Transitional Waters Bulletin
TWB, Transit. Waters Bull. 3(2007), 3-8
ISSN 1825-229X, DOI 10.1285/i1825229Xv1n3p3
http://siba2.unile.it/ese/twb

RESEARCH ARTICLE

Geochemical study of sediments from the Amvrakikos Gulf lagoon complex, Greece

Aristomenis P. Karageorgis

Hellenic Centre for Marine Research, Institute of Oceanography, 46.7 km Athens-Sounio Avenue, Mavro Lithari, 19013 Anavyssos, Greece

Abstract

1 - Grain-size parameters, organic carbon, major and minor elements were determined in a suite of 50 surface sediment samples obtained from the Amvrakikos Gulf lagoons Rodia, Tsoukalio, Logarou, and Tsopeli

2 - The shallow lagoon-floor (max. 3.1 m) was covered mainly by muddy sediments

3 - Most major and minor elements were found to be related with terrigenous aluminosilicates. Higher contents of S, Mo, Pb, organic C, and As were observed in Rodia lagoon, indicating temporary anoxic conditions. High Cr and Zr contents exhibited similar behavior with Si and were attributed to the presence of minerals chromite, zircon and quartz. Typical occurrences of biogenic elements (Ca, Sr) were also recorded. Relatively high heavy metal contents for V, Cr, Ni, and Zn were attributed to the natural weathering of metal-bearing ultra-basic rocks.

4 - The lagoon system is supplied by terrigenous material originating in the Rivers Arachthos and Louros and also directly by the weathering of rock formations. Due to the anticlockwise water circulation prevailing in Amvrakikos Gulf, particle-rich riverine waters from Arachthos entrain Logarou, whilst Tsoukalio and Tsopeli are mostly influenced by the neighboring Louros R.

Introduction

In the framework of the INTERREG Project TWReferenceNet, a geochemical investigation of lagoon surface sediments was undertaken. The scope of this work was: (a) to identify elemental variations between lagoons; (b) to understand sources and pathways of major and minor elements in the lagoons; (c) to study depositional mechanisms and lagoon-sea interactions and (d) to examine potential heavy metal enrichment.

The lagoon complex of Amvrakikos Gulf comprises several lagoons, out of which four have been selected for study, namely, Rodia, Tsoukalio, Logarou, and Tsopeli (Fig. 1); maximum water depths recorded were 3.1, 1.7, 1.6, and 1.4 m, respectively. Two major rivers influence the coastal environment of Amvrakikos Gulf, Arachthos, which flows into the NE sector of the Gulf and Louros, which flows into the NW sector and passes around the eastern border of Tsopeli lagoon (Fig. 1).

Material and methods

Surface sediments were collected during a single visit in the study area (24-28 October 2004). In total, 50 sediment samples were collected (Fig. 1), using a Hydro-Bios Lenz bottom sampler.

Grain-size measurements were undertaken using a Sedigraph 5100 system, after the separation of the sand fraction (>63 µm) by wet sieving.

Total (not sieved) and unwashed samples were analyzed for major (fused beads) and trace elements (powder pellets) by X-ray fluorescence in a Philips PW-2400 wavelength dispersive analyser, following the methods described by Karageorgis *et al.* (2005). Element concentrations are expressed on a salt-free basis.

Organic carbon was determined by a Fisons Instruments CHN elemental analyser type EA-1108, following the procedures described by Verardo *et al.* (1990), and Nieuwenhuize *et al.* (1994).

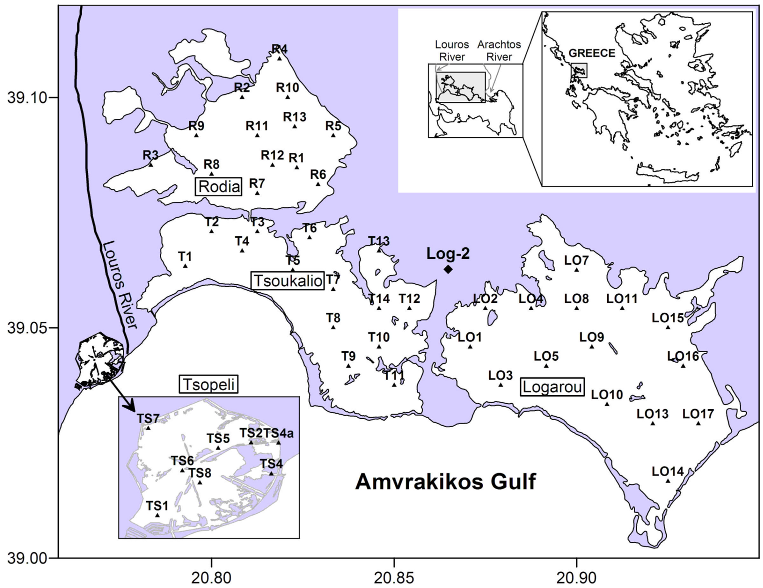

Figure 1. Surface sediment sampling stations location.

Results and discussions

Grain-size characteristics

Amvrakikos lagoon sediments are generally fine-grained, with moderate percentages of sand content (Tab. 1). Silt content predominates in Rodia lagoon (>80%), whilst clay content predominates in Logarou lagoon (>60%). Surface sediments of Tsoukalio and Tsopeli are generally muds, with silt content ~60-70%. In the absence of any direct input of sediments into the lagoons, which would supply coarser, sandy sediments, muddy sediments normally predominate; they originate in the weathering of adjacent rock formations. However, fine suspended particulate matter of riverine origin (Arachthos and Louros Rivers), probably entrains the lagoons through the narrow and man-controlled, natural and artificial connections of the lagoons to the open sea.

Organic carbon

Organic carbon content exhibits relatively low values in all lagoons (Tab. 1), with the exception of Rodia; here the highest value (9.05%) occurs in the central and eastern sector of the lagoon. These observations reveal that sediments have experienced anoxia or hypoxia. This is not surprising, as Rodia is the most isolated lagoon, and communicates to Tsoukalio through a narrow passage in the south. During the field measurements, the water column was found to be well oxygenated throughout the entire lagoon system. However, such high levels of organic carbon reveal that previously, low oxygen conditions have favored the accumulation and preservation of organic matter in Rodia.

Major and minor elements interrelations

Significant correlations of most major and minor elements against Al suggest their relation with terrigenous aluminosilicates. This group includes Ti, Fe, K, Mg, V, Co, Ni, Zn, Rb, Ba, and clay. Chromium and Cu are also positively correlated to Al. Inversely correlated to Al are Ca, Sr, sand, and silt, a group which relates to autochthonous biogenic carbonates, which are usually found in the coarser fractions of the sediment.

Mo, Pb, org. C, As, and silt exhibit high correlations against S, representing an anoxic phase in the surface sediments. Such sediments accumulate in environments where the rate of burial of particulate organic matter exceeds the rate of replenishment of dissolved oxygen (Calvert and Pedersen, 1993).

Chromium and Zr co-vary with Si. Silicon is on one hand structural element of terrigenous aluminosilicates, but is also abundant as pure quartz, a common mineral in sediments. Similarly, Zr in sediments is found as mineral zircon (ZrO_2); it is an element extremely immobile in the marine environment. Chromium may be attached to the lattice of clay minerals. It can also be introduced into the aquatic environment as a pollutant, mainly from leather tannery factories and fertilizers. However, its relation to immobile elements, i.e. Si and Zr, probably reflects its presence as chromite mineral, originating in the catchment area of the Rivers Arachthos and Louros.

Spatial distribution of major and minor elements

Aluminosilicate-related major and minor elements exhibit highest contents in Logarou lagoon, and particularly in the sector bordering the open sea (e.g. Al; Fig. 2). This distribution pattern suggests that the main source of sediment to Logarou is Arachthos River; the predominant anticlockwise circulation in Amvrakikos Gulf, transports suspended particulate matter to the west, and particulates entrain Logarou from a number of narrow connections. Similarly, riverborne particulates feed Tsoukalio. However, the connection of the latter lagoon to the open sea seems to be more restricted. The Rodia lagoon exhibits low aluminosilicate-related element contents, due to its natural isolation from the open sea; probably, it receives terrigenous material from small branches of Louros River. Tsopeli receives terrigenous particulates from Louros River, through a number of narrow connections.

Calcium and Sr, typical biogenic elements exhibit similar spatial distribution patterns (e.g. Sr; Fig. 2). Highest contents are observed in Rodia lagoon. Probably its natural isolation from the open sea, and freshwater inputs, favor growth of calcareous benthic organisms. Tsoukalio exhibits moderate abundance of biogenic elements, whilst Logarou shows the lowest Ca and Sr contents, similarly to Tsopeli, indicating that better communication to the open sea suppresses benthic calcareous organism abundance.

Sulphur, As, Mo and organic carbon exhibit similar spatial distribution patterns (e.g. As; Fig. 2), characterized by high contents in Rodia. In areas where dissolved oxygen supply is limited, organic matter degradation produces H_2S, as a by-product of bacterial sulphate reduction and surface sediments become anoxic (Froelich *et al*., 1979). Surface sediments of Rodia, particularly those obtained from the central and eastern sector exhibit a distinct dark brown to black color, which characterizes anoxic sediments. It is possible that during the winter period, and under heavy rainfall, large quantities of organic carbon are injected into the lagoon, from the Louros River branches, and thus consuming rapidly all available dissolved oxygen and trigger anoxia.

Silica, Cr and Zr follow similar spatial distribution patterns (Fig. 2). Higher element contents of this group are observed in the NW sector of Logarou, whilst in the other lagoons they show generally lower contents. This sector of Logarou in also characterized by relatively sandier sediments, thus elements of the group seem to be enriched in the sand fraction. Apparently, Si and Zr are not related to human sources, as they appear in sediments as minerals (SiO_2 and ZrO_2) and of course Si is also related to aluminosilicates. Therefore, it remains for Cr, to understand whether it is related to potential pollution sources or not. Chromium contents are very high (max. 422 ppm), about 4 times higher than the average shale and 7 times higher than the average shallow water sediment (Turekian and Wedepohl, 1961). Its relation, however, with Si and Zr, probably suggest that Cr is related to mineral chromite, which is found in the upper catchment of Arachthos R., in ultra-basic ophiolite formations. Nickel, which is also common in ophiolite formations, exhibits in Logarou high contents, as well (116-275 ppm).

Similarly, high Cr and Ni contents have been recorded in soils of the Aracthos River deltaic plain by Vryniotis and Papadopoulou (2004) and were attributed to the weathering of metal-rich rock formations.

Table 1. Mean values of measured parameters in the sediments of the four lagoons.

	Rodia	Tsoukalio	Logarou	Tsopeli
Sand (%)	20.7	21.7	14.8	19.1
Silt (%)	68.2	54.9	38.0	38.7
Clay (%)	11.1	23.4	47.2	42.2
Si (%)	17.0	22.5	22.4	24.5
Al (%)	4.35	4.99	6.83	6.19
Ti (%)	0.251	0.315	0.397	0.360
Fe (%)	2.83	3.16	4.74	3.98
K (%)	1.203	1.465	2.152	1.913
Na (%)	0.59	0.77	1.08	0.72
Ca (%)	9.65	6.60	4.39	5.04
Mg (%)	1.771	2.118	3.305	2.079
P (%)	0.074	0.072	0.070	0.068
S (%)	1.365	0.904	0.675	0.666
Cl (%)	4.29	2.92	2.74	1.65
V (ppm)	112	108	153	129
Cr (ppm)	231	274	302	295
Mn (ppm)	867	1191	922	665
Co (ppm)	16	18	27	21
Ni (ppm)	124	131	221	168
Cu (ppm)	37	31	44	48
Zn (ppm)	72	76	105	100
As (ppm)	18	14	11	10
Br (ppm)	181	90	58	275
Rb (ppm)	85	91	131	127
Sr (ppm)	574	407	325	267
Zr (ppm)	110	139	117	131
Mo (ppm)	12	6	4	4
Ba (ppm)	215	240	263	254
Pb (ppm)	36	26	25	26
tot. N (%)	0.797	0.573	0.415	0.367
org. C (%)	6.55	4.35	2.92	2.95
$CaCO_3$ (%)	23.4	16.7	10.2	11.8

Heavy metal pollution aspects

Comparing average heavy metal contents of sediments from the Amvrakikos Gulf lagoons to other Hellenic sites, we may infer that values for V, Cr, Ni, and Zn are considerably high. Although we have identified that most of the heavy metals are intimately and exclusively associated with aluminosilicate minerals, such high values require further examination, in order to clarify that sediments have not been influenced by anthropogenic activities. The best way to resolve this problem is to sample and analyze pre-industrial sediment. During March 2006, a 4-m core (Log-2; Fig. 1) was recovered, sub-sampled and analyzed for major and minor elements. Results show that the background of all metals is considerably high, throughout the core. For chromium, in particular, it originates from the weathering of flysch deposits, which are ubiquitous in the catchment area of Arachtos River. Flysch samples were also analyzed and have shown similarly high Cr contents. Therefore, heavy metal enrichment in the Amvrakikos lagoon sediments is attributed to natural processes, rather than anthropogenic activities.

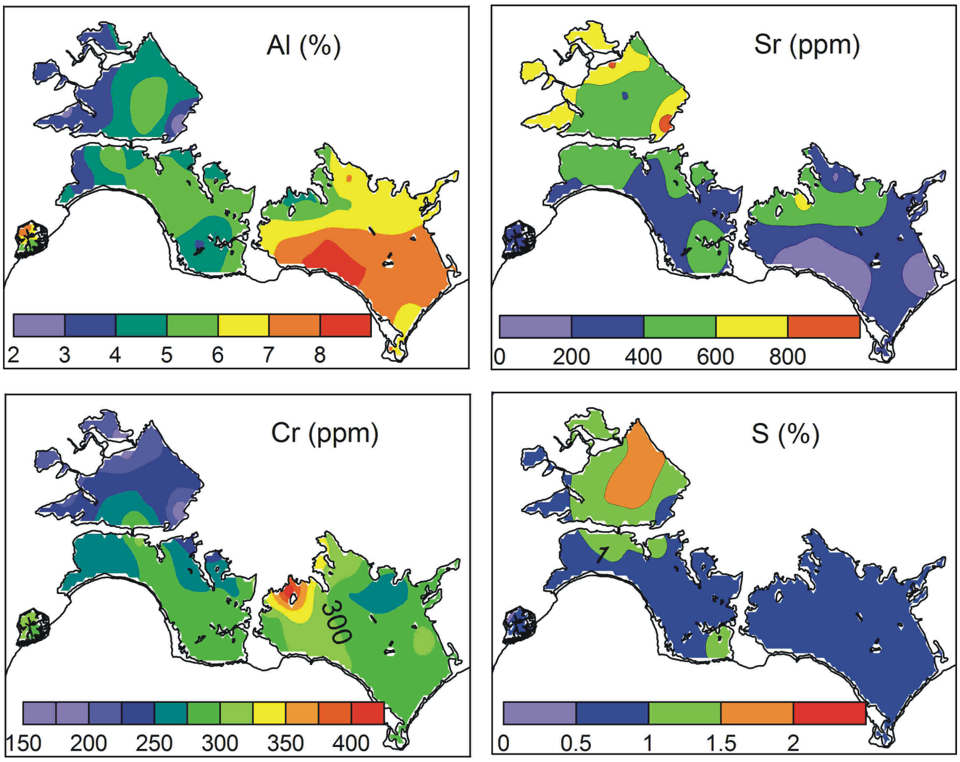

Figure 2. Spatial distribution of major and minor elements representing the four prevailing element groups

Acknowledgments

This paper was funded by an INTERREG IIIB CADSES grant to the project TWReferenceNET.

References

Calvert, S.E. and Pedersen, T.F., 1993. Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record. *Marine Geology*, **113**: 67-88.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica Cosmochimica Acta, **43:** 1075-1090.

Karageorgis, A.P., Anagnostou, C.L. and Kaberi, H., 2005. Geochemistry and mineralogy of the NW Aegean Sea surface sediments: implications for river runoff and anthropogenic impact. *Applied Geochemistry*, **20**: 69-88, DOI: 10.1016/j.apgeochem.2004.07.008.

Nieuwenhuize, J., Maas, Y.E.M. and Middelburg, J.J., 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. *Marine Chemistry*, **45**: 217-224.

Turekian, K.K. and Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. *Bulletin Geological Society of America*, **72:** 175-192.

Verardo, D.J., Froelich, P.N. and McIntyre A., 1990. Determinations of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer. *Deep-Sea Research*, **37**: 157-165.

Vryniotis, D. and Papadopoulou, K., 2004. The role of Aracthos and Louros Rivers in the development of sediments of the Arta's plain with the contribution of geochemical parameters. *Bulletin of the Geological Society of Greece*, **36**: 150-157.