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On the geochemistry of Gialova lagoon, SW Peloponnesus, Greece

Papakonstantinou M., Sergiou S., Dimas X., Fakiris E., Christodoulou D., Geraga M., and Papatheodorou G*.

Laboratory of Marine Geology and Physical Oceanography, Department of Geology, University of Patras, Greece, 26 504.

*corresponding author
e-mail: gpapathe@upatras.gr

Abstract. The spatial distribution of lithological characteristics, organic carbon and major / trace elements was studied in the surface sediments of the Gialova lagoon, a shallow water lagoon (<1.0 m) which is located at southwestern Peloponnesus (Greece). The sediment samples were collected on the basis of a detailed bathymetric map and the backscatter properties of the lagoon floor acquired using high resolution side scan sonar on board of an Unmanned Surface Vehicle (U.S.V.). Four main geochemical phases were identified based on the elements – grain size – organic carbon associations. Geoaccumulation index (Igeo) was estimated for heavy metal concentrations showed low to moderate contamination for Mo, Pb, Ni, and Cr.

Keywords: Lagoon, sediments, heavy metals, Igeo

1. Introduction

Lagoons are highly vulnerable environments, counted amongst the most threatened aquatic systems lying under various types of natural (such as global climate and sea level rise) and anthropogenic forces (intensive agriculture, aquaculture and input of heavy metals). The Gialova Lagoon is considered as an important wildlife refuge (Maneas et al. 2019). Even though it is protected by international conventions and belongs to the Natura 2000 European community Network as Special Protection Area (SPA) and Site of Community Interest (SCI), the lagoon has suffered from many human interventions during the last 70 years which resulted to the reduction of its extent from 7.5km^2 to 2.5km^2 (Avramidis et al. 2015, Maneas et al. 2019).

The lagoon is separated from the Navarino bay by a 3.3km long and 0.15km wide natural sand barrier. In this barrier, a narrow canal connects the lagoon with the bay. The surrounding geological setting of the Gialova Lagoon consists of Holocene alluvial deposits and sand dunes, Plio–Pleistocene deposits of conglomerates, marls and fine grained sandstones, and Eocene to Oligocene flysch deposits (Avramidis et al., 2015).

The main objectives of this study are to visualize the spatial distribution of sedimentological characteristics of the lagoon and to examine potential heavy metal enrichment, since bottom sediments grain size and geochemical characteristics are important geological and environmental factors.

2. Material and methods

2.1. Field work

The sampling survey was conducted during December 2020, on the basis of backscatter properties of the lagoon floor acquired using high resolution side scan sonar data on board of an Unmanned Surface Vehicle (U.S.V.). Subsequently, twenty-eight (28) surficial sediment samples were collected covering the entire different backscatter levels of the lagoon floor. Sediment samples were collected with the use of a Van-Veen grab while subsamples for laboratory analyses were taken from the central part of the grab to avoid contamination.

2.2. Analytical procedures

Sediment samples were subjected to macroscopic description, granulometry and chemical analysis. All samples were visually described in terms of colour and textural features. Grain size analysis was performed using a Malvern Mastersizer 2000 particle analyzer. Hydrogen peroxide (H_2O_2) treatment was applied prior to analysis to eliminate organic matter.

The definition of the main four grain size statistical parameters, mean (Mz), sorting (σi), skewness (Sk) and kurtosis (KG) were calculated with the GRADISTAT program (Blott & Pye, 2001) while sediment classification was based on Folk (1974) nomenclature.

Bulk geochemistry was determined by four acid digestion followed by ICP-MS finish. Total Organic Carbon (TOC) was measured using a LECO Carbon analyzer after HCL (25%) pre-treatment to remove carbonates. The spatial distribution of sediment characteristics was visualized using the Surfer 9 and ArcGIS software.

2.3. Contamination indices

Geoaccumulation index (Igeo) (Muller, 1979) was estimated for selected heavy metal concentrations in which,

$$Igeo = log_2[Cn/(1.5Bn)]$$

Cn is the measured concentration for the metal n in the sediment sample and Bn stands for the background value for the metal n. In this study, background values were based on global average shale data from Turekian & Wedepohl (1961).

3. Results and discussion

The detailed bathymetry acquired with U.S.V. showed that the Gialova lagoon is extremely shallow with a maximum water depth of 0.70m (Fig. 1). Despite the very shallow depth of the lagoon, three morphological parts were defined: (i) the western basin with maximum water depth of 0.65m, (ii) the eastern basin with slightly higher depth (0.70m) and (iii) the central and coastal part with water depth less than 0.55m (Fig. 1). The spatial distribution of the backscatter coincides well with the three morphological parts and the subaqueous vegetation of the lagoon (Papakonstantinou et al. 2021, in preparation).

The macroscopic description of the bottom samples revealed that the lagoon floor comprises very dark grey (5Y 3/1) mud with occasional presence of larger sized bioclasts (bivalve shells and gastropods) and plant residues. A thin (mm scale) dark grayish brown (2.5Y 4/2) mud layer is covering, in most sampling sites, the bottom sediments. Surface sediment granulometry also coincides well with the morphology of the lagoon floor. The western basin consists of very fine-grained sediments (mean Mz: 6.9 phi) with mean percentage of sand, silt, and clay at 5.1%, 61.3% and 33.6%, respectively. The eastern basin is covered by slightly coarser sediments (mean Mz: 6.8 phi) and mean percentage of sand, silt, and clay are 3.3%, 67.3% and 29.4% respectively. The central shallower part of the lagoon is covered by coarser sediments (mean Mz: 6.4 phi) compared to the previous two basins. The central part displays the highest sand mean percentage (11.2%), high silt (61.8%) and the lower clay percentage (27%). The spatial distribution of clay proportion clearly reflects the three different morphological parts of the lagoon (Fig 2b). The coarser sediments (Mz: 5.0-5.5 phi) associated with the higher sand proportion (23-35%) were obtained along the southwestern coast of the lagoon, just north of the sandy lagoon barrier separating the lagoon from Navarino Bay and near the canal (inlet). This relatively high sand content is probably related to the littoral sandy material of Navarino Bay that has been transported into the lagoon through the canal. Similar process has been proposed by Avramidis et al. (2015) based on sedimentological data collected 25 years ago.

The spatial distribution of the total organic carbon (TOC) seems to be affected by the morphology of the lagoon floor (Fig. 2d). The higher TOC percentages (1.7-2.0%) were measured in the two shallow basins where the very fine sized sediments dominate (Fig. 2b, c) while low concentrations (1.3-1.6%) were obtained along the sand barrier at the southwestern part of the lagoon and at the central part. This pattern highlights the high absorption of the organic matter in the fine silt - clay size fraction of the sediment texture. It also suggests that organic matter is primarily deposited in the shallow basins where burial process prevents oxidation and that the oxygenation of the lagoon is ascribed to the saline water inflows from the adjacent Navarino bay through the canal.

The minimum, maximum and mean concentrations of selected major (wt%) and trace elements (ppm) in the surface sediments of Gialova Lagoon are presented in Table 1. Based on the pattern of the spatial distribution and the correlation coefficient (r) of selected major and trace elements, four geochemical phases can be identified: (i) Al, Fe, Ti, Co, Ni, Cr, Cu, Pb, Sn, V, Zn, Zr, (ii) Ca, Sr (iii) Mg, Mn, Na, P and (iv) As, Cd, Mo.

The first geochemical phase represents the aluminosilicate minerals and the clay fraction of the sediments. It should be noted that the concentration of some heavy metals (Pb, Ni, Cr) may have been affected by activities of anthropogenic origin. Moreover, this geochemical phase is moderately correlated with organic carbon. The metals detected in that phase present similar spatial distribution with maximum concentrations obtained at the western shallow basin of the lagoon and moderate concentrations at the eastern basin (Fig 3a). The second geochemical phase stands for the biogenic calcareous fraction of the sediments showing a different spatial pattern compared with the previous phase, with maximum concentration at the central part of the lagoon floor and along the southwestern coast where sand proportion is also highest (Figs 2a, 3b). The third geochemical phase represents the moderate correlation of Mn and Mg with organic carbon suggesting that the organic phase seems to be an efficient scavenger of the heavy metals and the Mn is an important factor in the geochemistry of surface sediments of Gialova lagoon (Fig 3c). The fourth geochemical phase shows a different spatial pattern with maximum concentrations at the western basin and the central part of the lagoon suggesting a different source of those metals probably indicating anthropogenic inputs (Fig 3d).

The Igeo values for selected heavy metals indicate that the Gialova lagoon is moderately contaminated (Igeo:1-2) for Mo and slightly to moderately contaminated (Igeo: 0-1) for Pb, Ni and Cr. The highest Igeo values were found in the sediments of the western shallow basin and western end of the lagoon. The elevated concentrations of Ni may be attributed to the weathering of the bauxite surface deposits from the nearby geological formations. Similar explanation has been suggested by Varnavas et. al. (1987) for the high concentrations of Ni in the surface sediments of Navarino bay.

The Pb mean concentration in the Gialova Lagoon surface sediments (35.56 ppm) is higher than those reported in many Greek lagoons (Table 1). Similarly, Cr concentrations are higher than those of Messolonghi lagoon and Koumoundourou lake but significantly lower than those in the lagoons of Amvrakikos Gulf (Table 1). Zn and V concentrations are lower compared to others Greek lagoons (Table 1). On the contrary, Mn concentrations in Gialova lagoon is higher than those in others Greek lagoons (Table 1).

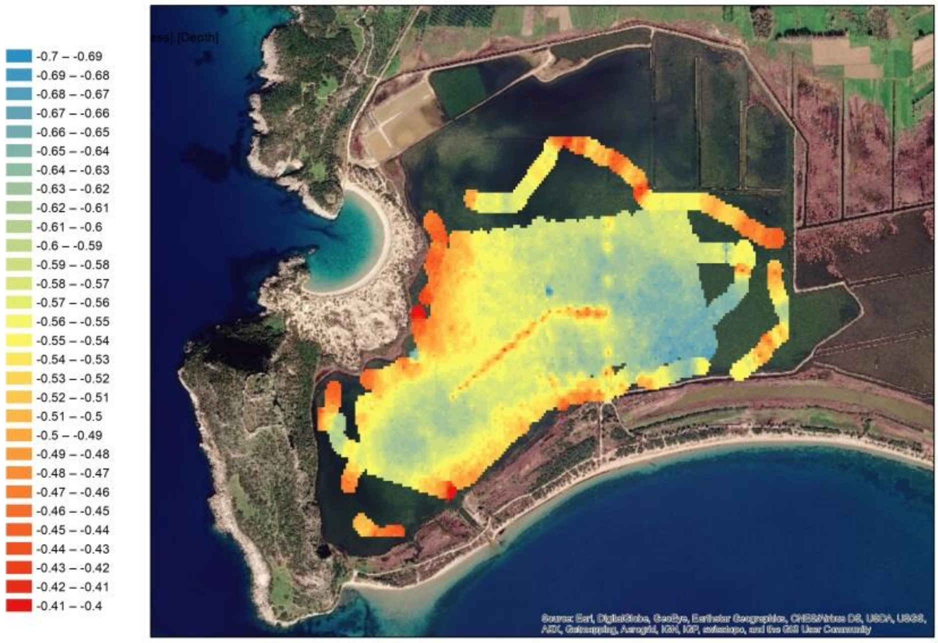

Figure 1. Bathymetric map of Gialova lagoon. The two very shallow basins are indicated by blue color.

Table 1. Mean, minimum and maximum values of heavy metals concentrations in the Gialova Lagoon compared to other Greek aquatic systems and average Shale's values.

Element	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
Element unit	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
Gialova Lagoon, mean[a]	0.13	122.50	30.50	3.20	1026.32	103.20	35.46	69.18	64.50
Gialova Lagoon, min – max[a]	0.10 - 0.16	91 - 151	20.50 - 36.50	2.13 - 3.84	646 - 1150	66.50 - 123.50	26.30 - 44.40	46.00 - 83.00	45.00 - 79.00
Gialova Lagoon, mean[b]	0.81	118.20	57.51	4.76*	1549*	172.11	36.29	69.24	98.47
Messolonghi Lagoon[c]	–	101.00	20.00	2.36*	630.00	84.00	16.00	75.00	60.00
Koumoundourou Lake[d]	–	58.00	21.00	0.58*	155.00	28.00	53.00	23.00	83.00
Alikes Lagoon[e]	–	251.67	29.17	3.59*	630.00	134.17	9.88	109.33	68.89
Aetoliko Lagoon[f]	–	140	88	4.17	837	75.6	–	–	122.2
Kleisova Lagoon[g]	–	–	13.00	1.64	562.00	62.00	–	–	29.00
Rhodia Lagoon[h]	–	231	37	2.83	867	124	36	112	72
Tsoukalio Lagoon[h]	–	274	31	3.16	1191	131	26	108	76
Logarou Lagoon[h]	–	302	44	4.74	922	221	25	153	105
Tsopeli Lagoon[h]	–	295	48	3.98	665	168	26	129	100
Navarino Bay – upper sediments[i]	–	–	66.00	–	–	151.00	–	–	352.00
Shales[j]	0.3	90	45	4.72	850	68	20	130	95

*Calculated concentrations using the appropriate molar ratio

References: [a]This study, [b]Avramidis et al. 2015, [c]Karageorgis et.al. 2012, [d]Karageorgis et.al. 2009, [e]Panagiotaras et.al. 2012, [f]Dassenakis et al. 1994, [g]Papatheodorou et.al. 2002, [h]Karageorgis, 2007, [i]Varnavas et.al. 1987, [j]Turekian & Wedepohl, 1961.

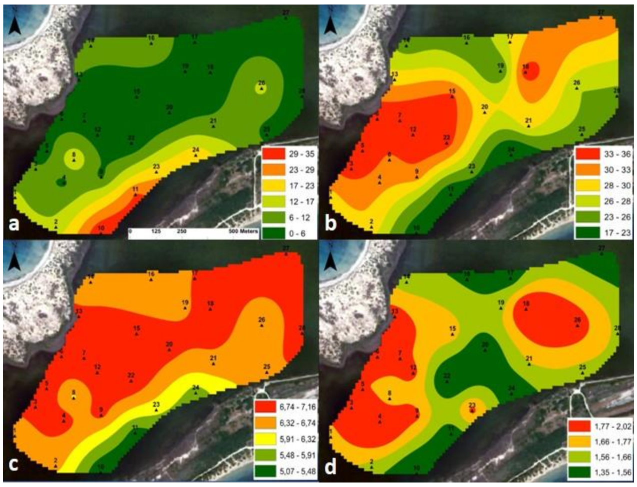

Figure 2. Spatial distribution of (a) Sand (%), (b) Clay (%), (c) Mz (phi) and (d) TOC (%)

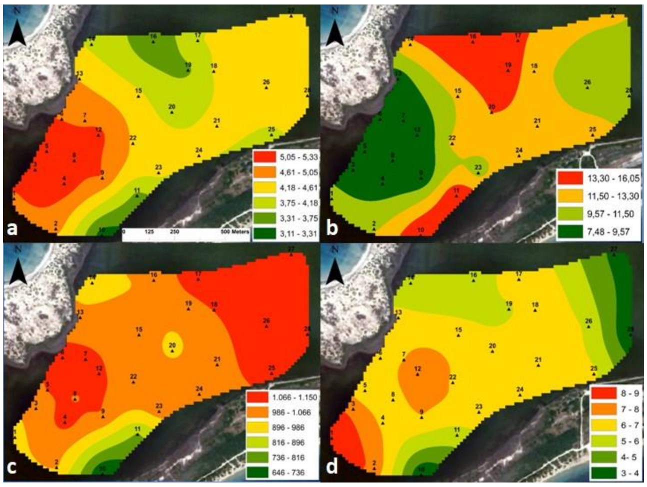

Figure 3. Spatial distribution of (a) Al (%), (b) Ca (%), (c) Mn (ppm) and (d) Mo (ppm)

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