RESEARCH ARTICLE

Ecological risk assessment of heavy metals in the sediments of a Mediterranean lagoon complex

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Abstract

This study examines the heavy metal contamination in the surface sediments of six coastal lagoons in Northern Greece (Nestos River and Vistonikos complexes) in relation to particle size distribution, organic carbon, total phosphorus and total Kjeldahl nitrogen. Furthermore, the contamination degrees and the ecological risks were assessed using different indicators. The study of heavy metals in lagoon's sediments is important in evaluating natural contamination against anthropogenic impact, and consequently, providing knowledge that could lead to management measures to reduce heavy metal environmental risks. Lafri Lagoon is characterized by the highest metal levels in all elements, while Agiasma and Porto Lagos by the lowest. Comparison of metal (As, Cd, Cr, Cu, Mn, Pb, Zn and Ni) levels with Sediment Quality Guidelines showed that As and Cr were found above the toxic effect threshold values. Potential toxicity (RI) seems influenced mostly by As and Cd. CD and PLI values classified the lagoons under study as "very highly contaminated" and "polluted", respectively.

Keywords Heavy metals · Surface sediments · Lagoons · Ecological risk assessment · Grain size distribution · Organic carbon

Introduction

Coastal lagoons are enclosed shallow water basins situated at the lower end of watersheds, receiving drainage from natural streams and/or canals draining adjacent land-based activities, strongly affected by air/sea interactions (winds, precipitation, evaporation, thermal fluxes), having limited exchange to the open sea [1, 2]. Lagoons act as transitional buffer zones for the transfer of freshwater and substances from the terrestrial to the coastal zones. They are mostly formed in river deltaic zones, where prominent longshore sediment transport favors the development of depositional sand bars, acting as barriers separating their basins from the open sea. In the microtidal Mediterranean environments (tidal range < 0.5 m), usually a single narrow inlet allows the water exchange, leading to poor tidal circulation and slow water renewal in the basin [3]. These characteristics portray the lagoon systems as highly productive and extremely vulnerable to nutrients overloading, functioning in fragile equilibrium to the entry of wastewaters and agricultural residues, the storage of substances at their sediments and the benthic-to-water column release of nutrients and metals, known as internal loading [4]. Lagoons' productivity in the water column and sediments is expressed by the high diversity of planktonic species and species in phyto-, meio- and zoo-benthos, negatively related to their basin confinement and circulation patterns [5]. Ecosystem degradation is related to the regular phytoplankton and macroalgal blooms, the presence and expansion of opportunistic species with high-ecological tolerance to nutrients and organically-enriched environments, the prevalence of anoxic events and the consequent reduction in system's diversity [6].

In parallel, most Mediterranean lagoons are exploited by local cooperatives for the fishery production of euryhaline fishes as Mugilidae: *Liza saliens*, *Liza aurata*, *Mugil cephalus*, Moronidae: *Dicentrarchus labrax*, Sparidae: *Sparus aurata*, Anguillidae: *Anguilla anguilla* through the construction of barrier traps at their inlets. The presence of substances as organic carbon, nitrogen and phosphorus compounds and heavy metals accumulated at the sediments of lagoons may affect the food web of these fishes and cause significant public health concerns. The analysis of spatial

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distribution of pollutants in sediments are useful to recognize the long-term degradation processes of lagoons, associate pollutants to sources and lead to better environmental management [7]. This is particularly important since the toxicity of trace metals is not directly linked to concentration. Although some trace metals (Zn, Fe, Cu, Mg and Mn) are considered as micronutrients, exceedance of certain levels makes them toxic for organisms, fish and humans. Other metals as Pb, Hg and Cd are highly toxic even at trace amounts. Trace metals evaluation of their contamination and risks in sediments should consider the assessment of natural versus anthropogenic contamination [8] and the induced ecological risks [9] following geochemical normalizations and the Sediment Quality Guidelines [10, 11].

Sixteen coastal lagoons situated at the deltaic zones of the Evros, Nestos and Strymon Rivers and in the Vistonikos Gulf, Northeastern Greece, formulate four wetland complexes protected by the Ramsar Treaty [12]. The systems receive limited freshwater inflows, enriched with residues from agriculture and livestock activities carried out at the adjacent deltaic plains. Six lagoons of the Nestos and Vistonikos complexes are at the center of attention of the present work: Eratino, Agiasma, Lafri, Porto Lagos, Xirolimni and Ptelea, all included in the EU Natura 2000 network. The main objectives of this study are (a) the determination of a broad range of heavy metals contamination (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Pb, Rb, Sr, V, U, Zn, Ni, Fe, B, Ge, Mo, Re, Ti, W, Zr) in the surface sediments at various sites of these six lagoons; (b) the interrelation of metals content to granulometry and concentrations in organic carbon (OC in %), total phosphorus (TP) and total Kjeldahl nitrogen (TKN) levels in sediments; (c) the assessment of the anthropogenic impact of these metals in the lagoon ecosystem; and (d) the discussion on the potential pollution sources and cycling, focusing on lagoon hydrodynamics and ecological safety. The obtained information may provide a better understanding on the management measures needed to minimize environmental risks of heavy metals contamination in sediments.

Materials and methods

Study area description

The present study examines the trace metals contamination in sediments, together with the associated ecological risks, at six fishery-exploited lagoons located in Northern Greece (Fig. 1). Eratino and Agiasma lagoons belong to the Nestos River complex. Eratino Lagoon covers approximately 3.9 km^2, with a length of about 5.9 km, a mean width of 0.7 km (maximum width of 1.5 km) and a perimeter of 32 km. The mean depth of the lagoon is 1.1 m and the maximum depth

is 4.5 m. The lagoon is connected to the open sea (Kavala Gulf) with an inlet channel approximately 30 m wide and 0.7 m deep [3]. Eratino receives freshwater by a natural, shallow, 2 km long channel in the northern part of the basin and agricultural runoff by direct drainage [2]. The system communicates with the adjacent Vassova lagoon through a narrow, shallow channel [3]. Agiasma is a shallow lagoon with a mean depth of 1 m, covering an area of 4.4 km^2, with a length of about 7 km, a mean width of 0.8 km and a perimeter of 18.3 km. It has two narrow outlets to the sea. The outlet in the middle of the basin remains open only during stocking, from mid-February to May, while the outlet in the southern part of the lagoon is always open. Agiasma is considered to be one of the less affected lagoons in the Nestos Delta complex [13].

Lafri is a small, shallow lagoon covering 2.0 km^2 located at the western part of Vistonikos Gulf. It has a mean depth of 0.4 m and it is connected to the Vistonikos Gulf with a northwest directed long channel. Porto Lagos is a shallow coastal lagoon, with an average depth of about 1 m and covers an area of 1.6 km^2. It is connected upstream to Vistonis Lake through two artificial channels and to Vistonikos Gulf through a canal of 170 m wide and 400 m long. Xirolimni lagoon is a shallow lagoon with an average depth of 0.6 m covering an area of 2.3 km^2. It has a narrow connection to the sea through a canal of 240 m long. Xirolimni receives fresh water from precipitation and direct runoff. Ptelea is a shallow system with an area of 3.6 km^2. It communicates with Elos lagoon through an inland canal and to the Thracian Sea through a narrow inlet.

The geometric and hydrologic parameters of these six lagoons are summarized in Table 1. All six lagoons are surrounded by farmlands (mostly cotton, maize, alfalfa), thus receiving agricultural runoff especially during flash flood events (Fig. 1). Lagoons are forced by similar tidal influence at their mouths (spring tidal range 0.4 m and neap tidal range 0.2 m) and they belong to the same Koppen climatic zone (Csb, warm summer Mediterranean climate). Mean annual precipitation is approximately 320 mm, ranging between 420 and 430 mm and air temperature between − 5 to 38 °C with annual mean temperature of 15 °C. In North Aegean Sea, winds blowing from the north and northeast dominate, while south-southwestern winds prevail in spring and summer.

Sample collection and analysis

Collection of samples

Sediment samples were collected from 21 stations positioned in each of the six lagoons (Fig. 1), mostly at the entrance and the wintering canals, from July to November 2014 using a stainless-steel corer. The samples were placed in plastic bags (previously cleansed in a 1 N nitric acid bath for 1 h
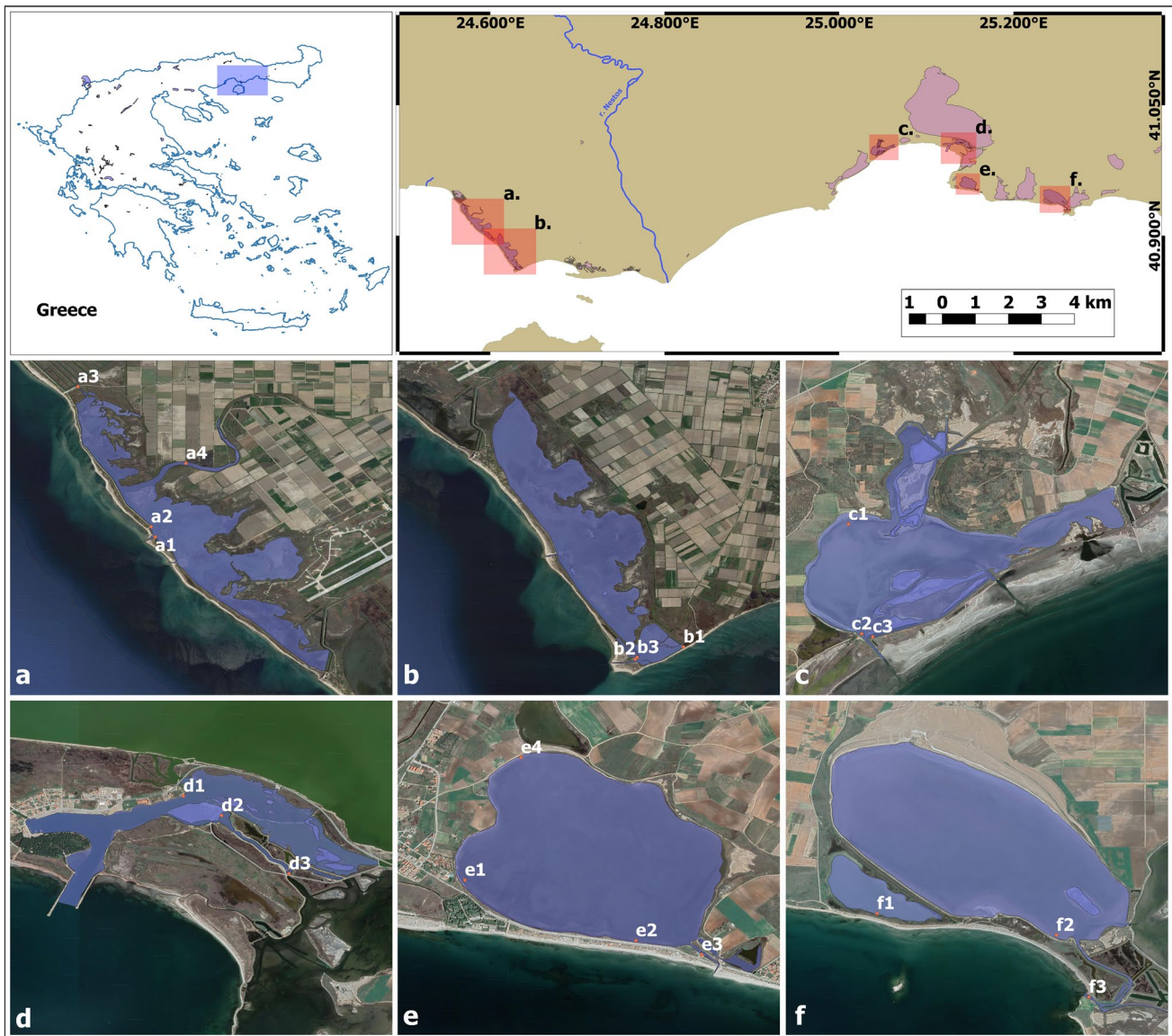
Fig. 1 The sampling stations at the six lagoons under study, where **a** Eratino, **b** Agiasma, **c** Lafri, **d** Porto Lagos, **e** Xirolimni and **f** Ptelea

Table 1 Geometric and hydrologic characteristics for the six lagoons

Lagoon	Latitude	Longtitude	A (km^2)	h (m)	V (km^3)
Eratino	40°54′57″ N	24°35′10″ E	3.9	1.1	0.0043
Agiasma	40°52′48″ N	24°37′16″ E	4.4	1.0	0.0044
Lafri	40°59′53″ N	25°02′31″ E	2.0	0.4	0.0008
Porto Lagos	41°00′29″ N	25°08′33″ E	1.6	1.0	0.0016
Xirolimni	40°57′34″ N	25°08′53″ E	2.3	0.6	0.0014
Ptelea	40°56′40″ N	25°14′45″ E	3.6	0.8	0.0029

where *A* lagoon surface area, *h* mean lagoon water depth, *V* lagoon water volume

and rinsed thoroughly with d.d. water) and kept and transported on ice to the laboratory. In the laboratory samples were air dried at room temperature (25 °C), sieved through a 1 mm sieve and then stored in polyethylene bags for further analysis.

Sediment grain size

Samples were sieved through nine standard sieves (2, 1, 0.85, 0.71, 0.60, 0,50, 0.25, 0.20, 0.15 mm) and sediment grain-size distribution per sample was determined. Statistical parameters were obtained from each distribution curve, as the diameter (expressed as D in mm or $\phi = -\log_2 D$) and the respective diameters corresponding to 5, 16, 25, 50, 75,

84 and 95 percentages were estimated. Then, the mean grain size M_ϕ as:

$$M_\phi = \frac{\phi_{16} + \phi_{50} + \phi_{84}}{3} \qquad (1)$$

the standard deviation as:

$$\sigma_\phi = \frac{\phi_{84} - \phi_{16}}{2} \qquad (2)$$

the skewness as:

$$a_\phi = \frac{M_\phi - \Phi_{50}}{\sigma_\phi} \qquad (3)$$

and the kurtosis as:

$$K = \frac{\phi_{95} - \phi_5}{2.44(\phi_{75} - \phi_{25})} \qquad (4)$$

were assessed. Grain-size distribution was defined according to sieving results, further tested using the Bouyoucos soil hydrometer to determine the sand, silt and clay percentage per sample.

Chemical analysis

The elemental concentration of metals in sediments: Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Li, Mn, Pb, Rb, Sr, V, U, Zn, Ni, Fe, B, Ge, Mo, Re, Ti, W, Zr and the content in total phosphorus (TP), total Kjeldahl nitrogen (TKN) and organic carbon (OC) were determined at the sediment fraction with diameter lower than 1 mm.

The elemental concentration in the collected samples was determined using Inductively Plasma-Mass Spectrometry (ICP-MS). A quantity of each sediment sample was digested using a mixture of acids (HNO_3, HCl, H_2O_2). Specifically, 3 g of dry sediment sample was transferred to a 250 ml volumetric block digestion tube. At first 10 ml 1:1 HNO_3 were added and heated for 15 min at 95 °C, then 5 ml of concentrated HNO_3 were added and heated for 30 min at 95 °C. Then, 3 ml of concentrated HCL were added and heated for 1 h. The digestion block is let to cool to 80 °C, then 3 ml of 30% H_2O_2 is added and heated for 15 min at 95 °C. After cooling at room temperature, the samples were filtered and diluted up to 100 ml. Two blank samples were pretreated in the same way as the samples.

TP in sediment samples was estimated by digestion with H_2SO_4 in the presence of $K_2S_2O_8$ (persulfate digestion method) and was determined colorimetrically using the Stannous Chloride Method (4500-P D). TKN was determined by the Kjeldahl method. An amount of 1–2 g sample was weighed and placed in a 500 mL Kjeldahl flask and then 50 mL of digestion reagent (H_2SO_4,

K_2SO_4, $CuSO_4$, H_2O) was added. The mixture was then digested at 170 °C for 1 h, at 230 °C for 30 min, at 280 °C for 1 h and at 380 °C for 45 min. The digest turned pale green. The digested samples were cooled, and 25 ml H_2O and 50 ml sodium hydroxide-thiosulfate reagent were added. TKN was determined by steam distillation and direct titration with H_2SO_4 0.01 N, using boric acid as an indicator for titrimetric finish. OC content in the sediment samples was determined by the wet oxidation method, according to the procedure described by El Wakeel, Riley [14].

Metals quality assurance

Pretreated sediment samples were analyzed in triplicates, in order to determine the Relative Standard Deviation (RSD). Three blank samples were run in the same way as the samples and the concentrations were determined using standard solutions. The mean RSD of the replicate samples was less than 10% of the mean concentration for all the metals, except for Be (15.6%), Ge (14.1%) and Re (14.6%) (Table 2). The high RSD for Be, Ge and Re is attributed to their low concentration in combination to the dilution in pretreated samples prior to the ICP-MS analysis. Analytical quality control was achieved using certified reference material for marine sediment (BCSS-1, National Research Council of Canada). The recoveries percentage for most metals ranged between 80 and 101%, with the exception of Al and Ba, Cu, Mo and U having recoveries below 80%.

Table 2 Mean relative standard deviation of the mean concentration in the studied heavy metals

Analyte	Mean RSD (%)	Analyte	Mean RSD (%)
Ag	5.7	Rb	2.6
Al	1.7	Sr	2.0
As	2.9	V	3.2
Ba	2.0	U	7.3
Be	15.6	Zn	4.3
Bi	5.7	Ni	9.0
Cd	9.8	Fe	2.8
Co	2.6	B	7.4
Cr	3.5	Ge	14.1
Cs	2.9	Mo	4.1
Cu	8.0	Re	14.6
Ga	3.0	Ti	3.8
Li	5.8	W	9.7
Mn	2.2	Zr	3.3
Pb	2.6		

Statistical analysis

Pearson correlation coefficients were calculated in order to interrelate the heavy metal concentration in sediments with the grain size characteristics and the concentrations of TP, TKN and OC.

Sediment contamination assessment

The trace metal variability of sediments may be natural or influenced to some degree by anthropogenic sources. The determination of the degree of contamination in a trace metal requires an unpolluted reference material (geochemical background).

Contamination factor (CF) and contamination degree (CD)

CF evaluates the enrichment in metals in relation to the background concentrations of each metal in sediments. CF is the ratio of each metal concentration in the sediment sample to the background value [9, 15].

$$CF = \frac{C_{Metal}}{C_{Background}} \tag{5}$$

where, C_{Metal} is the concentration of each metal in the sediment sample, and $C_{Background}$ is the uncontaminated background level of the metal, as reported by Wedepohl [16] and Rudnick, Gao [17]. While CF is calculated for individual elements, CD provides an overall assessment in the sediment contamination of the study sites. CD is expressed as:

$$CD = \sum_{i}^{n} CF \tag{6}$$

The classification of sediment samples based on the CF and CD is shown in Table 3.

Pollution load index (PLI)

PLI provides an overall assessment on the level of heavy metal contamination. PLI was determined using the following formula:

$$PLI = \left(CF_1 \times CF_2 \times ... \times CF_n\right)^{1/n} \tag{7}$$

where CF is the contamination factor and n is the number of heavy metals considered. According to Tomlinson et al. [18] a PLI value greater than 1 indicates that the site is polluted, whereas a PLI less or equal to 1 indicates no pollution.

Ecological risk assessment

A potential ecological risk index (RI) was used to assess the degree of heavy metal contamination in sediments, according to the toxicity of heavy metals.

$$Er = Tr_{Metal} \times CF \tag{8}$$

$$RI = \sum_{i=1}^{7} Er \tag{9}$$

where Er is the potential risk factor of a given metal, Tr_{Metal} is the toxic response factor of metals (As = 10, Cd = 30, Cu = Pb = 5; Zn = 1; Cr = Ni = 2) and CF is the contamination factor [9]. The various classes of the risk factors Er and RI are given in Table 4.

Results

Sediment properties

Figure 2 illustrates the ternary diagram for the sediment samples of the six examined lagoons. Sediments from Eratino lagoon appear dominated by sand (76.3–96.7%), followed by silt (2.2–16.9%) (Table 5). Agiasma lagoon exhibited similar pattern with higher composition in sand (84.8–98.1%) and lower composition in silt (1.2–7.3%).

Table 3 Classification for CF and CD

CF value	CD value	Contamination status
<1	<6	Low contamination
1—3	6—12	Moderate contamination
3—6	12—24	Considerable contamination
>6	>24	Very high contamination

Table 4 Description of the risk factors Er and RI

Er value	Contamination status	RI value	Contamination status
<40	Low ecological risk	<150	Low ecological risk
40—80	Moderate ecological risk	150—300	Moderate ecological risk
80—160	Considerable ecological risk	300—600	Considerable ecological risk
160—320	High ecological risk	>600	Very high ecological risk
>320	Very high ecological risk		

Fig. 2 Ternary diagram of particle size (mud, sand, coarse material) of the six lagoons sediments. Eratino lagoon is denoted with black squares, Agiasma lagoon with red circles, Lafri lagoon with blue up triangles, Porto Lagos lagoon with green down triangles, Xirolimni with orange diamonds and Ptelea lagoon with pink pentagons

Station b3 in Agiasma lagoon showed a higher proportion of silt (7.3%) and coarse material (6.4%), compared to the other two stations in the same lagoon. Lafri lagoon showed a lower proportion of sand (42.9–78.7%) with higher gravel (6.2–29.3%) and mud fractions (12.6–36.8%). Porto Lagos lagoon is dominated by sand (65.7–81.3%) and coarse material (14.0–23.1%), with low mud fraction (5.4–11.2%). The same pattern is followed by Xirolimni lagoon with more mud (8.8–24.7%) at the expense of sand (51.7–76.0%). In Ptelea, sand (56.1–71.4%) prevails, followed by mud (21.7–24.2%) and gravel (4.3–22.5%).

Eratino lagoon shows heterogeneity in the sediment composition ranging from very poorly sorted to moderately sorted, slightly gravelly sands and slightly gravelly muddy sands. Skewness varies from positive to very positive and in one of the stations (a3) to very negatively skewed sediments (Table 5). Agiasma lagoon sediments are characterized as slightly gravelly sands, poorly to moderately sorted, with positive skewness, ranging from very platykurtic (b1), platykurtic (b2) and leptokurtic (b3). Sediments in Lafri lagoon are considered as poorly to very poorly sorted gravelly muds and gravelly muddy sands. Skewness ranges from very positively skewed to almost symmetrical, varying from very leptokurtic to leptokurtic. Porto Lagos lagoon sediments are poorly sorted gravelly sands and gravelly muddy sands.

Table 5 Sediment grain size characteristics, sediment type and grain size ratios throughout the six lagoons

Stations	Coarse material	Sand	Silt	Clay	Sediment type	Sorting	Skewness	Kurtosis	D_{90}/D_{10}	D_{75}/D_{25}
a1	0.6	96.7	2.2	0.4	Slightly Gravelly Sand	MS	PS	VP	4.13	2.93
a2	2.5	80.5	14.1	2.8	Slightly Gravelly Muddy Sand	PS	VPS	EL	36.24	1.68
a3	1.8	93.7	3.7	0.7	Slightly Gravelly Sand	MS	VNS	M	4.99	2.32
a4	3.4	76.3	16.9	3.4	Slightly Gravelly Muddy Sand	VPS	VPS	EL	49.24	1.79
b1	0.5	98.1	1.2	0.2	Slightly Gravelly Sand	MS	PS	VP	3.85	2.72
b2	1.9	94.8	2.8	0.6	Slightly Gravelly Sand	MS	PS	P	4.09	2.74
b3	6.4	84.8	7.3	1.5	Gravelly Sand	PS	VPS	VL	6.90	3.05
c1	12.9	42.9	36.8	7.4	Gravelly Mud	VPS	PS	VP	283.67	51.02
c2	7.2	59.1	28.1	5.6	Gravelly Muddy Sand	VPS	VPS	P	122.46	20.52
c3	6.2	78.7	12.6	2.5	Gravelly Muddy Sand	PS	VPS	VL	45.77	3.30
c4	29.3	47.1	19.6	3.9	Gravelly Muddy Sand	VPS	N	M	175.93	13.46
d1	23.1	65.7	9.3	1.9	Gravelly Muddy Sand	PS	VPS	L	46.90	4.29
d2	14.0	81.3	3.9	0.8	Gravelly Sand	PS	VNS	P	12.07	4.01
d3	16.5	79.1	3.7	0.7	Gravelly Sand	PS	NS	P	9.37	3.95
e1	33.3	51.7	12.5	2.5	Muddy Sandy Gravel	VPS	VPS	M	89.94	8.09
e2	15.4	76.0	7.1	1.4	Gravelly Muddy Sand	PS	VNS	VL	13.23	2.83
e3	20.3	58.5	17.6	3.5	Gravelly Muddy Sand	VPS	PS	L	149.84	6.58
e4	18.2	57.1	20.6	4.1	Gravelly Muddy Sand	VPS	PS	L	179.13	7.00
f1	4.3	71.4	20.2	4.0	Slightly Gravelly Muddy Sand	VPS	VPS	EL	47.65	1.78
f2	13.4	64.9	18.1	3.6	Gravelly Muddy Sand	VPS	PS	VL	148.88	3.62
f3	22.5	56.1	17.8	3.6	Gravelly Muddy Sand	VPS	PS	L	153.44	6.82

Where *VWS* very well sorted, *WS* well sorted, *MS* moderately sorted, *PS* poorly sorted, *VPS* very poorly sorted, in sorting; *VNS* very negatively skewed, *NS* negatively skewed, *N* almost normality, *PS* positively skewed, *VPS* very positively skewed, and in kurtosis, *VP* very platykurtic, *P* platykurtic, *M* mesokurtic, *L* leptokurtic, *VL* very leptokurtic, *EL* extremely leptokurtic

The sediment composition shows a large heterogeneity in skewness ranging from very negatively skewed (d2), negatively skewed (d3) and very positively skewed (d1) and vary from platykurtic (d2 and d3) to leptokurtic (d1). Xirolimni shows poorly to very poorly sorted gravelly muddy sands and muddy sandy gravels. Skewness ranges from very negatively to very positively skewed and kurtosis ranges from mesokurtic to very leptokurtic. Ptelea sediments are characterised as very poorly sorted slightly gravelly muddy sands and gravelly muddy sands. Skewness ranges from positive to very positive and kurtosis from leptokurtic to extremely leptokurtic.

Table 6 presents the spatial distribution of organic carbon (%), TKN and TP (mg/g) content in each station of the six lagoons. The OC percentage ranges from 0.1 to 1 in all lagoons of this complex. Local maxima in OC are reported in Ptelea (f3: 2.27%) followed by Eratino (a4: 1.41%) and Lafri (c1: 1.33%). TKN concentration shows the same distribution pattern as OC%. TP values showed a wide variation in spatial scale. The TP concentration ranges from 0.64 to 14.1 mg/g in Eratino, 8.86–33.4 mg/g in Agiasma, 3.75–16.6 mg/g in Lafri, 33.7–48.5 mg/g in Porto Lagos, 5.08–9.66 mg/g in Xirolimni and 2.03–5.59 mg/g in Ptelea. The highest values were found in Porto Lagos lagoon and the lowest values in Ptelea lagoon.

Table 6 Organic carbon (OC), total nitrogen (TKN) and total phosphorus (TP), content in surface sediments from the six lagoons

Station	OC %	TKN (mg/g)	TP (mg/g)
a1	0.21	0.11	0.64
a2	0.21	0.20	12.0
a3	0.10	0.13	5.88
a4	1.41	1.17	14.1
b1	0.08	0.12	33.4
b2	0.08	0.13	8.86
b3	0.14	0.09	22.4
c1	1.33	2.29	4.61
c2	1.24	0.58	2.60
c3	0.22	0.13	16.6
c4	0.57	0.55	3.75
d1	0.50	0.33	33.7
d2	0.24	0.30	40.8
d3	0.25	0.34	48.5
e1	1.35	1.30	5.62
e2	1.04	1.01	5.08
e3	0.41	0.43	7.53
e4	0.62	0.53	9.66
f1	0.47	0.38	4.03
f2	0.58	0.34	2.03
f3	2.27	0.89	5.59

Metals in sediments

The trace metal contents for every station in the six lagoons sediments under study are presented in Table 7. The metal concentration in sediment showed a wide spatial variation. Lafri lagoon is characterised by higher trace metals levels in all elements, while Agiasma and Porto Lagos presented the lowest values.

The highest values for each trace metal were all found in station c1 in Lafri Lagoon (As: 169 µg/g, Cd: 2.20 µg/g, Cr: 572 µg/g, Cu: 198 µg/g, Mn: 7,262 µg/g, Pb: 282 µg/g, Zn: 664 µg/g, Ni: 296 µg/g). Most of the lowest metal levels were measured in Agiasma lagoon, but also Cr was found at low levels in Porto Lagos and Zn in Eratino Lagoon.

Pearson correlation analysis carried out on the surface sediments, revealed a strong positive correlation between As, Cr, Cu Mn, Pb, Zn and Ni and weak correlation between the previous metals with Cd (Table 8). As, Cd, Cr, Cu, Mn, Pb, Zn and Ni showed a positive correlation with the D_{90}/D_{10} ratio, implying that higher metal concentrations occur in sediments with a higher factor of variation. OC was found positively statistically significant to Cd, Cu, Mn, Pb, Zn, Ni and TKN and negatively to D_{10}. TP showed a negative correlation with Cd, Cr, Ni and the D_{90}/D_{10} ratio showing the preference of TP in more monosized material with limited metal content.

Assessment of sediment contamination

Table 9 summarizes the results of contamination indicators (CF, CD, PLI) for metals in sediments for all stations throughout the six lagoons. According to the CF values, all stations in these six lagoons exhibited considerable to very high contamination for As (with the exception of two stations in Agiasma and one in Lafri which showed moderate contamination). Very high contamination was shown for Cr, with six of the stations ranging between low to considerable contamination. Cr showed moderate contamination, low to moderate contamination for Cu (except of c3 which showed considerable and c4 with very high contamination), moderate to considerable contamination for Mn, although there are stations with low (a1, b1, b2, c2) and one (c4) with very high contamination. Sediments experience moderate to very high contamination for Pb, low to considerable contamination for Zn, except of c4 and d3 showing very high contamination, and low to moderate contamination for Ni, except of d3 and f2 with considerable and c4 with very high contamination.

CD values indicate very high contamination levels, although there are two stations exhibiting moderate contamination (b1 and d2) and three with considerable contamination (a3, b2 and d3) (Fig. 3). According to PLI values, most of the stations may be characterized as "polluted" and only four of them as "non-polluted" (b1,

Table 7 Trace metals concentrations (in µg/g) in surface sediments observed at the six lagoons (*n.d.* not detected)

Stations	Ag	Al	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Ga	Li	Mn
a1	14.9	4,493	19.2	52.1	1.14	1.27	1.55	7.89	445	4.69	11.2	7.67	34.3	303
a2	8.84	11,360	18.7	143.4	2.25	1.05	1.02	20.4	226	10.8	1.93	17.0	78.6	905
a3	5.16	7,847	14.5	99.0	1.25	1.04	0.60	16.0	168	7.13	3.76	11.9	53.1	804
a4	10.5	24,036	45.0	263.1	5.28	2.52	1.20	37.8	306	19.5	67.0	32.3	134	2,496
b1	6.77	5,306	6.36	82.2	1.43	0.80	0.22	9.40	119	4.81	2.69	8.41	36.3	381
b2	10.8	4,039	10.9	51.2	1.21	0.49	0.63	7.48	102	3.94	6.79	6.31	30.7	277
b3	6.81	7,697	99.2	127.9	1.11	16.3	n.d	17.9	240	11.1	0.45	15.6	21.6	715
c1	14.9	65,704	169.4	459	15.6	3.82	2.20	105	572	37.8	198	n.d	317	7,262
c2	10.4	16,465	21.2	248	2.73	0.80	0.66	34.2	240	19.5	3.41	29.5	92.9	1,419
c3	8.38	13,483	23.9	247	2.84	0.52	0.35	26.6	168	18.5	30.4	n.d	96.1	1,215
c4	9.02	38,695	64.5	636	8.35	1.35	0.70	75.4	383	39.0	83.1	68.9	289	2,906
d1	3.34	5,925	18.3	76.8	1.50	0.28	0.55	20.8	98.1	5.26	24.1	8.96	9.17	2,479
d2	2.30	3,176	12.8	40.9	0.82	0.10	0.16	10.6	76.8	3.39	9.71	4.78	n.d	413
d3	2.07	5,706	29.6	80.6	1.90	0.33	0.07	20.2	110	4.39	116	8.99	0.95	732
e1	4.88	23,170	15.5	284	5.48	1.09	1.02	38.0	245	10.2	79.9	30.2	56.4	1,469
e2	3.15	20,536	24.3	182	4.87	0.85	0.82	30.2	217	9.29	60.8	24.4	46.4	1,081
e3	2.07	19,066	24.0	560	5.56	0.82	0.47	36.5	221	10.3	51.2	33.5	28.2	881
e4	1.83	15,620	23.5	287	3.92	0.70	0.59	33.4	153	6.62	45.5	21.9	42.2	1,267
f1	2.10	32,505	35.0	666	7.59	1.15	0.64	43.6	251	13.4	63.5	46.2	146.9	2,438
f2	1.17	17,215	31.1	140	4.56	0.64	0.62	28.3	156	7.76	38.7	19.4	36.2	1,481
f3	3.12	24,536	79.8	147	5.88	1.45	1.34	41.7	251	9.36	63.5	26.7	54.8	1,569

Station	Pb	Rb	Sr	V	U	Zn	Ni	B	Ge	Mo	Re	Ti	W	Zr
a1	28.5	47.7	374	147	2.36	2.33	26.9	21,728	74.6	0.77	7.80	0.84	614	6.29
a2	28.4	141	357	119	3.84	127	57.1	50,119	7.36	0.51	3.03	0.19	n.d	2.36
a3	35.8	89.7	422	99.6	5.13	65.7	36.0	40,677	n.d	0.25	1.62	0.10	1270	1.66
a4	89.8	252	940	219	21.4	292	114	111,482	18.9	0.51	28.1	0.10	3326	2.04
b1	20.1	56.6	80.8	62.5	2.49	6.11	22.9	24,378	n.d	0.16	0.10	0.05	783	1.39
b2	23.1	42.5	190	54.5	1.86	26.9	17.6	21,147	n.d	0.13	0.28	0.02	515	0.78
b3	23.1	158	221	140	n.d	9.67	18.4	47,202	n.d	0.12	0.30	0.01	2364	0.85
c1	282	501	2339	488	13.0	664	296	280,236	517	0.53	17.0	0.02	1869	0.97
c2	56.4	265	1236	180	1.32	190	80.0	82,065	98.8	n.d	4.79	0.01	4071	0.53
c3	36.1	244	2389	150	3.43	219	76.9	68,827	9.05	0.16	0.80	0.01	2996	0.32
c4	83.7	578	460	374	6.08	599	227	188,004	203	0.35	8.23	0.01	7742	0.68
d1	54.0	53.0	2412	69.5	5.39	51.6	47.3	30,683	2210	0.12	12.9	0.06	287	0.24
d2	31.9	30.6	883	40.9	1.37	20.7	25.9	17,450	40.0	n.d	6.82	n.d	294	0.03
d3	57.3	48.5	996	64.2	2.80	81.4	42.8	36,039	n.d	n.d	n.d	n.d	143	n.d
e1	116	163	1621	192	5.85	202	141	93,204	144	0.03	12.4	0.01	136	0.36
e2	92.5	142	1709	169	5.22	126	99.1	78,921	146	0.10	11.3	0.01	134	0.22
e3	75.2	140	530	139	3.15	117	108	77,589	92.4	0.07	1.55	0.01	93.8	0.09
e4	115	116	891	146	4.72	94.4	89.1	60,219	n.d	n.d	n.d	n.d	n.d	n.d
f1	150	235	2795	200	4.30	252	129	105,404	n.d	n.d	n.d	n.d	n.d	n.d
f2	59.9	119	3259	127	6.85	109	83.7	61,475	237	0.05	n.d	n.d	364	0.05
f3	103	154	3408	216	9.88	249	164	100,098	97.9	0.11	8.23	0.02	30.1	0.04

b2, b3 and d2). The highest PLI values were reported at two stations in Lafri Lagoon (c1 an c4, 12.4 and 5.93 respectively), receiving agricultural residues from adjacent fields. PLI values for all three stations in Agiasma

Table 8 Pearson correlation matrix for the heavy metals and other sediments parameters

Parame-ter	As	Cd	Cr	Cu	Mn	Pb	Zn	Ni	OC	TP	TKN	D$_{10}$	D$_{50}$	D$_{90}$	D$_{90}$/D$_{10}$	D$_{75}$/D$_{25}$
As	1.000															
Cd	**0.519***	1.000														
Cr	**0.702***	**0.804***	1.000													
Cu	**0.672***	**0.524***	**0.567***	1.000												
Mn	**0.784***	**0.648***	**0.681***	**0.800***	1.000											
Pb	**0.696***	**0.657***	**0.629***	**0.866***	**0.879***	1.000										
Zn	**0.690***	**0.579***	**0.718***	**0.760***	**0.854***	**0.755***	1.000									
Ni	**0.701***	**0.646***	**0.709***	**0.820***	**0.851***	**0.863***	**0.945***	1.000								
OC	0.418	**0.592***	0.390	**0.479***	**0.479***	**0.456***	**0.573***	**0.634***	1.000							
TP	− 0.187	**− 0.588***	**− 0.551***	− 0.088	− 0.245	− 0.245	− 0.347	**− 0.460***	− 0.377	1.000						
TKN	**0.648***	**0.718***	**0.620***	**0.816***	**0.804***	**0.875***	**0.716***	**0.812***	**0.742***	− 0.296	1.000					
D$_{10}$	− 0.298	− 0.306	− 0.276	− 0.340	**− 0.525***	**− 0.511***	**− 0.585***	**− 0.643***	**− 0.536***	0.426	**− 0.437***	1.000				
D$_{50}$	− 0.295	− 0.243	− 0.287	− 0.209	− 0.306	− 0.360	− 0.424	− 0.416	− 0.234	0.399	− 0.251	0.350	1.000			
D$_{90}$	0.196	0.044	− 0.014	**0.477***	**0.477***	0.233	0.214	0.396	0.339	0.122	0.380	− 0.222	0.059	1.000		
D$_{90}$/D$_{10}$	**0.609***	**0.514***	**0.529***	**0.634***	**0.716***	**0.734***	**0.727***	**0.833***	**0.540***	**− 0.449***	**0.643***	**− 0.704***	**− 0.446***	**0.514***	1.000	
D$_{75}$/D$_{25}$	**0.749***	**0.602***	**0.671***	**0.690***	**0.843***	**0.767***	**0.727***	**0.733***	0.400	− 0.246	**0.753***	− 0.333	− 0.300	0.277	**0.749***	1.000

Bold numbers with one and two asterisks refer to the correlation at different statistical level

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Table 9 Estimated degree of anthropogenic impact based on contamination factor (CF), degree of contamination (CD) and pollution load indices (PLI)

Station	CF								CD	PLI
	As	Cd	Cr	Cu	Mn	Pb	Zn	Ni		
a1	4.01	17.22	4.84	0.40	0.58	1.67	0.03	0.57	29.32	1.12
a2	3.89	11.31	2.46	0.07	1.72	1.67	1.90	1.22	24.23	1.63
a3	3.02	6.70	1.82	0.13	1.53	2.10	0.98	0.77	17.05	1.36
a4	9.16	13.31	3.32	2.39	4.74	5.28	4.36	2.43	45.00	4.75
b1	1.32	2.43	1.30	0.10	0.72	1.18	0.09	0.49	7.63	0.59
b2	2.26	7.05	1.10	0.24	0.53	1.36	0.40	0.37	13.32	0.91
b3	20.66	0.00	2.60	0.02	1.36	1.36	0.14	0.39	26.53	0.74
c1	35.28	24.46	6.21	7.09	13.78	16.56	9.91	6.30	119.59	12.35
c2	4.41	7.33	2.60	0.12	2.69	3.32	2.84	1.70	25.02	2.14
c3	4.99	3.85	1.82	1.08	2.30	2.12	3.26	1.64	21.07	2.37
c4	13.44	7.83	4.16	2.97	5.51	4.92	8.93	4.84	52.61	5.93
d1	3.80	6.07	1.07	0.86	4.70	3.18	0.77	1.01	21.45	1.99
d2	2.67	1.83	0.83	0.35	0.78	1.88	0.31	0.55	9.19	0.88
d3	6.17	0.73	1.20	4.14	1.39	3.37	1.22	0.91	19.12	1.81
e1	3.24	11.37	2.66	2.85	2.79	6.82	3.02	3.00	35.74	3.85
e2	5.06	9.15	2.35	2.17	2.05	5.44	1.88	2.11	30.22	3.18
e3	5.00	5.23	2.40	1.83	1.67	4.43	1.75	2.30	24.60	2.76
e4	4.91	6.57	1.66	1.62	2.40	6.73	1.41	1.90	27.20	2.80
f1	7.29	7.07	2.73	2.27	4.63	8.83	3.80	2.74	39.36	4.38
f2	6.49	6.85	1.69	1.38	2.81	3.52	1.62	1.78	26.14	2.72
f3	16.62	14.93	2.72	2.27	2.98	6.04	3.71	3.49	52.76	4.94

Fig. 3 Distribution of CD and PLI values in the six lagoons
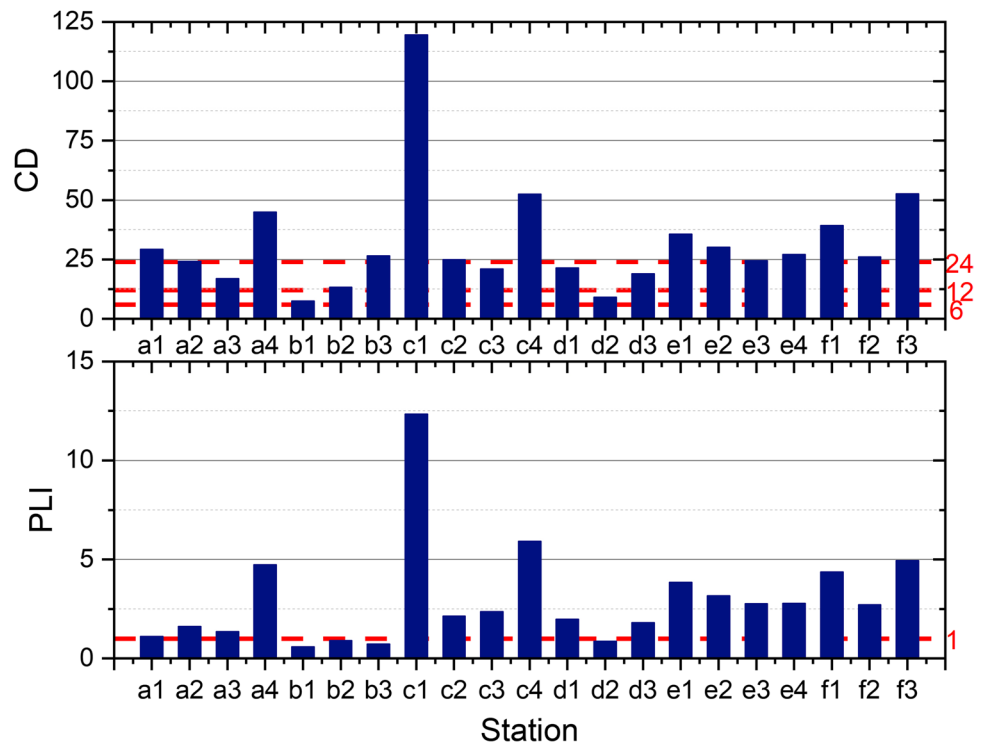
Table 10 Calculated values of Er and RI for metals in the sediments of the six studied lagoons

Station	Er							RI
	As	Cd	Cr	Cu	Pb	Zn	Ni	
a1	40.06	516.70	9.67	2.00	8.37	0.03	1.14	577.99
a2	38.87	339.36	4.91	0.35	8.36	1.90	2.43	396.18
a3	30.16	201.01	3.65	0.67	10.52	0.98	1.53	248.53
a4	91.61	399.34	6.64	11.96	26.42	4.36	4.87	545.20
b1	13.24	72.88	2.59	0.48	5.91	0.09	0.98	96.18
b2	22.61	211.43	2.21	1.21	6.80	0.40	0.75	245.41
b3	206.60	0.00	5.21	0.08	6.79	0.14	0.78	219.60
c1	352.82	733.84	12.43	35.43	82.80	9.91	12.60	1239.82
c2	44.07	220.02	5.21	0.61	16.60	2.84	3.40	292.75
c3	49.85	115.53	3.65	5.42	10.62	3.26	3.27	191.62
c4	134.44	234.90	8.32	14.85	24.60	8.93	9.67	435.72
d1	38.02	181.97	2.13	4.30	15.88	0.77	2.01	245.08
d2	26.65	54.82	1.67	1.73	9.38	0.31	1.10	95.67
d3	61.69	21.82	2.39	20.68	16.85	1.22	1.82	126.47
e1	32.35	341.00	5.32	14.27	34.11	3.02	6.00	436.06
e2	50.62	274.63	4.71	10.85	27.20	1.88	4.22	374.11
e3	50.00	156.77	4.80	9.15	22.13	1.75	4.61	249.20
e4	49.05	197.00	3.32	8.12	33.66	1.41	3.79	296.36
f1	72.90	212.08	5.46	11.33	44.17	3.80	5.47	355.22
f2	64.87	205.50	3.38	6.92	17.62	1.62	3.56	303.47
f3	166.21	447.79	5.45	11.34	30.21	3.71	6.98	671.69

lagoon were found below zero, thus being considered as a "non-polluted" lagoon (Fig. 3).

Ecological risk assessment

Table 10 presents the calculated values of the potential risk factor for metals in the sediments of the six studied lagoons. Cd and As reported the highest ecological risk. The highest Er-values for Cd were reported in: c1 in Lafri, a1 in Eratino and f3 in Ptelea lagoon. Most of the stations (71.5%) were considered to be of "high" to "very high" ecological risk for Cd, while the remaining indicated "low" to "considerable risk". For the 76.2% of sampled stations, the Er-values for As indicated "low" to "moderate" ecological risk, while the rest were considered as "considerable to very high" ecological risk. Er-values for Cr, Cu, Zn and Ni were calculated below 40, indicating "low ecological risk" at all stations. Most of the stations were considered of "low" ecological risk for Pb, except of two locations: f1 in Ptelea, being at "moderate" and c1 in Lafri at "considerable" ecological risk. The ecological risk among all the stations in the six lagoons was found "moderate" to "considerable", with three stations indicating "low" (b1, d2 and d3) and two indicating "very high" (c1 in Lafri and f3 in Ptelea) ecological risk (Fig. 4).
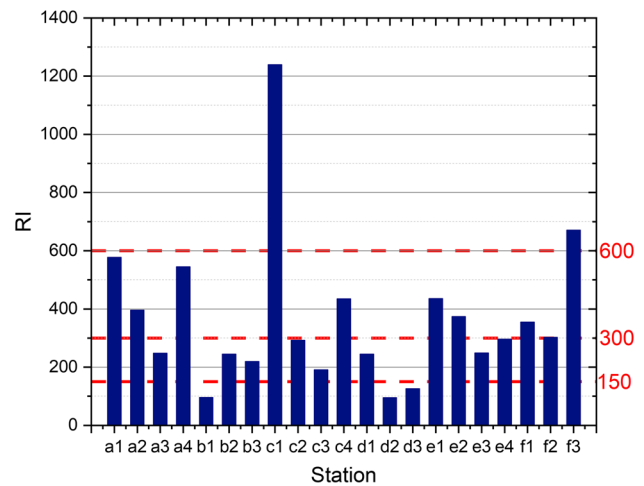
Fig. 4 Distribution of RI values in the six lagoons

Discussion

In this study, the heavy metal concentrations were examined in accordance to granulometry, OC, TP and TKN in the sediments of six lagoons in Northern Greece, receiving freshwater effluents from the intense, adjacent agriculture activities. Several indices and guidelines were employed

to assess sediments according to their contamination level and their induced ecological risks.

The average absolute concentration of heavy metals follows the order:

Eratino: Mn > Cr > Zn > Ni > Pb > As > Cu > Cd.

Agiasma: Mn > Cr > As > Pb > Ni > Zn > Cu > Cd.

Lafri: Mn > Zn > Cr > Ni > Pb > Cu > As > Cd.

Porto Lagos: Mn > Cr > Zn > Cu > Pb > Ni > As > Cd.

Xirolimni: Mn > Cr > Zn > Ni > Pb > Cu > As > Cd.

Ptelea: Mn > Cr > Zn > Ni > Pb > Cu > As > Cd.

Lafri Lagoon is characterised by the highest metal levels in all elements, while Agiasma and Porto Lagos showed the lower levels. Agiasma is mentioned in previous studies as one of less impacted lagoon of the Nestos River complex [19]. Metal levels were compared to Standard Quality Guidelines (SQGs) to assess the heavy metal pollution. Two criteria were used: the Lowest Effect Level (LEL) and the Toxic Effect Threshold (TET). The concentrations of As and Cr were higher than TET stated in SQGs, with the exception of some

sites where metal concentration was found lower (Fig. 5). Cd concentrations were lower than the TET value, and in nine of the stations were found even lower than LEL and considered as "non-polluted". The levels of Cu and Zn classify all stations from "non-polluted" to "moderately polluted", with the exception of c1 in Lafri and d3 in Porto Lagos, exceeding the Cu-TET level and c1 and c4 in Lafri, exceeding the Zn-TET level. Sediments concerning Pb concentration are considered as "non-polluted" to "moderately polluted". Station c1 in Lafri is an exception again, as it exceeds the Pb-TET threshold. Ni concentrations classify the sediments from "moderately to heavily polluted". Mn is not included in the SQGs as it is considered not to have adverse effects on marine organisms.

Most stations are characterized by high Ti concentrations, which indicate the possible influence by the Ti-rich garnets found in the broader Maronia area (Western Thrace) [20]. Pearson correlation matrix carried out on the surface sediments, revealed a positive correlation between As, Cd, Cr, Cu Mn, Pb, Zn. Such correlations between the above heavy
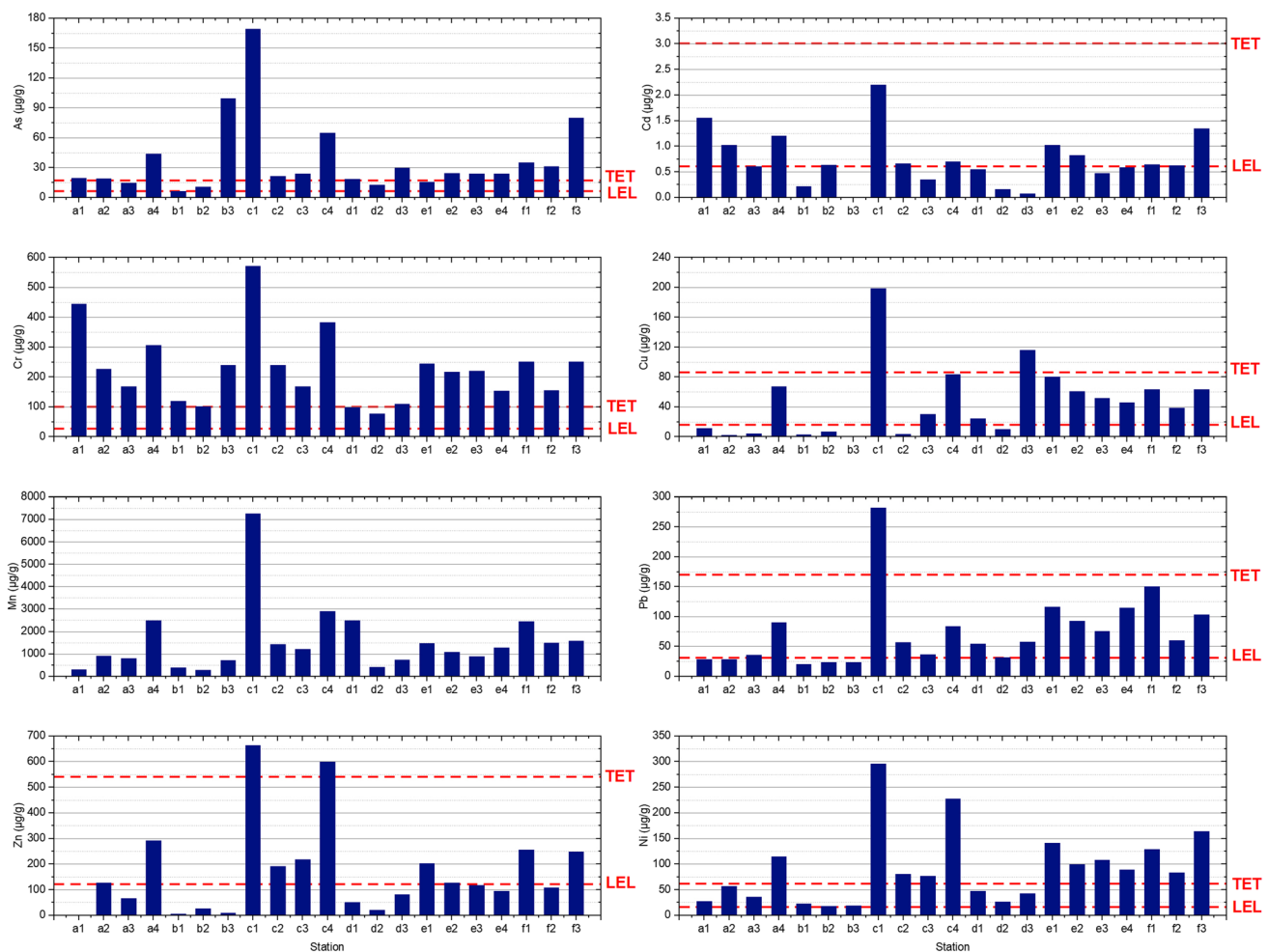
Fig. 5 Concentrations of trace metals in sediments for the six lagoons. LEL: Lowest Effect Level, TET: Toxic Effect Level, as stated in Standard Quality Guidelines

Table 11 Mean values and ranges (min -max) of heavy metal concentrations in the sediments for the six lagoons under study and those found in sediments from some other lagoons of the Mediterranean Sea

Lagoon	Metal concentration (µg/g)							
	As	Cd	Cr	Cu	Mn	Pb	Zn	Ni
Eratino, Greece	24.1±13.4 (14.5–44.0)	1.09±0.39 (0.60–1.55)	286±120 (168–445)	21.0±30.9 (1.93–67.0)	1127±950 (303–2496)	45.6±29.7 (47.7–252)	122±124 (2.33–292)	58.6±39.3 (26.9–114)
Agiasma, Greece	38.8±52.3 (6.4–99.2)	0.28±0.32 (0.00–0.63)	154±75 (102–240)	3.31±3.21 (0.45–6.79)	458±229 (277–715)	22.1±1.73 (20.1–23.1)	14.2±11.1 (6.11–26.9)	19.7±2.87 (17.6–22.9)
			130 [m] (20.0–112)	25.0 [m] (10.0–37.0)		76.4 [m] (20.0–158)	65.0 [m] (30.0–70.4)	40.8 [m] (10.0–59.0)
Lafri, Greece	69.7±69.3 (21.2–169.4)	0.98±0.83 (0.35–2.20)	341±178 (168–572)	78.8±86.3 (3.41–198)	3200±2810 (1215–7262)	114±113 (36.1–282)	418±248 (190.-663)	170±110 (76.9–296)
Porto Lagos, Greece	20.2±8.6 (12.8–29.6)	0.26±0.25 (0.07–0.55)	95.0±16.9 (76.8–110)	49.9±57.6 (9.71–116)	1208±1112 (413–2479)	47.7±13.8 (31.9–57.3)	51.2±30.4 (20.7–81.4)	38.7±11.2 (25.9–47.3)
Ksirolimni, Greece	21.8±4.2 (15.5–24.3)	0.73±0.25 (0.47–1.02)	209±39.4 (153–245)	59.3±15.1 (45.5–79.9)	1175±252 (881–1469)	99.5±19.4 (75.2–116)	134±46.7 (94.4–202)	109±22.5 (89.1–141)
Ptelea, Greece	48.6±27.0 (31.1–79.8)	0.87±0.41 (0.62–1.34)	219±55.1 (156–251)	55.2±14.3 (38.7–63.5)	1829±529 (1480–2438)	104±45.2 (59.9–150)	204±82.7 (109–255)	126±40.3 (83.7–164)
Antinioti[a], Greece		1.18±1.05 (0.14–3.42)		39.0±20.0 (12.0–75.0)	220±73.0 (140–350)	27.8±16.1 (4.05–66.1)	75.6±37.8 (9.23–121)	
Santa Gilla[b], Italy			30.0±10.0 (0–52.0)			122±44.3 (45.8–216)	92.0±22.0 (51.0–140)	20.0±4.10 (12.1–28.8)
Pialassa Piomboni[c], Italy	4.00±3.00 (<2.00–15.0)		128±17.0 (78.0–160)	42.0±24.0 (20.0–187)		32.0±35.0 (11.0–257)	167±69.0 (81.0–383)	71.0±13.0 (33.0–93.0)
Valli di Comacchio[d], Italy	6.90 (5.70–9.30)	0.20 (0.10–0.30)	72.5 (35.9–97.5)			21.00 (12.10–28.00)		59.0 (44.7–75.4)
Venice[e], Italy	6.60±3.10 (2.30–21.4)		15.9±7.80 (4.20–57.2)	19.3±13.0 (2.30–108)	239±65.0 (80.0–573)	15.2±8.6 (2.40–60.4)	90.0±80.0 (16.0–715)	13.0±5.70 (3.20–39.8)
Burullus Lake[f], Egypt		0.69±0.11	53.9±6.77	23.6±4.16		22.8±7.66	75.1±16.3	
Bizerte[g], Tunisia		(6.60–12.0)	(155–210)	(0.30–22.0)	(320–598)	(100–190)	(163–257)	(52.0–88.0)
Gialova[h], Greece		0.59	82.3	45.7		44.2	73.7	108
Karavasta[i], Albania			(163–257)	(30.0–90.8)		(32.3–67.0)		
Berre[j], France		0.23±0.41 (0.20–1.40)	58.7±30.4 (17.1–119)	31.0±12.7 (7.00–60.7)		41.7±29.5 (12.0–104)	120±52.6 (56.5–215)	
Messolonghi[k], Greece			101±29.0 (33.0–138)	20.0±11.0 (4.00–35.0)	630±176 (375–899)	16.0±6.00 (7.00–31.0)	60.0±21.0 (19.0–83.0)	84.0±30.0 (25.0–122)
Homa[l], Turkey		0.11±0.03 (0.06–0.19)	10.3±15.2 (83.9–129)	18.5±4.84 (10.3–25.8)	562±88.4 (410–729)	10.5±5.05 (2.43–17.2)	71.0±15.7 (46.2–91.9)	85.1±13.9 (58.1–108)

[a] Botsou et al. [28]

[b] Atzori et al. [31]

[c] Pignotti et al. [23]

[d] Pitacco et al. [24]

[e] Zonta et al. [25]

[f] El-Amier et al. [30]

[g] Mna et al. [33]

[h] Avramidis et al. [32]

[i] Koto et al. [34]

[j] Arienzo et al. [26]

[k] Karageorgis et al. [29]

[l] Uluturhan et al. [27]

[m] Christophoridis et al. [19]

metals indicate that they have the same distribution characteristics or they are released from a similar contamination source [21]. Pearson correlation coefficients showed the significant positive correlation between OC, Cd, Cu, Mn, Pb, Zn and Ni which indicates that OC influences the abundance of trace metals in the studied samples [22]. As, Cd, Cr, Cu, Mn, Pb, Zn and Ni showed a positive correlation with the D90/D10 ratio indicating that higher metal concentrations occur in sediments with heterogeneity.

Additionally, metal concentrations in the six lagoons under study were compared to other Mediterranean lagoons reported by previous works (Table 11). The As content in the studied lagoons was found significantly higher, compared to three lagoons in Italy [23–25]. The Cd-values observed in Agiasma and Porto Lagos were comparable to those observed in Valli di Comacchio [24], Berre lagoon [26] and Homa lagoon [27]. The highest Cd concentrations were measured in Eratino and Lafri, being at similar levels to those observed in two other Greek lagoons: Antinioti [28] and Messolonghi [29]. The Cr levels measured in the studied lagoons were found higher compared to the other Mediterranean lagoons, except of Porto Lagos. Their levels appear comparable to Pialassa Piomboni lagoon [23], Burullus Lake [30] and Messolonghi. The higher Cu content was measured in Lafri, Porto Lagos and Xirolimni. The lower Cu content was found lower in Eratino, at the same level to Venice [25], Bullurus, Messolonghi and Homa lagoons. Mn levels were found higher in the studied lagoons (apart of Agiasma), compared to the lagoons reported in Table 11 [25, 27–29]. Concentrations of Pb measured in Lafri, Xirolimni and Ptelea were found at similar levels as in Santa Gilla lagoon [31], and significantly higher than the other lagoons. The Pb levels in Agiasma were the lowest and comparable to Antinioti, Pialassa Piomboni, Valli di Comacchio, Venice and Bullurus lagoons. Zn levels in Porto Lagos were found to be almost at the same level as Antinioti, Santa Gilla, Venice, Burullus, Gialova, Messolonghi and Homa lagoons. Zn concentrations were comparable with the ones found in Pialassa Piomboni lagoon. This study reports that the highest Zn concentration was measured in Lafri and the lowest in Agiasma. Ni content in Agiasma was found similar to Sant Gilla and Venice lagoons, and a little lower than Porto Lagos. Ni levels in Xirolimni were comparable to Gialova [32], Messolonghi and Homa lagoons.

Christophoridis et al. [19] conducted a study in Agiasma lagoon measuring Cr, Cu, Pb, Zn, Ni and Hg concentrations in sediment cores. Comparing the present results to Christophoridis et al. [19], it occurs that the maximum measured values herein were found lower for Cu, Pb, Zn and Ni trace metals, except for Cr having levels considerably higher.

The elevated values of CF for As, Cd and Pb, range from considerable to very high contamination in the sediments, registering these trace metals on the top of environmental concern. The same conclusion is reached when examining the Potential Toxicity RI, where the RI value is influenced

mostly by Cd and As. High levels of the above trace metals can be related to agricultural processes in general. Specifically, they could originate from impurities in fertilizers, pesticides, waste from pig and poultry production and sewage sludge [35]. The extensive use of phosphate fertilizers in agriculture can lead to increased concentration of As and Cd and their accumulation in agricultural soils [36]. CD and PLI values classify the majority of the stations under study as "very high contaminated" and "polluted", respectively. Based on the above indices, Agiasma is considered as the least contaminated lagoon amongst the six studied.

Conclusion

The contamination extent and the anthropogenic impact in six lagoons of Northern Greece was assessed, by collecting surface sediment samples from each lagoon and then using the contamination factor (CF), the contamination degree (CD), the pollution load index (PLI), the potential risk factor (Er) and the potential ecological risk index (RI) to assess metal concentrations. Heavy metal levels and sediment contamination indices reveal that Lafri lagoon is the most heavily impacted, while Agiasma and Porto Lagos are the less impacted lagoons. According to the LEL and TET guidelines, sediments appear particularly contaminated with Cr and As throughout the six lagoons under study. Finally, it is understood that the sediments are contaminated due to agricultural drainage water from agriculture and livestock activities from the adjacent to the lagoon areas.

Declarations

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