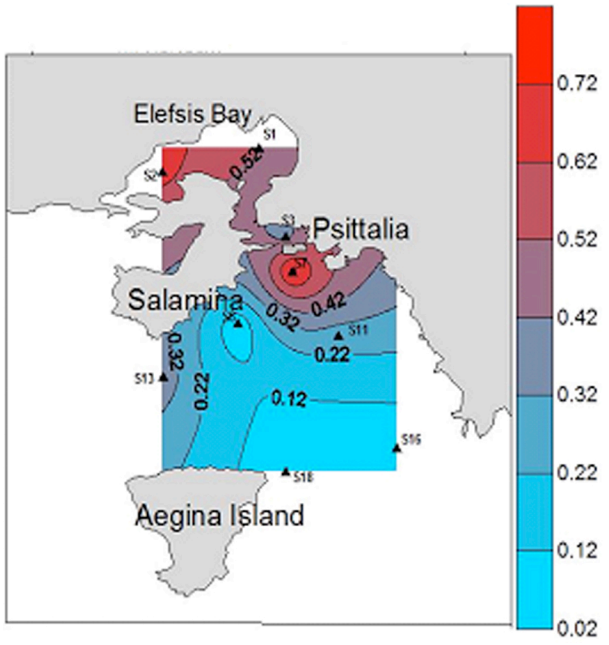

Fig. 5. Surface distribution of particulate Zn in µg/l (August 2009)

the waste water treatment outfall in the second (Fig. 4-5). However, the concentrations of Zn were below toxic levels (USEPA 2009) even in the most affected areas.

The study of Zn in Saronikos over the last 25 years (Fig.6) has shown a clear decrease in the Eastern part of the gulf after 1994, attributed to the operation of the wastewater treatment plant of Athens. The similar decrease in Elefsis can be attributed both to the wastewater treatment plant, as before 1995 untreated waste effluents were discharged in smaller depths closer to the gulf of Elefsis, but also to the minimization of the Elefsis industrial zone with some factories terminating their activities in the last 10 years.

The levels of Zn in Saronikos Gulf are comparable to those of other Greek coastal areas.

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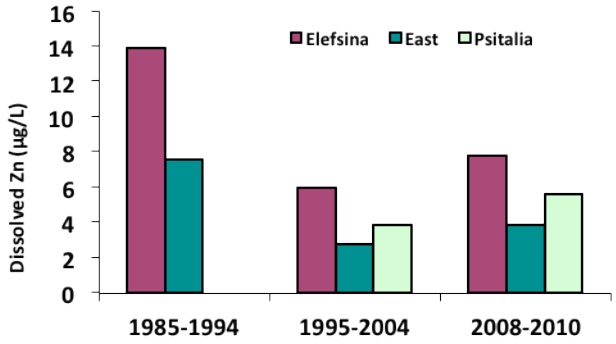

Fig. 6. Comparison of dissolved Zn data of Saronikos Gulf

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