SPATIAL AND TEMPORAL MONITORING OF HEAVY METALS IN THE SEAWATER OF PALEOCHORA, CHANIA- CRETE (GREECE).

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ABSTRACT

The concentrations of Cu, Ni, Zn, Fe, Mn, Cr, Pb and Cd were monitored in the Paleochora sea from June 2007 through August 2008, at sixteen coastal sampling sites. Heavy metals were determined by using graphite furnace Atomic Absorption Spectrometry. The concentrations of the studied metals were low indicating negligible heavy metal pollution according to the literature review.Spatial and temporal variations of heavy metal concentrations were observed, maybe due to human activities. Lead and cadmium were measured below detection limits. Also, there were no significant variations in the concentrations of the studied metals in the seawater column (sea surface layer and bottom water). The relative abundance of the heavy metals in the seawater followed the order: Fe>Zn> Cu> Ni> Cr>Mn>Pb> Cd.

Keywords
Seawater; heavy metals; pollution; Paleochora.

1. INTRODUCTION

Heavy metals in the costal environmentsare among the most common pollutants andtheirpresence is due to natural occurrence or as a result of anthropogenic activities including riverine or atmospheric inputs, coastal and seafloor erosion, biological activities, water drainage, agricultural runoffs and discharge of urban and industrial wastewaters (Perez-Lopez et al, 2003;Christophoridiset al, 2009). Metals, such as Cd, Ni, Cr, Pb and Hg are toxic in aquatic organisms mainly because of the oxidative potential whereas other metals, such as Fe, Zn, Cu, Se and Mn are essential for their metabolism but become toxic when their concentrations are excessive (Vlahogianniet al, 2007).Heavy metals can affect the ecosystems through bioaccumulation and biomagnification processes and they can represent a threat to marine life and to humansthrough seafood consumption (AydinOnenet al, 2011;Wang et al, 2010).

There are many researches, around the world, concerning the occurrence and distribution of heavy metals in the coastal, bay and sea environments, but the most of them were focused on heavy metals in the sediments and only a few on heavy metals in the seawater, due to the smaller variations in sediments than in the water phase (Dai et al, 2009). The aim of this study was to evaluate the spatial and temporal the distribution of selected heavy metals in the coastal area of Paleochora.

2. MATERIALS AND METHODS

2.1 Study Area

Paleochora is located 77 km south of Chania, at the southwest coastline of Crete– Greece (figure 1). It’s built on a small peninsula of 400m width and 700m length which divides the coastal zone bordering the Libyan Sea into two parts, the eastern and the western part.The population of Paleochora is about 2500. The main human activities in the area are the agriculture, the tourism, especially in the summer period and the fishery. The most common cultivations in the broader area are olive trees, vineyards and vegetables. Also, in the coastal zone there are many greenhouses. At the edge of peninsula there is a small harbourand next to the harbour, the municipal sewage pipe is submerged on the sea bottom and the untreated sewage is discharged to the sea.In addition, the sea receives inputs from three streams which they flow mainly during the winter period.

2.2 Sampling and Analysis

Water samples were collected at 16 sampling sites selected all along the coastal areaof Paleochora(figure 1). The sampling sites were chosen according to potential metal contamination sites (greenhouses, estuaries, harbour, residential area and sewage pipe).The sampling sites can be separated in two groups. The first group consists of 10 sampling sites next to the coastal line (0.5 m depth from the water surface) and the second group consists of 6 sampling sites along the coastal line at a depth of 10m. In the first group, water samples were collected from the sea surface in an acid-cleaned polyethylene bucket. In the second group, water samples were collected from the sea surface and 10m depth along the contour of 10m using an acid-cleaned polyethylene bucket and a Niskin sampler respectively. The water samples were placed in 2 l acid-cleaned polypropylene bottles, and they were transportedin a portable refrigerator, to the laboratory at ± 4 °C. Eight sampling campaigns were carried out in each site of the first group and six of the second group, during June 2007 to August 2008. In all sampling campaigns the sea was calm (no wavy).

The water samples, without filtration, acidified to pH<2 with high-purity nitric acid. Total metals in water samples were determined according to U.S.EPA Method 200.12 (Creed and Martin, 1997). 100ml of a water sample were placed in a beaker and were added 2ml of 50% concentrated high-purity nitric acid. The samples were heated gently for about 2h at 85^o Cuntil reduction to the sample volume at about 20ml. Then the samples were transferred quantitatively to a 100-mL volumetric

flask and were diluted to volume with reagent water. The concentrations of the metals were measured by graphite furnace Atomic Absorption Spectrometry (Perkin Elmer, AAnalyst 700).All water samples were treated in duplicate.The relative standard deviations (RSD) of the method and each run were <5%. The detection limits of the method were determined for Cu: 1.2 μg/l, for Ni: 1.5μg/l, for Pb: 2μg/l, for Fe: 5μg/l, for Cr: 0.115μg/l, for Mn: 1μg/l, for Cd: 0.009μg/l and for Zn: 3.5μg/l.
The spatial distribution of the studied metals in the coastal area of Paleochora is visualized on maps produced by ARC GIS V9.2 software.

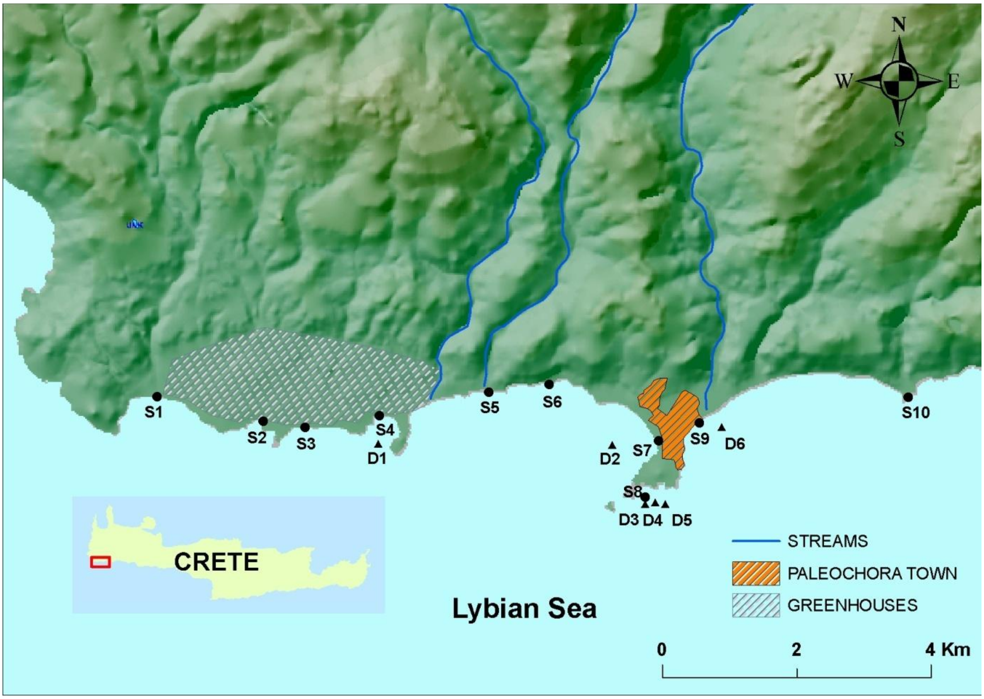

Figure 1. Map of coastal area of Paleochora with sampling sites. Cycles: sampling sites from the first group; Triangles: sampling sites from the second group.

3. RESULTS AND DISCUSSION

3.1 Source attribution and spatial distribution of heavy metals

As already mentioned, the selected sampling sites along the coast are close to human activities and to the estuaries of the three streams, where possibly,sewages and olive mill waste waters from the surround villages,have been discharged.In particular, the sampling sites S1, S2, S3, S4, and D1 are close to greenhouses, the sampling site S5 in the estuary of Pelekaniotis' stream, the sampling site S6 next to hotels and the sampling sites S7, D2, S9 and D6 are close to the small town of Paleochora. Also, there are many touristic units in the residential area and the estuary of Kakodikianos' stream. The sampling site S8 is located inside the harbour and the sampling sites D3, D4 and D5 next to the sewage pipe. In the sampling site S10 there are no human activities.

The studied heavy metal concentrations in theseawater of the coastal area of Paleochora are given in Table 1. The concentrationsof the heavy metals which are shown in Table 1have been arisen from the average of all the measurements (all the dates which were carried out sampling campaigns) in each sampling site. For the calculation of the average concentration in the sampling sites the values which were below detection limits were considered as zero. The symbolnd is used only in the case which all the measurements (all the dates which were carried out sampling campaigns) in a sampling site werebelow detection limits.

TABLE 1. Average metal concentrations (μg/ l) in seawater of the studied area

Element	Range	Mean	Median
Cu	nd – 3.80	1.28	0.93
Ni	nd– 3.07	0.91	0.73
Pb	nd- 0.43	0.03	nd
Fe	5.70- 15.39	9.67	9.05
Cr	0.15 – 0.72	0.46	0.34
Mn	0.13 – 0.66	0.45	0.33
Cd	nd	nd	nd
Zn	3.57 – 21.42	8.06	6.67

nd: below detection limit

Table 2 summarizes the metal concentrations in seawater from other coastal areas of Greece and from Mediterranean sea. In the same table reported data for unpolluted seawater. The studied heavy metal concentrations were found lower in comparison to the reported literature data for unpolluted seawater, with the exception of chromium,which seems to have a higher value, but much lower than the coastal areas of Thessaloniki and Aegean respectively. According to the literature review, the seawater of the coastal area of Paleochora can be considered unpolluted of heavy metals.
The mean metal concentrations in seawater of the coastal area of Paleochora decreased in the following order: Fe> Zn> Cu> Ni> Cr>Mn>Pb> Cd. Similar relative abundance of heavy metals was observed in the seawater of an Aegean coastal area and followed the order: Fe > Zn >Pb> Cu > Cr > Cd, except of Pb which was higher than Cu and Cr (Akcali and Kucuksezgin, 2011). In another study which also concerns an Aegean coast, the metal concentrations in seawater decreased in the order: Fe > Zn >Mn> Cu >Pb> Cr > Cd (AydinOnenet al, 2011). Iron and zinc seems to be the most abundant metals and cadmium the less abundant in Mediterranean sea.

The spatial distribution of the average concentrations of the studied metals in the sampling sites of the coastal area of Paleochora are shown in the following maps (Figure 2a, b respectively). The highest concentrations of heavy metals were found in the proximity of the residential area, the sewage pipe and the greenhouses, indicating anthropogenic origin. The lowest heavy metal concentrations were observed in the sampling site S10 (named Gialiskari or Anydroi) where there are no human activities. Lead and cadmium were measured below detection limits in all sampling sites with the exception of lead which, in sampling site S9, was found only once 3.44 μg/l (on 7/15/20008).

TABLE 2. Heavy metal concentrations (μg/ l) in various coastal areas of Mediterranean sea

	Cu	Ni	Pb	Fe	Cr	Mn	Cd	Zn
ThermaikosGulf[a]	1.18-2.08	0.5-1.2	3.5-20.0	-	-	4.1-7.0	0.16-0.47	13.4-17.2
KavalaGulf[a]	0.7-1.22	0.5-1.5	5.5-20.5	-	-	6.5-7.3	0.33-0.52	18.8-23
Thessaloniki bay [b]	0.8-5.5 (3.2)	-	12.3-24.4 (17.5)	-	0.4-5.4 (2.1)	-	-	16.5-75.9 (40.0)
Anavissos Bay[c]	1.08–7.26 (3.13)	0.60–3.63 (1.31)	1.45–10.49 (4.71)	-	-	0.16–8.02 (3.75)	0.08–0.59 (0.32)	1.96–8.45 (4.23)

Eastern Aegean coast Turkey [d]	0.83-4.9	-	1.1-1.8	6.9-21.5	0.77-1.2	1.4-4.5	0.17-0.24	3.7-8.5
Unpolluted seawater[e]	3	0.7-7	0.03	-	-	-	0.11	10.00
Unpolluted coastal area Sicily-Italy [f]	1.6	-	1.77	-	0.16	-	0.24	7.20

a:Fytianos and Vasilikiotis, 1983; b:Christophoridis et al, 2009; c:Ladakis et al, 2007; d: Aydin Onen et al, 2011 e: Campanella et al, 2001; f: Roth and Hornung, 1977 . The numbers in parenthesis are the mean concentrations.

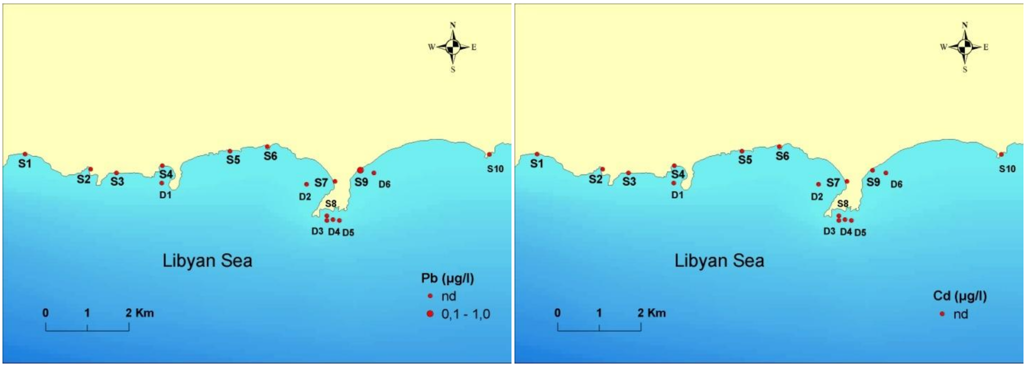

Figure 2a. Spatial distribution of Pb and Cd in the seawater of the coastal area of Paleochora.

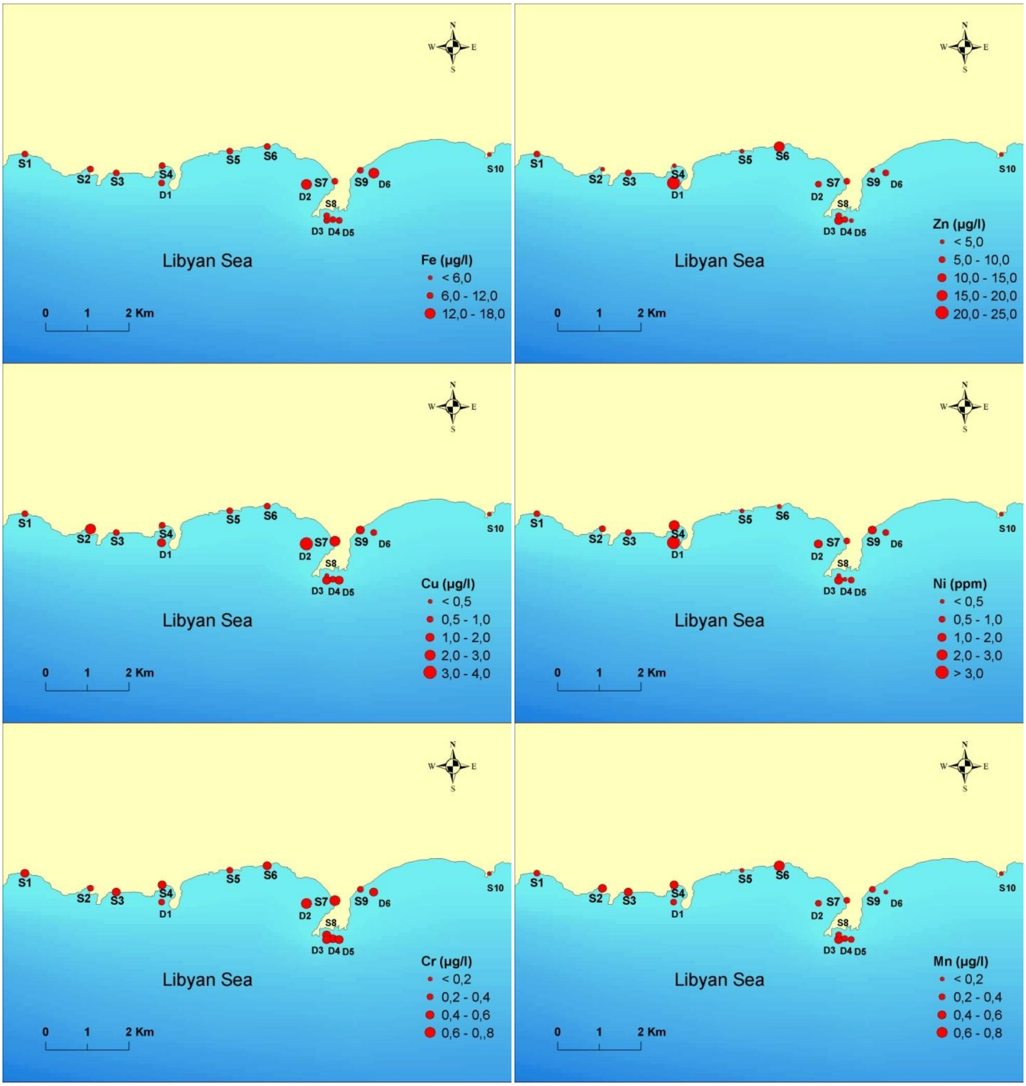

Figure 2b. Spatial distribution of Fe, Zn, Cu, Ni, Cr and Mn, in the seawater of the coastal area of Paleochora.

3.2 Temporal monitoring of heavy metals

In order to evaluate the temporal variations of the heavy metals in the seawater of Paleochora, the seawater samplings were separated in two periods, in the dry and in the wet period. The dry period consisted of sampling campaigns which were carried out from May to October and the wet period from November to April. In each period there are different physical or human activities where can cause heavy metal pollution in the seawater of the studied area. In the wet period the streams are flowing to the sea due toprecipitationand are cultivated vegetables in the greenhouses. In the dry periodis carried out the leaching of the greenhouse soils and are operated the touristic units and many tourists visit Paleochora for short or long vacations.

Figure 3 shows the temporal variations of the averageheavy metal concentrations in the surface seawater of Paleochora (sampling sites S1-S10) during dry and wet period. In the dry period,the concentrations of the studied metals were higher than in the wet period.The lower concentrations in the wet period is probably due to high rainfall and to reduced quantity of sewage where wasdischarged into the sea. The total rainfall of the studied area for the wet period (from November 2007 to April 2008) was about 600mm and for the dry period was 80mm respectively.Maximum variations were observed in copper and minimum in chromium. Also, lead and cadmium were below detection limits. The low average concentration of Pb is due to the measurement in the sampling site S9 on 7/15/2008 which as it was mentioned was found 3.44μg/l.On the other hand, Srinivasa Reddy et al, (2005) found the highest concentrations of heavy metals in the winter period.

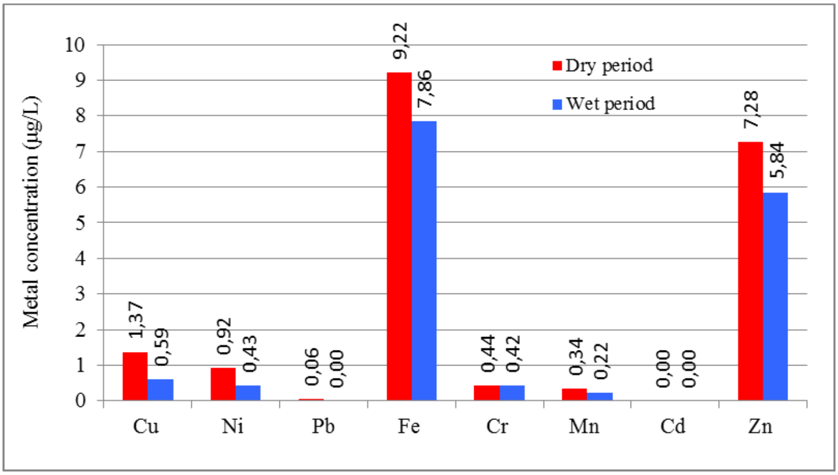

Figure 3. Metal concentrations (μg/l) in the surface seawater of the coastal area of Paleochora between dry and wet period.(The value 0.00 is considered nd).

3.3 Heavy metal concentrations in seawater column

For the investigation of heavy metals in the seawater column, were compared the average metal concentrations in the sea surface and at depth 10m, at the sampling sites D1-D6.Figure 4 shows the variations of theheavy metals between the surface water and thebottom water,along the contour of 10m. There are no significant variations in the heavy metal concentrations between the surface and the bottom seawater. In opposition, Cuong et al (2008), found the highest concentrations of heavy metals in the bottom waters.

4. CONCLUSIONS

This study investigated the spatial and temporal distribution of heavy metals in the seawater of the coastal area of Paleochora – Chania. The seawater of the studied area can be considered uncontaminated of heavy metals, since the metal concentrations were generally low. Especially, lead and cadmium were measured below detection limits. The relative abundance of the heavy metals followed the order Fe> Zn> Cu> Ni> Cr>Mn>Pb> Cd. The highest concentrations of heavy metals were observed close to human activities, such us in the residential area and in greenhouses. Significant variations were found between dry and wet period for the studied metals mainly due to anthropogenic activities. In the dry period were observed higher concentrations. Also, insignificant variations were found in the mean metal concentrations in the seawater column.

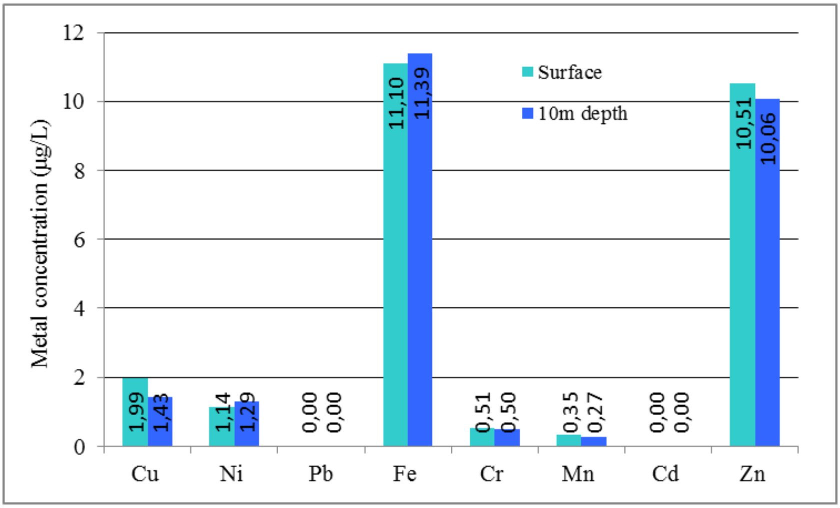

Figure 4.Metal concentrations (µg/l) in the surface and bottom (10m depth) seawater in the coastal area of Paleochora.(The value 0.00 is considered nd).

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