Anthropogenic metal pollution in Saronikos gulf: historical evolution and risk assessment based on selected sediment cores

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Abstract. Anthropogenic metals (Cd, Cu, Hg, Pb, Zn) are chemical elements known for toxic effects when present in elevated concentrations. There are various sources of these metals to marine sediments. The presence and levels of anthropogenic metals in sediments may cause adverse implications to ecosystem and human health. The present paper is a preliminary presentation of anthropogenic metal levels in selected short sediment cores obtained during a 2017 sampling campaign in the various sub-areas of Saronikos (Elefis bay, Eastern, Western and Outer). The vertical distribution of Cd, Cu, Hg, Pb and Zn along with sediment quality evaluation are discussed. In the background sediment layers (below 15-20cm) the ranges of Cu, Pb, Zn, Hg and Cd (in mg/kg) are 9.3-37.3, 18.8-35.1, 16.8-85.3, 0.019-0.033 and 0.041-0.090 respectively. In upper sediment layers affected by anthropogenic pollution the ranges of Cu, Pb, Zn, Hg and Cd (in mg/kg) are 13.7-138, 33.9-181, 35-435, 0.031-1.73 and 0.051-0.65. The metal contents in the sediments of Saronikos generally do not exceed the ERL (effects range low) and ERM (effects range median) sediment quality guidelines widely used as risk indicators to benthic biota. However, most metals in Elefsis bay and Hg in Elefsis and other locations of Saronikos as well, present elevated concentrations above the quality limits posing risk to marine biota and possibly to human health.

Keywords: Industrial pollution, Urban pollution, Background levels, Sediment Quality assessment

1. Introduction

Trace metals are known pollutants. Some are essential to biota participating in biochemical functions but can be toxic in elevated concentrations (e.g., Co, Cu, Zn) and others are only toxicants with no biochemical roles (e.g., Hg, Cd, Pb) (Morel et al., 2003).

Sediments are generally considered as sinks of contaminants and thus are widely used to assess metal pollution in coastal marine areas. Sediments cores are known to serve as records of pollution events and their deeper layers are used to determine local metal background levels. Thus, the study of sediments in a coastal marine area can provide both spatial and temporal information on metal pollution (Birch, 2017; Chiaia-Hernández et al., 2022).

The aims of the present paper are; (a) to present the spatial distribution of the most common anthropogenic metals (Cd, Cu, Hg, Pb, Zn) in Saronikos gulf sediments along with sediment quality assessment and (b) to comment on their temporal evolution with comparison to background values from sediment cores.

2. Materials and methods

2.1. Study area - Sampling

Saronikos Gulf is the marine area bordering the largest cities of Greece, Athens and Piraeus, with ~4 million inhabitants and extensive industrial areas. The main sources of trace metals to the seawater and sediments of Saronikos are: (1) the industrial zones of Elefis Bay and Thriasio on the north coast hosting oil refineries, shipyards, food processing, iron steelworks, cement factories, cable manufacturing, waste recycling plants, landfills, military installations; (2) Piraeus port, one of the largest in the Mediterranean, with increased marine traffic; (3) the Athens wastewater treatment plant (Psitalia WWPT) on Psitalia island and (4) the atmospheric emissions by vehicle traffic and heating systems of the urban area. Furthermore, a smaller industrial zone, with a major oil refinery and smaller food processing and cable manufacturing installations, is situated on the north-western coast of Saronikos (Valavanidis et al. 2006, Paraskevopoulou et al. 2014).

Sediment samples (5 surface and 13 short cores) were collected in October 2017 by the R/V AEGAEO of HCMR from the various sub-areas of Saronikos gulf. In this paper we present metal content from some selected cores and surface sediments. Station S1 (core), inside Elefsis bay, is affected mostly by industrial activities.

Stations S7 (surface sediment), S8 and S11 (cores) are located in East / Inner Saronikos and S7 is closest to the outfall of the Psitalia WWTP. Stations N2, UN12A, S21 and S22 (cores) are located in East / Outer Saronikos, while MOT16A and UN6 (cores) are in West Saronikos. Finally, station S13 (core) is located in the strait between Salamina and Aegina. Figure 1 presents a map of Saronikos gulf with station locations and indicative pollution sources.

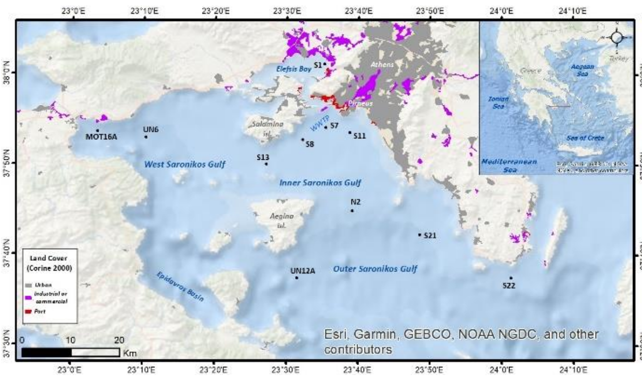

Figure 1. Map of Saronikos gulf with station locations and indicative pollution sources

2.2. Analytical procedures

The sediment were frozen after sampling. The cores were cut in the lab in 1cm or 2cm layers above and below 10cm respectively. All samples (surface and core layers) were stored frozen until further processing. Water content was removed by freeze drying. Subsequently, grain size analysis via dry sieving was performed using 1mm and 63μm stainless steel sieves. The gravel (>1mm), sand (> 63μm) and muddy (<63 μm) fractions were separated for the calculation of the respective percentages to the total sediment. The gravel fraction was discarded, the two other fractions were mixed again for further analysis and the concentrations of heavy metals refer to sediment particles below 1mm.

The total metal contents (Cu, Pb, Zn) were extracted via complete dissolution of sediments with an acid mixture of HNO_3-$HClO_4$-HF after four evaporation steps in Teflon beakers on a hotplate at temperature above 80°C (ISO-14869-1:2000). The extraction for Hg and Cd was performed with concentrated HNO_3 acid digestion in closed Teflon beakers for at least 8 hours on a hot plate (70-80 °C). The metal concentrations were measured by Atomic Absorption Spectroscopy (AAS) techniques (Flame AAS for Cu, Pb and Zn, Graphite Furnace AAS for Cd and Hydride Generation AAS for Hg). Quality assurance of measurements included duplicate digestion / analysis of a few selected sediment samples and digestion /analysis of reference materials with each batch of unknown samples. The repeatabilities from the duplicate analyses ranged from below 1 to 6 (% relative standard deviation) and the recoveries for the reference materials ranged between 90-110%.

3. Results and Discussion

The metal contents in the surface and the deeper layer of each core are presented in Table 1. The evaluation of sediment quality is based on the quality guidelines (SQG) of "effects range low" (ERL) and "effects range median" (ERM). Metal concentrations below the ERL value indicate that effects on biota are rare. Concentrations between the ERL and ERM and above the ERM are reported to occasionally and frequently affect biota. The ERL limits for Cd, Cu, Hg, Pb and Zn are 1.2, 34, 0.150, 46.7 and 150 mg/kg respectively. The ERM limits for these metals are 9.6, 270, 0.710, 218 and 410 mg/kg (Long et al., 1995).

The sedimentation rates have been reported at 0.11 – 0.13cm/yr in Elefsis (S1) and 0.08 cm/yr or lower the rest of Saronikos (Karageorgis et al. 2020, Prifti et al., 2021). Therefore, the sediment layers below 15-20 cm can be considered as pre-industrial (before the 1900's).

The highest surface sediment concentrations for all metals, except Cd, are measured in station S1 (Elefsis bay). The sediments at this location are affected by multiple anthropogenic activities i.e., the extended industrial zone and densely populated areas of Athens.

The highest Cd concentration in station S7, which is 3 to 15-fold above the levels in sediments of other stations, is caused by the outfall of the Athens WWTP. All other metals also present high concentrations in station S7. In the surface sediments of stations S1 and S7 Hg content exceeded the ERM quality limit while Cu, Pb and Zn exceeded the ERL limit. Cd concentrations did not exceed the sediment quality limits ERL and ERM in any of the stations but in S7 the Cd content of 0.981mg/kg is very close to the ERL limit of 1.2mg/kg. In stations UN6, N2, S21 and UN12A Pb concentrations also slightly exceeded the ERL limit.

As a general trend in the deeper sediment layers the lowest Cd Cu, Pb and Zn values are found in stations S1, S13, S11 and S22 and the highest in stations S8, S21, N2, UN12A, MOT16A and UN6. This can be attributed to the different granulometric composition. The sediments of the former stations are coarse-grained with grain size ratios ranging from equal fractions of sand and mud in S1 to dominant sand fractions (60-80% at S11 and S22 and 100% sandy material at S13, while the sediments of the latter stations are finer with mud content above 90%. Thus, in consistency to the theory on trace metal affinity (Salomons and Forstner, 1984) the finer deep layer sediments of the study area generally contain higher levels of metals. However some exceptions, i.e. Cd and Zn in S22, Zn in S1 and Pb in S11 could be attributed to the facts that at S11 and S22 the deep horizons are more recent, S1 core layers contain a significant amount of finer muddy material and S1 is closer to the shoreline affected by anthropogenic activities even in pre-industrial times.

The pre-industrial levels of Hg were very low in most of the cores (0.019-0.033mg/kg) consistent with reported background values for average rocks and sediments (Wedepohl, 1995). The median pre-industrial Hg contents (mg/kg) of S11 (0.039), S8 (0.056), S13 (0.056) were slightly elevated and the highest pre-industrial levels of Hg are found in station S1 inside Elefsis bay (0.211mg/kg). These findings cannot be attributed to grain size effects since the cores in question, except S8, contain coarser particles. The reason for elevated deep layer levels of Hg in these stations may be the proximity to shore where human presence even in pre-industrial times could contribute Hg to the environment i.e. from biomass burning or use of Hg salts as medication (Elbaz-Poulichet et al., 2011).

Table 1. Metal contents in the surface and deeper layers of the analyzed sediment cores (Max value in another layer in parenthesis. Values above the ERL in ***bold italics*** and values above the ERM in **bold** writing. S7 surface sample only.)

Station / Area / Depth	Layer	Hg (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
S1 / Elefsis / 20m	(0-0,5cm)	**1.73**	0.300 (0.650)	***133 (138)***	***157 (181)***	***399 (435)***
	(31-35cm)	**0.196**	0.0	16.6	14.4	74.3
S7 / East -Inner / 70m	(0-1cm)	**0.888**	0.981	***107***	***102***	***251***
S8 / East -Inner / 90m	(0-1cm)	**0.199 (0.226)**	0.156 (0.160)	26.7 (33.4)	40.3 (49.6)	83.1 (99.4)
	(24-26cm)	0.034	0.134	22.0	36.9	74.8
S11 / East -Inner / 77m	(0-1cm)	**0.168 (0.226)**	0.051 (0.069)	18.0 (18.4)	42.7 (47.0)	36.8 (42.3)
	(16-17cm)	0.039	0.041	9.3	27.4	18.8
S13 / East / 87m	(0-1cm)	***0.111***	0.057	13.2 (14.3)	33.9	39.1 (42.2)
	(18-20cm)	0.034	0.052 (0.069)	10.7	18.8	19.2
MOT16A / West / 100m	(0-1cm)	0.044	0.137	22.6 (22.9)	20.4 (25.7)	48.3
	(30-32cm)	0.024	0.131	22.1	28.1	44.1
UN6 / West / 200m	(0-1cm)	0.082 (0.084)	0.102 (0.128)	***36.7***	***52.9***	92.1
	(24-26cm)	0.033	0.091	28.5	32.5	62.4
N2 / Outer / 180m	(0-1cm)	0.050 (0.056)	0.207 (0.332)	26.3	***61.1***	114 (127)
	(22-24cm)	0.034	0.163	20.1	2.3	61.4
S21 /Outer / 220m	(0-1cm)	0.057	0.255 (0.346)	30.7 (31.6)	***64.1 (78.1)***	140 (151)
	(38-39cm)	0.033	0.140	23.1	30.3	85.3
S22 / Outer / 193m	(0-1cm)	0.026	0.154	14.6 (14.8)	38.7 (44.9)	49.0
	(12-13cm)	0.019	0.112	11.4	15.2	27.7
UN12A / Outer / 216m	(0-1cm)	0.058	0.150	29.3 (30.3)	***57.5 (61.7)***	106
	(28-30cm)	0.031	0.139	29.1	***60.2***	93.2

The comparison between upper layers, excluding the heavily polluted stations S1 and S7, reveals some exceptions to the rule of higher metal contents in finer sediments. Especially in the case of Hg and Pb, some coarser surface sediments (S11, S13, S22) contain elevated levels which can be attributed to the proximity to pollution sources or to geological factors Another observation is that among fine-grained sediments for Cd, Cu, Pb and Zn the highest values are found in the stations farthest from the shore, while in the case of Hg in station S8 in East Saronikos closer to Attiki. This may indicate differences in sources, routes and rates during metal transport and deposition to the sediments.

Regarding the vertical distribution of metals in the sediment cores there are differences between stations and metals. The Hg profiles are similar in all stations with lower concentrations in the deeper layers and clear increase in the upper layers depicting anthropogenic polluting activities. In most stations the peak Hg concentration is found at the top layers (0-2cm) but in station S8 (Figure 2a) at 4-5cm depth stabilizing to slightly lower levels above. In the most affected stations the Hg increase in the surface layers is 5 to 10-fold while in the stations farthest from shore the increase is only 2-fold. The continuing increase of Hg in the surface layers of sediments could be mainly attributed to fossil fuel combustion (Elbaz-Poulichet et al., 2011).

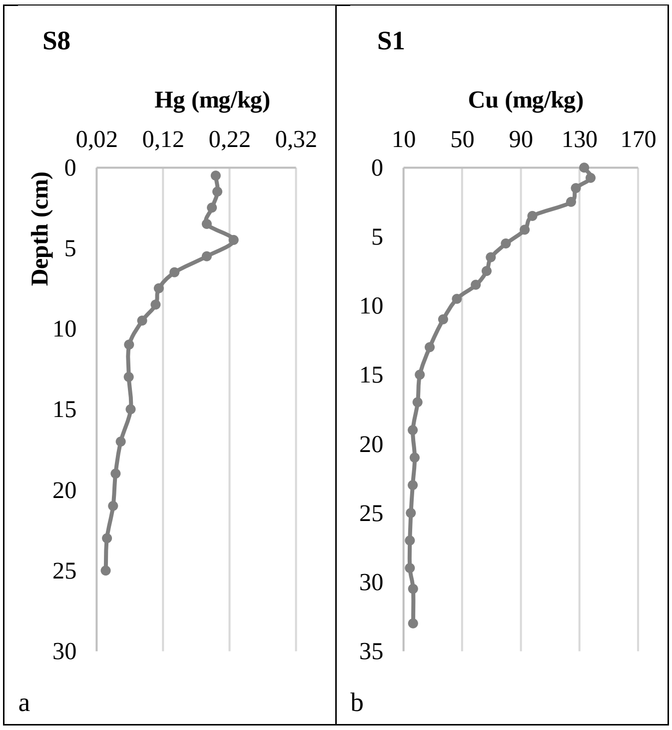

Figure 2. Selected vertical profiles of metal concentrations in Elefsis and Saronikos sediment cores

The other anthropogenic metals present 3 types of vertical profiles. In some of the cores the metal contents present constant increase towards the surface with maximum levels at the top layers 0-2cm. For example Cu in S1 (Figure 2b). In other cases, the deeper layers of sediment present lower values, there is a peak concentration at an an intermediate depth and at the upper layers there is stabilization to lower concentrations but not to pre-industrial levels (similar profiles to Hg in Figure 2a). The metal concentration peaks are found between 8 and 3cm ranging between stations. Taking into account the sedimentation rates mentioned above the peak concnetrations generally correspond to the era of maximum industrial activity in Attiki. Finally, in some cases the concentration variation throughout the core is minimal and there is no pronounced decreasing or increasing trend.

4. Conclusions

This paper presents some preliminary findings arising from the study of sediment cores collected from Elefsis bay and Saronikos gulf in 2017. Vertical profiles of Hg and Cd in sediment cores have not been presented before. It is clear that the sediments of Elefsis are the most heavily impacted due to anthropogenic activities in the greater area of Athens and Attiki. In some of the cores there are signs of recovery with decreasing concentrations in the upper layers due to limitation of industrial activities or application of Best Available Techniques in production and anti-pollution procedures. However, in other cases, such as the most toxic metal Hg there are continuing increasing trends to levels considered harmful to benthic biota.

This dataset is to be expanded with evaluation of other metals in the studied cores, such as Ni, Cr, Fe and Al. Furthermore, there are pending analyses to three additional cores, in Elefsis bay and Inner Saronikos near pollution sources. In the West area of Saronikos more cores have been analyzed and the findings have already been published (Filippi et al., 2023). Thus, an extended review and presentation of the full dataset of Saronikos sediments is under preparation and will allow for a more detailed presentation of the spatial distribution and temporal evolution of metals in this marine area.

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