Journal of Geochemical Exploration 146 (2014) 105–118

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Investigation of major and trace element distribution patterns and pollution status of the surficial sediments of a microtidal inner shelf influenced by a transboundary river. The case of the Alexandroupolis Gulf (northeastern Aegean Sea, Greece)

A. Karditsa [a,*], S.E. Poulos [a], F. Botsou [b], D. Alexakis [c], M. Stamatakis [a]

[a] Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, 15784 Attiki, Greece
[b] Laboratory of Environmental Chemistry, Faculty of Chemistry, National and Kapodistrian University of Athens, 15784 Attiki, Greece
[c] Centre for the Assessment of Natural Hazards and Proactive Planning, Laboratory of Reclamation Works, National Technical University of Athens, 9 Iroon Polytechniou Street, Athens, 15773, Greece

ARTICLE INFO

Article history:
Received 17 October 2013
Accepted 11 August 2014
Available online 23 August 2014

Keywords:
Overall Enrichment Index (OEI)
Transboundary river
Sediment Quality Guidelines
Modified degree of contamination
Enrichment factor

ABSTRACT

The present investigation examines the distribution patterns of major and trace elements of surficial sediments of the Alexandroupolis Gulf (NE Aegean shelf) which are influenced by the influxes of the transboundary river Evros. Fifty-three surficial sediment samples were analysed for 25 major and trace elements, together with the $CaCO_3$, TOC and mud content. Factor analysis was conducted in order to reveal the major processes that control their behaviour. Pollution indices (enrichment factor, modified contamination degree) were used to evaluate pollution levels, the most widely used SQGs criteria (i.e. ERL/ERM and TEL/PEL) were used for the association with adverse effects on aquatic organisms whilst a new Index (OEI) was introduced to examine the Overall Environment status.

The overall mineralogical and chemical elemental status of the Alexandroupolis Gulf is mainly dominated by the riverine inputs of Evros system, whereas, localised point sources contribute to the pollution status of the study area. According to the pollution indices used element enrichment and associated potential pollution were found to be related mostly to mud-sized sediments (10–30 m depth), whilst increased element concentrations are observed, spatially, close to Evros river mouths, within the harbour, and along the NW coast of the study area. The application of the SQGs on Cr, Cu, Ni, Pb and Zn showed that almost half of the sampling sites may occasionally be associated with toxic effects. However, according to the OEI, only Zn and Pb provide a widespread positive overall enrichment in the study area.

1. Introduction

The distribution of major and trace elements within the marine sediments is governed by complex natural processes (e.g. hydrodynamic activity, riverine or atmospheric inputs, biological activities), as well as human activities (e.g. discharges of urban, agricultural and industrial wastewater). Sediments accumulate higher levels of hazardous contaminants than water, causing serious problems to biota due to their toxicity and bioaccumulation (Larner et al., 2008; Morillo et al., 2007).

During the last decades, direct (e.g. untreated waste) and indirect (e.g. agricultural runoff) human activities have increased the risk of environmental degradation, especially in coastal areas (Clark, 1993). Riverine inputs are the dominant transport pathway for contaminants, including trace elements, from the continents to the sea (Ip et al., 2007; Radakovitz et al., 2008). In the case of transboundary rivers, the management of their water/sediment fluxes and the related water and sediment quality issues is much more complex, since there are "upstream–downstream" interdependencies between the sharing countries (Wiering et al., 2010).

The Evros River is the second biggest river in the Balkans after the Danube River and it is shared by Bulgaria, Turkey and Greece. Flood events with severe socio-economic and environmental impacts constitute a major problem particularly for the downstream countries (Greece and Turkey) (Skias et al., 2013). Furthermore, a number of studies report the deterioration of the surface water quality in the Bulgarian part (Bird et al., 2010a), as well as in the Greek part (e.g. Lekkas et al., 2004; Skoulikidis, 2009; Dimitriou et al., 2012). All the above cited studies recognize transboundary pollution problems and agree to the need for an integrated management at a river basin scale.

The management of the Evros River basin is, probably, the case of the highest complexity in SE Europe according to Skias et al. (2008), with the

* Corresponding author. Tel.: +30 210 7274195.
E-mail address: kkarditsa@geol.uoa.gr (A. Karditsa).

http://dx.doi.org/10.1016/j.gexplo.2014.08.004
0375-6742/

major constrains concerning the co-operation of the three neighbouring countries with respect to information exchange, administrative shortcomings, political diversities and geographic complexities (Mylopoulos and Kolokytha, 2008). Although these problems are commonly encountered in many transboundary rivers (e.g. Comair et al., 2013; McGlade, 2002), the fact that the river course acts as the natural borderline between Greece and Turkey gives rise to particular and complicated engineering, national defence, and eventually political problems of different nature, dimensions and intensity (Skias et al., 2013) for its lower route and deltaic plain. Existing bilateral agreements and co-operation in the Evros basin cover issues of flood protection and joint infrastructure projects (UN.ECE, 2011), whereas, the only trilateral co-operation was signed in the framework of EU INTERREG IIIA/PHAE CBC Programme Initiative (Skias and Kallioras, 2007).

Apart from the riverine inputs, harbour activities have often been associated with the degradation of the environmental status of bottom sediments in coastal areas, either within the harbour basin and/or in the neighbouring area with pollution related to three main reasons (after Guerra et al., 2000): (i) the decrease of hydrodynamic energy and, therefore, of the ability of the water and seabed sediments to be renewed within the harbour basin; (ii) the presence of human activities (e.g. loading and unloading of raw materials) and (iii) the presence of a nearby coastal city which is associated with the disposal of urban and industrial wastes.

To identify environmental issues in river influenced coastal sediments, including those of semi-closed embayments and/or harbour basins, the distribution of certain major and trace elements in bed sediments has been widely used as pollutant indicators. Such studies, during the past decade, have been conducted along the Mediterranean coast including the Gulf of Lion (Roussiez et al., 2006), Gulf of Izmir (Turkey) (Bergin et al., 2006), Port of Bagnoli (south Italy) (Romano et al., 2004), Gulf of Trieste (Covelli et al., 2006), Algeciras Bay (South of Spain) (Diaz-de Alba et al., 2011) and Eastern Morocco (Makhoukh et al., 2011), reporting in most cases local enrichments related to point sources of pollution (e.g. harbours, fluvial inputs, nearby cities).

The present study examines the pollution status of the surficial seabed sediments of the Alexandroupolis Gulf (NE Aegean shelf), which receives the riverine fluxes from the transboundary and largest Balkan river Evros, through the investigation of the distribution pattern of major and trace element concentrations and the application of state-of-the-art pollution indicators. Previous studies in the area have assessed the distribution of major and trace elements in shallow core sediments only (Kanellopoulos et al., 2006) or focused around the harbour area (Poulos et al., 2007).

2. Study area

2.1. Physico-geographical setting

The Gulf of Alexandroupolis (Fig. 1), which belongs to the inner continental shelf of the NE Aegean Sea (Samothraki Plateau), has a smooth relief with very low gradients (<1%). The seabed has a zonal granulometric distribution with the nearshore sediments (<10 m depth) consisting of sand, the sediments extending to the middle area (10–30 m water depth) consisting of fine-grained (muddy) material, whilst sediments in the offshore area (water depths larger than 30 m) are characterised as muddy sands, representing a transitional zone to relict sandy deposits (Karditsa and Poulos, 2013), which are present at water depths >60 m, at a distance of ~40 km from the coastline (Pehlivanoglou et al., 2000; Perrisoratis et al., 1987). The carbonate content increases seawards from ~10% near the coast up to ~50% in water depths >40 m (Karditsa and Poulos, 2013; Perrisoratis et al., 1987).

The Evros River debouches on the eastern coast of the Gulf (Fig. 1) Its drainage basin is 52,500 km^2 and it is the largest watershed draining the Balkan Peninsula, of which 66% belongs to Bulgaria, 27% to Turkey and 7% to Greece. The Evros River discharges annually approximately 3.2 $\times 10^6$ tones of sediment (Pehlivanoglou, 1989) and 9.5 km^3/year of freshwater (Sari and Çağatay, 2001). The delta of the Evros River is one of the most important wintering areas for birds in the Mediterranean and, as such has been designated as a Ramsar Site, Special Protected Area as well as a Natura 2000 site (in Greece). Similarly, about 33% of the Bulgarian part of the drainage basin has also been designated as a Natura 2000 site, whereas in the Turkish part, the areas of ecological importance are under national protection status (UN.ECE, 2011).

Geologically, the catchment area belongs to the Rhodope geotectonic zone, consisting of more than 50% of clastic formations (i.e. fluvial/deltaic deposits, conglomerates and terrigenous sediments). The remaining 50% consists of Triassic schists, limestones, dolomites, marbles, Plio-Quaternary deposits, granites/diorites, flysch, ultramafic rocks, volcanic/pyroclastic and plutonic rocks and some Precambrian crystalline rocks/migmatites (Kanellopoulos et al., 2008). On the west coast of the study area outcrop the Jurassic to Lower Cretaceous-aged formations of Makri Unit (marbles, dolomites, limestone, calcitic schists,

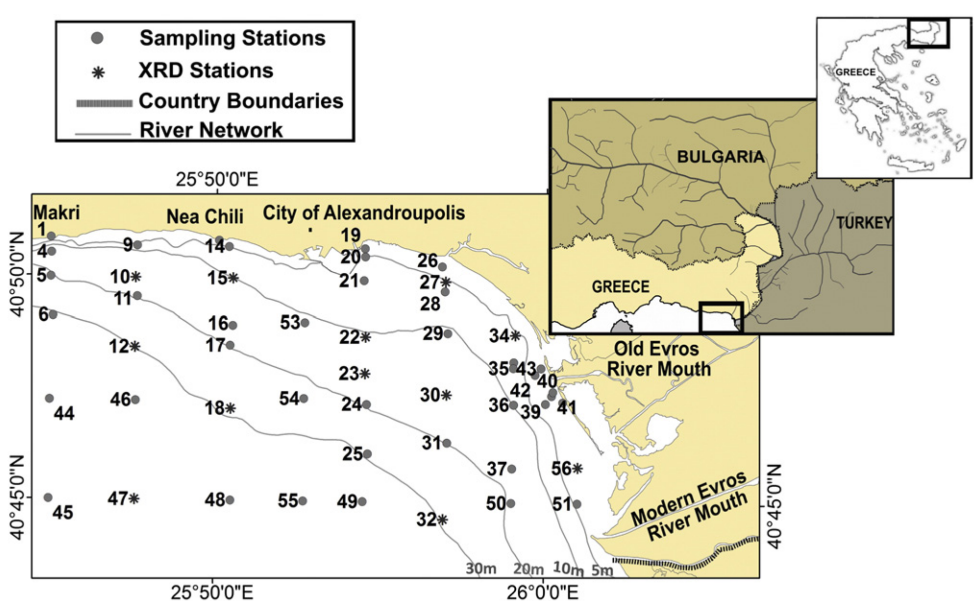


Fig. 1. Location of sampling sites in the Alexandroupolis Gulf and Evros River network system.

sericitic phyllites and greenschists) (Kouris, 1980) and the Upper Cretaceous (Kouris, 1980) or Jurassic–Lower Cretaceous (Papadopoulos, 1982) shales, marls, sandstones, conglomerates and volcano-clastics of Drymos–Melia unit.

The distribution pattern of the Evros River plume is rather variable; it is mainly directed either southwards under the influence of the Samothraki anticyclonic circulation (Olson et al., 2007) or westwards under the combined influence of the prevailing NE winds and the Coriolis Effect.

2.2. Human activities

Human activities within the transboundary Evros River catchment are closely related to industrial waste, urban sewage and agricultural discharge increasing its content in organic and inorganic matter, nutrients and several trace elements (Angelidis and Athanasiadis, 1995).

Since the 1950s, anthropogenic activities near or in the flanks of the Evros River have also been responsible for the hydrological and morphological changes in its delta region. In Bulgaria, the discharge of untreated urban wastewater constitutes a major source of pollution (untreated wastewater and agriculture). Industrial activities (including food production, production of non-ferrous elements and chemicals) are considered to be a potential source of trace elements, organic and nitrogen pollution, although of local importance. In addition, mining activities in mountainous areas are related to surface, groundwater and sediment pollution. In Turkey, untreated domestic wastewater discharges of the Ergene tributary are also one of the main sources of pollution (UN.ECE, 2011). In addition, illegal waste disposal, industrial discharges and unsustainable agricultural practices are additional pressure factors.

Moreover, draining and irrigation works in conjunction with the alignment and settlement of the lower part of the Evros river course, approximately 7 km southern from its natural mouth, in 1950s have modified significantly, qualitatively and quantitatively its water/sediment fluxes in the Gulf of Alexandroupolis.

Amongst human constructions that are expected to have a significant environmental impact on the Gulf are the harbour of the city of Alexandroupolis, the coastal stations of fuel loading located a few km east of the harbour, the outflow of the waste treatment plant discharging west of the harbour, whilst the nearby airport may also be regarded as an indirect pollution source. The Alexandroupolis harbour was first constructed in 1870 (named Dedeağaç at the time) and used as a small piscatorial shelter. After a series of expansions and artificial deepening, it is now one of the main commercial harbours in the NE Aegean Sea.

3. Materials and methods

3.1. Sampling and preparation to analysis procedure

A total of fifty-three (53) surficial sediment samples were collected from the area under investigation, with the use of a van Veen grab, during a sampling campaign in September 2008 (for station locations see Fig. 1). Subsequently, samples were washed out, dried at room temperature (<25 °C) and stored into clean polyethylene (PE) bags. All samples were sieved in sequence through 2 mm and 0.2 mm nylon sieves. Fragments of shells and plant debris were handpicked and removed prior to homogenization in an agate tema mill. Contact with metallic tools and equipment was avoided throughout sediment sample preparation to avoid laboratory contaminations.

3.2. Mineralogical analysis

To identify the mineralogical composition of the collected samples X-ray Diffraction (XRD) analysis was applied to twelve selected samples from diverse water depths, representative of the whole area. The analysis was conducted in the 0.2 mm fraction of sediments, using a Siemens D5005 Diffractometer (Faculty of Geology and Geoenvironment, University of Athens). Although actual concentrations of each mineral could not be defined, a semi-quantitative estimation was carried out based on Cook et al. (1975) methodology, according to which each mineral reflectance to the XRD diffractogram corresponds to a percentage proportion of each mineral in the examined sample.

3.3. Major and trace element analysis

The major and trace element content of the homogenized and pulverized sediment samples was determined after total digestion of the sediment with a mixture of HNO_3–$HClO_4$–HF–HCl acids. The concentrations of Al, Ca, Fe, K, Mg, Na, P, Ti, Ba, Be, Co, Cr, Cu, La, Mn, Nb, Ni, Pb, Sc, Sr, Th, V, Y, Zn and Zr in the solutions were determined by inductively coupled plasma mass spectrometry (ICP-ES, Spectro Arcos) at the ACME Analytical Labs, Vancouver Canada.

3.4. Statistical analyses

Factor analysis was performed, using the SPSS Software (IBM 21.0) in order to reduce the original variables to a set of factors representing the prevalent geochemical processes and/or element sources. The data set included 25 major and trace elements, as well as $CaCO_3$, TOC and mud content which were obtained from Karditsa and Poulos (2013).

Before applying the factor analysis, all individual variables were screened for outliers and skewed distributions by means of box plots and descriptive statistics (skewness and kurtosis). The variables with asymmetric distributions were log transformed. Principal axis factoring was applied at the correlation matrix with the orthogonal Varimax (variance maximizing) rotation.

Factor scores were used for the production of spatial distribution patterns, with the use of the Surfer tool following a kriging method.

3.5. Application of pollution indicators

3.5.1. Enrichment factor (EF)

The enrichment factor (EF) was used to estimate the anthropogenic impact on sediments and define the number of times the natural or reference content of element is exceeded (Tanner et al., 2000); it is calculated using the formula:

$$\mathrm{EF} = ([\mathrm{M}]\mathrm{s}/[\mathrm{R}]\mathrm{s})/([\mathrm{M}]\mathrm{rf}/[\mathrm{R}]\mathrm{rf}) \tag{1}$$

where M is the element concentration, R is the normalizer concentration, s is the sediment sample, and rf is the background value. The normalization procedure and the selection of the background value are described in detail in Section 4.3.1.

The various classes of the level of contamination of sediments, based on enrichment factor, are given in Table 1 (Sutherland, 2000, modified after Roussiez, Roussiez et al., 2006).

3.5.2. Modified degree of contamination (mC_D)

The degree of contamination is a modified pollution factor, introduced initially by Hakanson (1980) and simplified by Abrahim and Parker (2008). It is calculated by the formula:

$$\mathrm{mC_D} = \Sigma \mathrm{Cf}/\mathrm{n} \tag{2}$$

Table 1
Levels of contamination based on EF values (Sutherland, 2000 modified after Roussiez et al., 2006).

EF value	Level of contamination
<1.5	Deficiency to low enrichment
1.5–5	Moderate enrichment
5–20	Significant enrichment
20–40	Very high enrichment
>40	Extreme high enrichment

where n is the total number of samples and Cf = Mx / Mb (where Mx is the mean concentration of the target element in at least five sub-samples and Mb is the concentration of the element in the selected background value).

The degree of contamination is being classified as shown in Table 2.

3.5.3. Sediment Quality Guidelines (SQGs)

The SQGs are used to evaluate sediment quality relative to the potential of adverse effects on sediment-dwelling organisms. The most widely used SQGs criteria are the ERL/ERM (Effects Range Low/Effects Range Median) and the TEL/PEL (Threshold Effects Level/Probable Effects Level) introduced by Long et al. (1995, 1998) and MacDonald et al. (1996), respectively. The TEL/PEL values were derived using concentrations associated with both effects and no observed effects, whereas calculations of the ERL/ERM values were derived using only chemical concentrations associated with adverse effects. The ERL and TEL values represent concentrations below which effects are rarely observed, whereas the ERM and PEL values represent concentrations above which adverse effects on marine organisms are likely to occur. Intermediate frequencies of adverse effects are expected at concentrations between the ERLs and ERMs and between the TELs and PELs. Table 3 presents the SQGs for five trace elements (Long et al., 1995; MacDonald et al., 1996) determined in this study.

4. Results and discussion

4.1. Mineralogical analysis

The mineralogical analysis of the bottom sediments of the Alexandroupolis Gulf revealed that the silicate and aluminosilicate minerals predominate over carbonate minerals (Table 4). Quartz is the single silicate phase, whereas aluminosilicates are represented by K-feldspars, plagioclase, and illite/muscovite. Amphibole, kaolinite and chlorite exist in minor amounts. Heavy minerals such as barite and magnetite are also detected. The carbonate phases are mainly aragonite and minor calcite and Mg-calcite. Dolomite is detected in one sample.

Quartz, K-feldspar, plagioclase, chlorite and amphibole are common minerals not only in the metamorphic rocks of the basement, mainly schists, as well as in the overlain Tertiary tuffs and lavas of acidic composition, but also in younger sedimentary deposits of detrital origin. The presence of muscovite and kaolinite is also attributed to the altered lavas that occur in wide zones north of the town of Alexandroupolis. Barite presence is most likely related to the epithermal mineralisation of Pb–Zn–Au–Ag (Voudouris, 2006). Illite and chlorite are common clay minerals in the fine-grained sedimentary deposits. Aragonite and Mg-calcite are metastable minerals and commonly occur in recent sediments of biogenic origin. In the samples studied, aragonite predominates over all carbonate phases detected. Calcite can be derived from the alteration of marble substrates and/or chemical/biogenic deposition. Dolomite is also related to the weathering of marble substrates. Finally, magnetite is attributed to the metamorphic, ophiolitic and granite rocks and has been detected as Ti-rich variety since 1960s in the Alexandroupolis nearshore zone (Marinos et al., 1976).

Table 2
The various classes of the degree of contamination according to modified pollution factor (mC_D).

mC_D values	Degree of contamination
$mC_D < 1.5$	Zero to very low
$1.5 < mC_D < 2$	Low
$2 < mC_D < 4$	Moderate
$4 < mC_D < 8$	High
$8 < mC_D < 16$	Very high
$16 < mC_D < 32$	Extremely high
$mC_D \geq 32$	Ultra high

Table 3
The values of ERL (Effects Range Low), ERM (Effects Range Median), TEL (Threshold Effects Level) and PEL (Probable Effects Level) concentrations (in mg/kg) for the chemical elements Cu, Pb, Zn, Ni and Cr (after Long et al., 1995,1998 and MacDonald et al., 1996).

	ERL	ERM	TEL	PEL
Cr	81.0	370	52.3	160
Cu	34.0	270	18.7	108
Ni	20.9	51.6	15.9	42.8
Pb	46.7	218	30.2	112
Zn	150	410	124	271

4.2. Major and trace elements

4.2.1. Major and trace element concentrations

The descriptive statistics of major and trace element concentrations (in dry weight) of the surficial sediments of the Alexandroupolis Gulf are presented in Fig. 2.

In order to provide information about the relative homogeneity of the data the relative standard deviation (RSD) = stdev / mean ∗ 100 for its element was investigated. Thus, the major elements Al, Fe and Mg display relative low variability which correspond to RSDs equal to 27.5%, 32.5% and 28.1%, respectively, whereas Ca is found with the extreme heterogeneity of 83.1%. In turn, K and Na display lower RSD (18.7% and 17.4%, respectively) implying homogeneous distribution patterns throughout the study area, whilst, P varies more significantly (39.0%).

Concerning trace elements, Cu, La, Pb, Sr, Th, Zr and Zn vary widely displaying RSD >50% (77.1%, 60.3%, 60.2%, 69.0%, 66.5%, 66.1% and 55.7%, respectively), whereas Ba, Be, Co, Mn, Ni, Nb, Sc, V, and Y present a better homogeneity having RSD <50% (22.3%, 30.1%, 24.7%, 31.8%, 41.8%, 36.0%, 36.5%, 29.9% and 44.5%).

4.2.2. Factor analyses

A model of four factors was retained as the most important which explained 92.2% of the total variance. Factor loadings are given in Table 5, whereas the distribution patterns of the factor scores are illustrated in Fig. 3. Some elements (e.g. Sr, Ti, K, Cr) show high loadings in more than one factor, indicating their complex behaviour.

Factor 1 (F1) represents the largest proportion of the variance of the dataset, accounting for 65.9% (Table 5); it presents high loadings for the major elements Mg, Al and Fe, as well as for mud content and TOC, and moderate loadings for K and Ti. F1 incorporates the majority of trace elements (Ni, Cu, Zn, Pb, Zr, Co, Be, Sc, Nb, Cr), and to some extent V and Th. On the other hand, Ca and Sr show moderate negative loadings.

The presence of major elements (Al, Fe, Mg, K) in this factor characterises the terrigenous aluminosilicate assemblage, which is abundant within the mud (silt and clay) fraction of sediment. Aluminosilicate minerals, together with TOC, are efficient scavengers for trace elements, thus all these variables group together in F1. According to the results of XRD analysis (Table 4), illite is present in the sediment samples. This is in agreement with the work of Pehlivanoglou et al. (2000), reporting that illite is the predominant mineral (52%), followed by smectite (33%) and kaolinite (15%), whereas interstratified illite/smectite is present in small amounts. The negative loadings for Ca and Sr in F1 imply the negative correlation of terrigenous fine-grained aluminosilicates with autochthonous carbonates (see F3).

On the spatial scale, Factor 1 has the highest scores in the muddy sediments that are observed at 10–30 m depths (Fig. 3). Thus, it can be argued that fine-grained sediments of fluvial origin enriched in trace metals and TOC are dispersed by the river plume and then advected and deposited offshore under the prevailing hydrodynamic conditions (Karditsa and Poulos, 2013) in a west-northwest oriented muddy zone. According to Pehlivanoglou et al. (2000), the Evros River supplies the Alexandroupolis Gulf with more than 1,000,000 m^3 of suspended material annually. On the basis of our results, the Evros

Table 4
XRD analysis results of selected bottom sea sediment samples from the Alexandroupolis Gulf (where major component = 3, moderate component = 2 and minor or trace component = 1).

Sample	Depth (m)	Illite/muscovite	Amphibole	Chlorite/kaolinite	Quartz	K-feldspar	Plagioclase	Calcite	Mg-calcite	Dolomite	Magnetite	Aragonite
10	14.9	3	1	1	2	2	2	1		1	1	2
15	10.1	3	1	1	2	1	2				1	2
12	20.5	3	1	1	2	1	1	1			1	2
34	5.0	2	1	1	1	2	3					
27	5.3	2	2	2	1	2	1		1		1	1
18	29.5	1		1	3	1	3	1	1			2
23	15.0	3	1	1	2	2	2	1	1			1
22	11.0	3	1		2	2	2				1	1
30	14.6	3	2	1	2	2	2				1	2
32	29.0	3		1	2	1	1	1			1	2
47	34.5				3	1	2	1	2			3
56	6.0	2	1	1	3	2	3					

River seems to be the major supplier of trace metals to the marine environment, too.

Factor 2 explains 14.1% of the total variance of the dataset, showing positive loadings for P and Ti, very high loadings for La, Y and Th, and moderate loadings for Nb, Sc, Zr, and Cr. The co-variance of Ti, Nb, Sc, Zr and Cr in Factors 1 and 2 most likely signifies their association with two distinct phases; the first phase is abundant in the muddy sediments (Factor 1), whereas the second phase is abundant in the coarser-grained sediments being related to heavy minerals as mentioned by Perissoratis et al. (1987). Subsequently, F2 represents heavy minerals enriched in REE. Spatially, the highest scores of F2 are confined in rather restricted zones in the western as well as the southeastern part of the study area, close to Evros river mouth. Lower scores of F2 are observed to the east of the old river mouth. As heavy minerals are not easily resuspended due to their high specific gravity, these accumulations are most probably related to long-lasting fluvial influence, especially during the period prior to 1950 when the old mouth of the Evros River was active.

Factor 3 accounts for 8.2% of the variance. This is a bipolar factor with high positive loadings for Ba, Na and K and negative loadings for carbonates ($CaCO_3$), Ca and Sr. The co-variance of Sr with Ca and carbonate contents indicates its substitution for Ca in carbonates. The high Sr contents, reaching 1500 mg/kg in the sandy sediments of the southwestern part of the study area, are common in aragonite rich sediments (Karageorgis et al., 2005 and references therein). Whilst the Sr–Ca-carbonate assemblage represents the biogenic carbonates, the association of K and Na with this factor is attributed to the presence of K-feldspars and Na-plagioclase. Mica and feldspars have been found to be enriched in Ba in the sediments of northern Greece (Karageorgis et al., 2005), therefore, the high loadings of Ba in F3 could be explained. The mica and feldspars' component is enriched in the near-shore sediments pronouncing their terrigenous origin. On the contrary, the carbonate component is abundant in the offshore sediments, in the transitional zone to the relict sands (Karditsa and Poulos, 2013). The inverse covariance of these two components of Factor 3 most likely signifies the dilution effect of the autochthonous biogenic carbonates on the terrigenous minerals.

Factor 4 explains only 4.0% of the total variance and is dominated by strong positive loadings for Mn and V. Other elements that are moderately associated with this Factor include P, Ti, Co, Fe and Cr. The highest scores of F4 are recorded in the northwestern sector near-shore sediments, as well as the southeastern sediments in front of the current Evros River mouth. Much lower factor scores occur in the muddy sediments of the intermediate zone (Fig. 3).

The presence of Mn in F4 implies that Mn occurs predominantly in the form of oxides and hydroxides, rather than being held on aluminosilicates (F1). Thus, the accumulations of Mn, V, Ti and P in front of the Evros River mouth could be attributed to the presence of secondarily formed oxides and hydroxides. These secondary minerals may occur either individually or form coatings on other minerals and are considered, in addition to fine aluminosilicates, the most important components of recent origin in surface sediments, serving as scavengers for other elements (e.g. Cr, Co) as well (De Lazzari et al., 2004). On the other hand, the high factor scores in the northwestern part of the

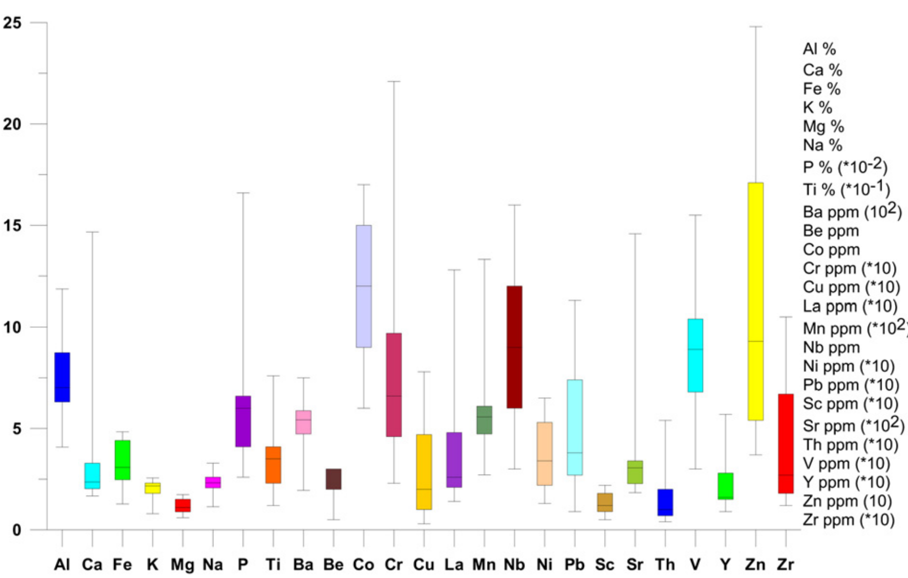


Fig. 2. Box plots of the elemental concentrations of the surficial sediments of the Gulf of Alexandroupolis.

Table 5
Factor loadings and percentages of explained total variance. Key variables of each factor are in bold.

	Factor			
	F1	F2	F3	F4
Al	**.737**	.468	.361	.059
Ca	−.434	−.030	**−.839**	−.281
Fe	**.752**	.413	.073	.503
K	.551	.132	**.789**	−.090
Mg	**.878**	.378	.042	.258
Na	−.045	.052	**.843**	−.021
P	.270	.553	.440	.573
Ti	.494	.495	.409	.537
Ba	.057	−.025	**.920**	−.004
Be	**.766**	.214	.437	.192
Co	**.800**	.178	.133	.517
Cr	**.624**	.476	−.049	.492
Cu	**.913**	.263	.082	.157
La	.349	**.911**	.003	.195
Mn	.176	.405	.162	**.807**
Nb	**.605**	.535	.332	.435
Ni	**.919**	.201	.086	.312
Pb	**.817**	.308	.128	.068
Sc	**.699**	.526	.046	.401
Sr	−.597	−.059	−.564	−.504
Th	.429	**.837**	.134	.297
V	.534	.438	.070	**.711**
Y	.400	**.840**	−.052	.323
Zn	**.877**	.255	.177	.234
Zr	**.814**	.501	.098	.079
CaCO3	.166	−.065	**−.806**	−.413
TOC	**.745**	.322	−.029	.026
Mud	**.896**	.096	.119	.205
% of variance	**65.9**	**14.1**	**8.2**	**4.0**
% cumulative variance	**65.9**	**80.0**	**88.1**	**92.2**

study area in the near-shore sediments could be attributed to the anomalously high concentrations of Mn that could be related to local erosion processes along the coast of Nea Chilli, as mentioned by Xeidakis et al. (2006).

4.3. Pollution indicators

4.3.1. Enrichment factor (EF) — normalization procedures

The elements tested as candidate normalizers are Al, Sc, Zr and Ti, which have been widely applied in geochemical studies (e.g. Ackermann, 1980; Loring, 1990). Amongst these elements, Al and Zr exhibit the strongest correlation coefficients with mud content, thus could effectively compensate for grain size effects. Zirconium has a much larger coefficient of variation (CV) than Al (66% and 27%, respectively) and, also, exceeds the CV of the majority of all other elements; therefore, in order to avoid spurious correlations between the normalized variables (van der Weijden, 2002), Al is eventually chosen for normalization.

The reference values that are considered for the determination of EF include the average shale (after Turekian and Wedepohl, 1961), the offshore surficial sediment from station 45 (see Fig. 1) and the average values of the lower layer (178–224 cm) of a sediment core obtained at a distance of ~2.5 km off the Evros present mouth area (water depth ~10 m) (i.e. core EV01, Kanellopoulos et al., 2008); ^{210}Pb radio-dating showed that this sediment layer was deposited at the beginning of the 20th century (Kanellopoulos et al., 2008).

As shown in Fig. 4 and with respect to average shale as reference background values, the sediments of the Alexandroupolis Gulf are significantly enriched in Pb (EF mean ± sd: 2.53 ± 1.15) and depleted in all other elements. Apparently, the average shale values do not compensate for the lithological particularities of the Evros catchment area, consequently leading to an underestimation of the EF. This is in accordance with the critical aspects reported in literature about the use of the average shale as reference value (e.g. Loring, 1991; Reimann et al., 2002; Salomons and Forstner, 1984; van der Weijden, 2002). Compared to the other two candidate reference values the EV01 core is advantageous over the offshore surficial sediment samples, as it corresponds to pre-industrial depositions, and it is finer-grained presenting lower carbonate content; thus, it precludes the dilution effects on elements of anthropogenic origin. Furthermore, although the rate of sedimentation at the offshore stations is low (about 0.3 mm/year; Kanellopoulos et al., 2008), the sediments deposited in water depths >30 m still bear the signature of recent anthropogenic loads. Hence, the sub-surface cored sediments seem to be more advantageous for the calculation of EFs.

Fig. 5 shows the box-plots of EFs for all the elements for which a reference value in the pre-industrial depositions (cored sediments) was available. According to Fig. 5 and Table 1, the surficial sediments of the Alexandroupolis Gulf are significantly enriched in Pb, moderately enriched in Ca, P, Cr, Cu, Mn, Sr and Zn and deficient in Fe, K, Mg, Ti, Ba, Ni and V.

Considering Pb first, enrichment is evident for all sediment samples (Fig. 5), implying widespread contamination. The highest EF values,

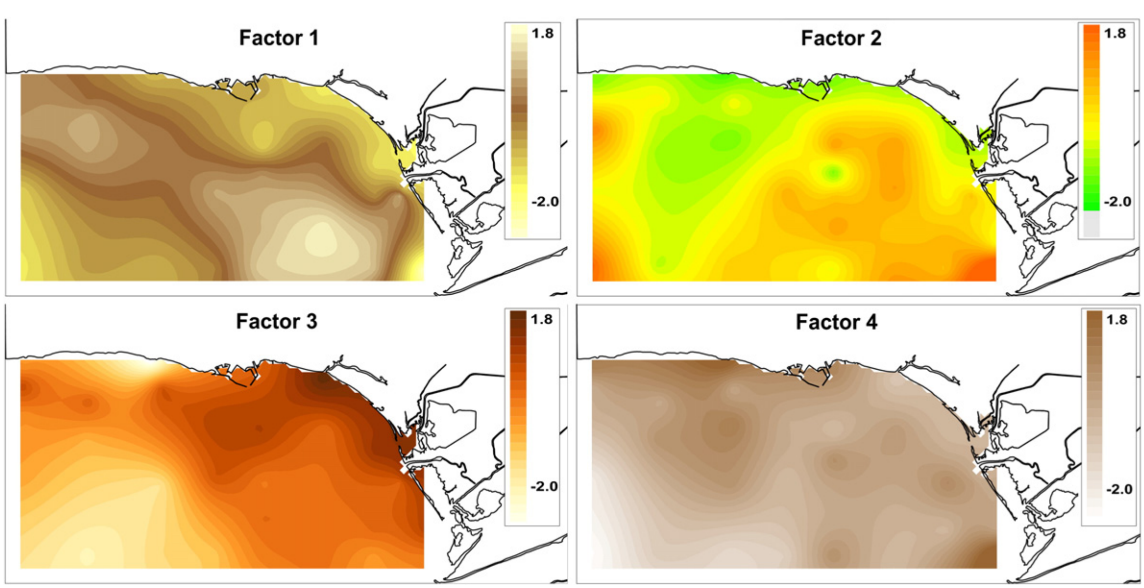
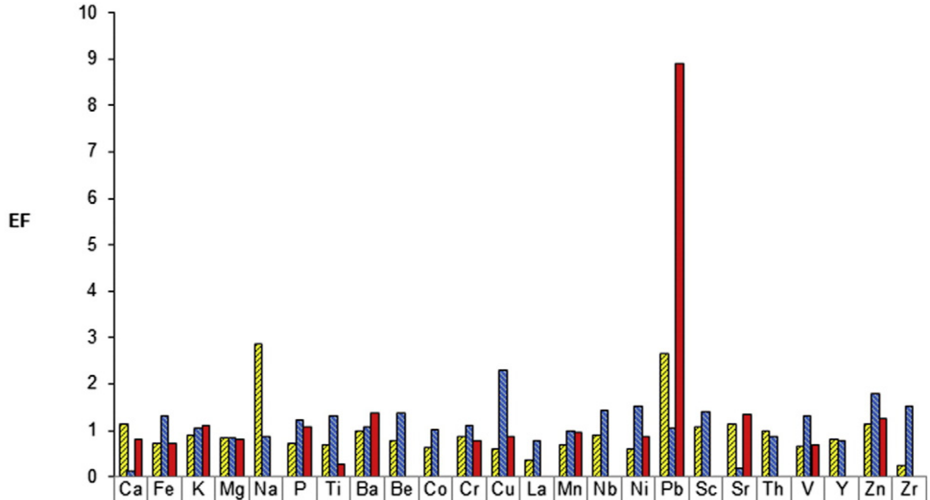


Fig. 3. Distributions of the four factor scores in the Alexandroupolis Gulf.



	Ca	Fe	K	Mg	Na	P	Ti	Ba	Be	Co	Cr	Cu	La	Mn	Nb	Ni	Pb	Sc	Sr	Th	V	Y	Zn	Zr
av. shale	1,1	0,7	0,8	0,8	2,8	0,7	0,6	0,9	0,7	0,6	0,8	0,5	0,3	0,6	0,8	0,5	2,6	1,0	1,1	0,9	0,6	0,8	1,1	0,2
offshore surf. sed.	0,1	1,3	1,0	0,8	0,8	1,2	1,2	1,0	1,3	1,0	1,1	2,2	0,7	0,9	1,4	1,5	1,0	1,3	0,1	0,8	1,3	0,7	1,7	1,5
loc. cored sed.	0,8	0,7	1,1	0,8		1,0	0,2	1,3			0,7	0,8		0,9		0,8	8,9		1,3		0,6		1,2	

Fig. 4. Comparison of Enrichment Factors (median values) estimated using reference values a) the average shale, b) the local cored sediments and c) an offshore, surface sediment sample.

however, are observed in the Alexandroupolis port, indicating a significant point source of pollution (Fig. 6). Lower, yet significant, enrichments are observed throughout the muddy sediments in 10–30 m depth, which coincide with the zone of fluvial depositions from the Evros plume (Fig. 6). Thus, the elevated EF values in the muddy zone could be attributed to the intensive mining activities in the Evros catchment area.

Bird et al. (2010b) used the Pb isotope signature to identify the origin of contaminant metals and established patterns of downstream sediment dispersal within the Evros River catchment; they found that approximately 50% of the channel sediment load within the Evros River originates from the tributaries that are directly affected by mining activities and smelter waste storage. These contaminated sediments are expected to be reduced downstream due to dilution by sediment inputs from other sources. Nevertheless, Bird et al. (2010a) reported that apart from the sediments of the contemporary Evros River channel, significant metal enrichments occur in the floodplain sediments, too. Trace elements associated to floodplain sediments could re-enter the river channel sediments through erosion or flood events. Thus, despite the downstream reduction of contaminated sediments significant contaminant loads could eventually reach the Aegean Sea through erosion and redispersal of floodplains and mine tailings.

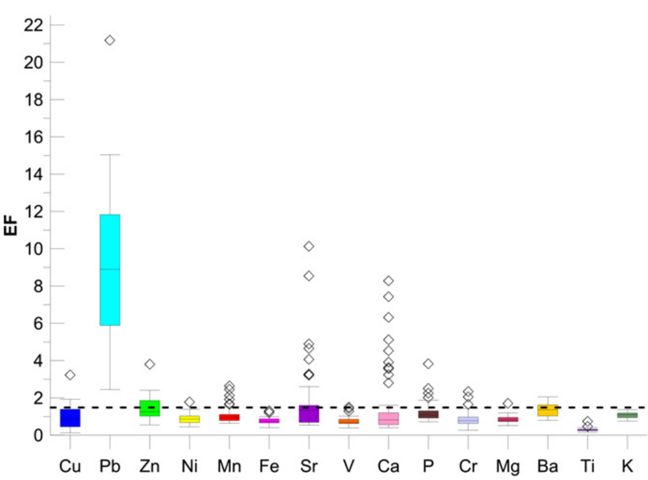


Fig. 5. Box plots of the Enrichment Factors for a suite of elements estimated in relation to local background levels (cored sediments). The dotted line represents the EF threshold value (1.5) above which at least a moderate enrichment is implied.

The spatial distributions of the EFs for Cu and Zn (Fig. 6) are similar to that of Pb; the highest EF values are related to the Alexandroupolis port activities, whereas EF values between 1.4 and 2.2 for Zn and 1.0 and 1.8 for Cu in the muddy sediments are related to the mining activities of Pb–Zn and Pb–Zn–Cu ores of the Rhodope metallogenic zone.

The highest EF values for P and Cr, illustrated as outliers in Fig. 5, are found in the vicinity of the Evros River mouth (Fig. 6); urban waste water as well as industrial effluent and sludges could be responsible for these enrichments. Agricultural runoff could also contribute to P enrichment.

As illustrated in Fig. 5, although the median EF values for Ca and Sr are lower than 1.5, there are a number of samples with EF > 1.5. These sediment samples were obtained from >30 m water depths in the transitional zone to relict sands, which are rich in biogenic carbonates.

Finally, sediments with the highest EF values for Mn (Fig. 6) are mainly located in the western coastal part, where the Makri Quaternary deposits are being eroded (Xeidakis et al., 2006). The same distribution pattern is observed for the EF for Ni which, although in general it has low values, it shows its highest values in the western nearshore zone.

Table 6 presents the EF values for the common "anthropogenic elements" of the sediments of the Alexandroupolis Gulf together with published data for other coastal areas. This approach allows for the direct comparison of contamination in various areas, ensuring conclusions are not influenced by the respective local lithologies. The ranges of EF values of the Alexandroupolis Gulf are, in general, comparable to those reported for Thermaikos Gulf (Christophoridis et al., 2009), Southern Barcelona (Puig et al., 1999), Gulf of Lion (Roussiez et al., 2006), Ligurian Sea (Martin et al., 2009) and Sardinia (Schintu et al., 2009). The high EF values for Cr reported in southern Barcelona are attributed to fluvial inputs of the nearby Besos River (Puig et al., 1999). Higher EF values for Cu and Pb have been reported for the Harbour of Malta (Huntingford and Turner, 2011) and for Cu, Pb and Zn in Toulon (Tessier et al., 2011) which are related to the shipwrecks from the 2nd world war. Finally, Izmir Bay presents high EFs for Cu and Zn (Atgin et al., 2000), which are attributed to long term untreated discharges of leather industries.

4.3.2. Degree of contamination (mC_D)

The degrees of contamination (mC_D) of the examined elements are presented in Fig. 7. According to the median values, all the elements

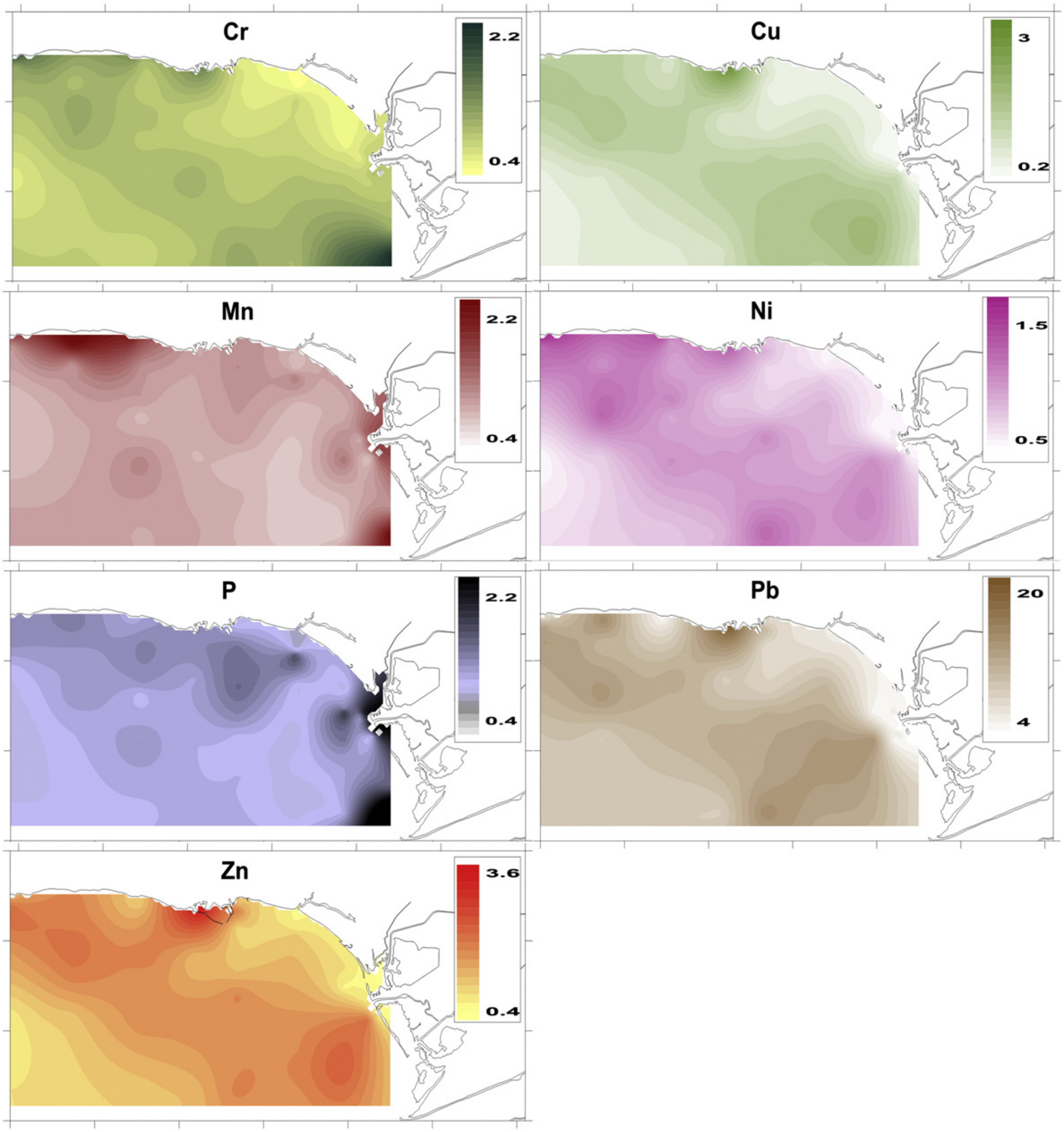


Fig. 6. Spatial distributions of the Enrichment Factors (EFs) for the elements that according to Table 1 show moderate to significant enrichment.

Table 6
Comparison of EF values (ranges and mean value) estimated for the surficial sediments of the Alexandroupolis Gulf and other coastal areas.

Study area	Reference value	Cr	Cu	Ni	Pb	Zn
Current study	Local background	0.27–2.35	0.13–3.23	0.45–1.79	2.45–21.18	0.55–3.81
Thermaikos Gulf[a]	Average shale		0.8–7.7 (2.9)		0.7–15.4 (5.1)	0.7–3.5 (1.7)
Gulf of Lions[b]	Local background		0.7–2.3	1–8.5	2.0–3.8	1.5–2.9
Izmir Bay[c]	Soil composition		0.5–17 +	1.3–1.6	0.8–10	0.9–9.5
Southern Barcelona[d]	Local background	0.3–30 +	1.1–3.4			1.85–3.7
North Ligurian Sea (NW Med Sea)[e]	Local background	1.1–2.5	1.4		1.5	1.2
Malta Harbours[f]	Local baseline (beach sand)		5.97–9.94		5.98–8.69	1.07–1.76
Toulon Bay (SE France)[g]	Local background	0.27–0.53	0.8–83.6		1.1–31.0	1.2–40.2
Coastal sediments of Sardinia (Italy)[h]	Local background	0.2–3.6	0.3–2.5			0.5–2.4

[a] Christophoridis et al. (2009).
[b] Roussiez et al. (2006).
[c] Atgin et al. (2000).
[d] Puig et al. (1999).
[e] Martin et al. (2009).
[f] Huntingford and Turner (2011).
[g] Tessier et al. (2011).
[h] Schintu et al. (2009).

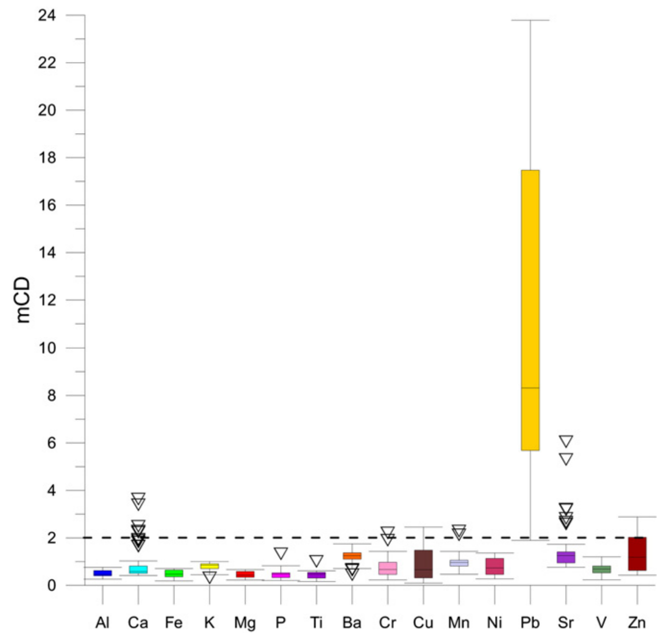


Fig. 7. Degree of contamination (mC_D) of the surficial sediments of the Alexandroupolis Gulf.

show zero to very low degree (<2) of contamination with the exception of the very high degree (>8) of contamination related to Pb concentrations. Even considering the highest concentrations, only Cu and Zn present high degrees of contamination of the sediments, whilst Ca, Cr, Mn and Sr indicate some outliers to moderate degree of contamination.

4.3.3. Sediment Quality Guidelines (SQGs)

Table 7 presents the percentages of samples in the three ranges of SQGs where the concentrations of Cu, Pb, Zn, Ni and Cr in the studied sediments could be rarely (≤ERL and ≤TEL), occasionally (between ERL–ERM and TEL–PEL) and frequently (≥ERM and ≥PEL) associated with adverse effects on the biota.

For both sets of SQGs, ERL/ERM and TEL/PEL, Ni concentrations in a relatively large proportion of samples (32.1% and 45.3%, respectively) exceed the probable effects-range (≥ERM and ≥PEL). However, the reliability of the mid range SQGs (ERM and PEL) for Ni is relatively low compared to the guidelines for most other chemicals, for which SQGs have been established. Therefore, the probabilities of observing toxicity in the samples that exceed only the SQGs for Ni would be much lower (Long et al., 1998). Furthermore, it should be noted that the local background level of Ni, established by the analysis of pre-industrialized cored depositions (Section 4.3.1), equals the mid-range SQGs and is 2–3 times higher than the low-range SQGs. Apparently, the SQGs for Ni are over-conservative for the study area.

Apart from Ni, the local background levels exceed the low-range SQGs (both ERL and TEL) for Cr and the TEL value for Cu, hence the

Table 7
Percentages (%) of the total sediment samples amongst ranges of Sediment Quality Guidelines (for threshold values see Table 3).

	<ERL	(%)	ERL–ERM	(%)	>ERM	(%)
	<TEL	(%)	TEL–PEL	(%)	>PEL	(%)
Cu	56.6	43.4	0.0		47.2	52.8
0.0	Pb	52.8	47.2	0.0		28.3
67.9	3.8	Zn	64.2	35.8	0.0	
52.8	45.3	1.9	Ni	17.0	50.9	32.1
	1.9	52.8	45.3	Cr	60.4	39.6
0.0		35.8	60.4	3.8		

number of samples that is in the occasional effects-range for these elements is overestimated. This is a common finding for several elements, particularly for Ni and Cr in other study areas, too (e.g. Aptiz et al., 2007; Guerra et al., 2009). In such cases, Chapman et al. (1999) recommend the replacement of SQGs with the background values. By replacing the ERL for Ni with the background level, the percentage of samples that could occasionally or frequently be associated with adverse effects decreases from 83% to 36%. Similarly, following this approach for the ERL and TEL values for Cr, the number of samples that is in the occasional effects-range decreases from 39.6% to 24.5% and from 60.4% to 20.8%, respectively.

As far as Pb and Zn are concerned, all SQGs are higher than the estimated background levels of these elements. The concentrations of Pb exceed PEL values only in two out of fifty three sediment samples. These sediments were obtained off the old river mouth (stations 39 and 30) and have the greatest potential of causing adverse effects on sediment-dwelling organisms. The concentrations of Zn exceed the respective PEL only in the sediments from the port of Alexandroupolis. For Pb and Zn, a relatively large proportion of samples (36% to 64%; Table 7) are in the occasional effects-range. These sediments are found mainly in water depths of 10–30 m, associated to the fine grained (muddy) sediments.

Finally, taking into consideration the local background levels, in 49% and 26% of samples no ERLs and TELs are exceeded respectively for any of the trace elements studied. These samples with the lowest probability for observing toxicity are located mainly at the sandy stations of Evros river mouth, eastwards the harbour area and in the transitional zone to relict sands (water depths >30 m).

4.4. Overall Enrichment Index (OEI)

In order to investigate the degree of the overall enrichment status in the study area, a new index is introduced, which combines all the applied aforementioned indices (EF, mC_D, SQGs). According to this index, sediments are characterised as having positive OEI (positively enriched) when they appear to be at least moderately enriched (EF > 1.5), moderately contaminated (mC_D > 2) and possibly toxic (element concentration > ERL threshold value, as given by SQGs), simultaneously. Although there are several studies that assess sediment quality by the application of pollution indicators (e.g. Christophoridis et al., 2009; Seshan et al., 2010; Kalender and UÇar, 2013; Gredilla et al., 2014; Zhuang and Gao, 2014), this innovative approach (OEI) attempts to concentrate, combine and visualise the overall degradation of sediment quality.

The application of OEI in the study area (Fig. 8) shows a positive enrichment for Pb and Zn throughout a broad zone extending between 10 and 30 m of water depth. Sediments within this zone are fine-grained, thus, the distribution pattern of the OEI for Pb and Zn underlines that these fine aluminosilicates are the major carrier phase for trace elements (Roussiez et al., 2006; Loring, 1990 and references therein; Salomons and Forstner, 1984). In addition, positive OEI appears for the sediment samples taken from the inner harbour, as well as for one sample to the east of the harbour, where the station of fuel loading is located. Accumulations of trace elements in the harbour sediments are reported by Chen et al. (2007), Cukrov et al. (2011), Abdollahi et al. (2013), Briant et al. (2013) and Huerta-Diaz et al. (2014). Transboundary pollution through international rivers is also reported in literature (e.g. Hills et al., 1998; Kalender and UÇar, 2013; Suleymanov et al., 2010; Zhao et al., 2012). Although pollution control measures of point sources could be considered for the protection or restoration of the sediment quality, this is a rather complex task in the case of transboundary riverine inputs, where co-operation at an institutional, legal and political level is a prerequisite.

As far as Cu is concerned, sediments displaying positive OEI originate from the harbour basin, close to the Evros mouth, as well as at the north-western part of the study area and are muddy in texture. The OEI for Ni and Cr shows positive enrichments only in one sediment sample, taken

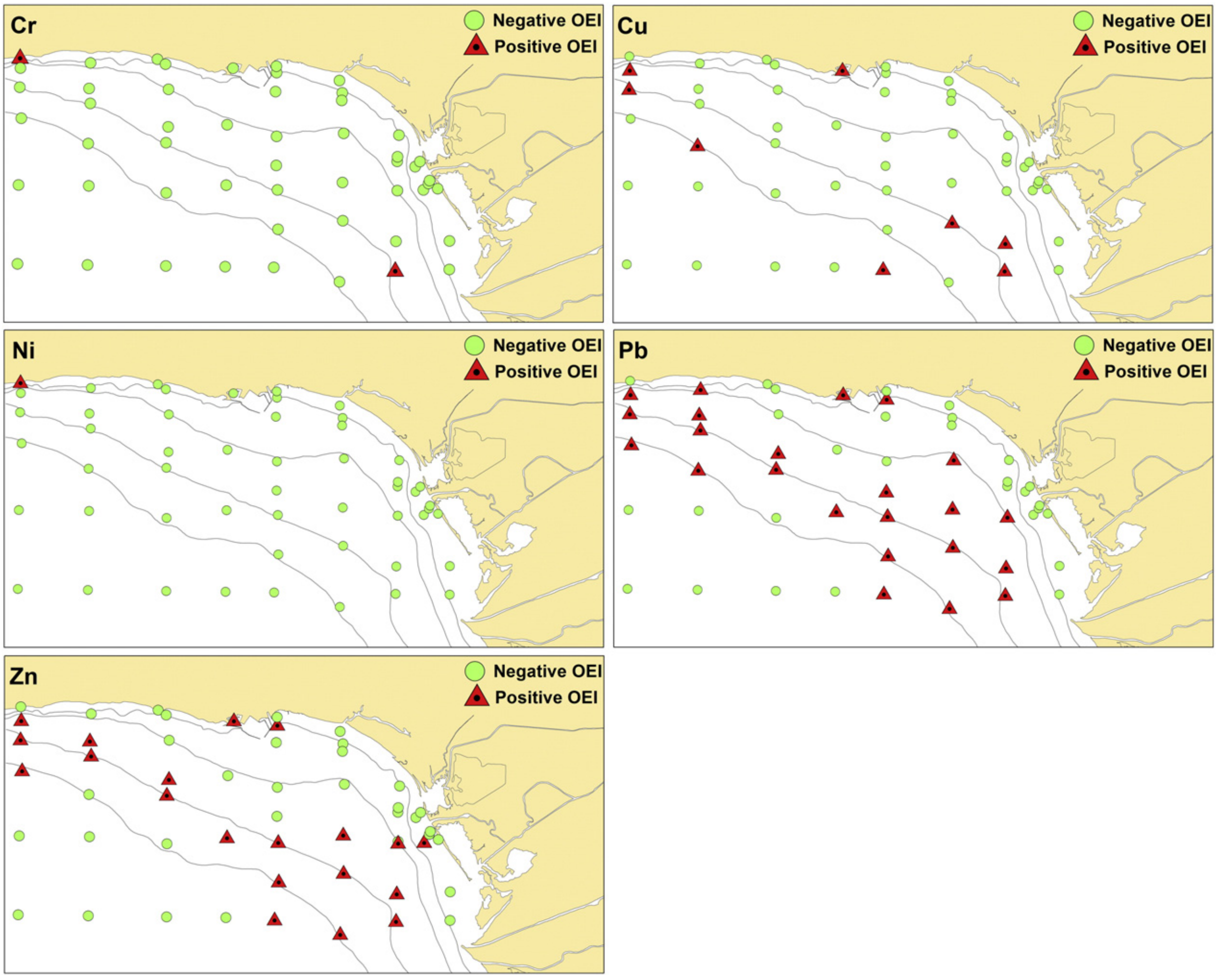


Fig. 8. Overall Enrichment Index for Cr, Cu, Ni, Pb and Zn (i.e. EF > 1.5, mC_D > 2 and elements concentrations > ERL values) for all sampling sites.

from the northwestern part of the study area, close to the shore. These enrichments could be related to the ophiolitic formations of the Makri Zone that underlie Quaternary formations (Meinhold and Kostopoulos, 2013). An additional sediment sample positively enriched in Cr is observed close to the Evros mouth, associated with fine grained sediments.

5. Conclusions

The overall enrichment status of the Alexandroupolis Gulf is mainly dominated by the riverine inputs of the Evros system, whereas, localized point sources contribute to the pollution status of the study area. This conclusion is indicated by the application of pollution indices performed for 25 elements together with the $CaCO_3$, TOC and mud content and supported by the newly introduced OEI. Increased trace element concentrations are observed spatially in the nearshore area close to Evros river mouths, within the harbour, in the offshore area extending between the 10 m and 30 m bathymetric contours, and in the NW nearshore area. The same areas are also related to the increased elemental enrichment according to pollution indices (EF, mC_D).

With respect to the Sediment Quality Guidelines and regarding Cr, Cu, Ni, Pb and Zn, more than half of the sediment samples could be occasionally, or frequently, connected to toxic effects on aquatic organisms. However, regarding Ni, Cr and Cu, a large proportion of samples exceeding the ERM and ERL thresholds are estimated to be over-conservative, because of the local background levels. In this case, toxic concentrations decrease significantly when replacing SQGs with the background values. As far as Pb and Zn are concerned, a relatively large proportion of samples are in the occasional effects-range and only in some localized samples (off the old river mouth for Pb and within the Alexandroupolis harbour for Zn) they exceed PEL concentrations.

The Overall Enrichment Index (OEI) infiltrates the results given by the application of pollution indices (EF, mC_D, SQGs) and indicates extensive positive enrichment in the Alexandroupolis Gulf for Zn and Pb, whilst Cu displays a positive OEI only in the harbour basin, close to the Evros mouth, as well as in the muddy sediments of the northwestern part of the study area. Finally, Ni and Cr are positively enriched only locally in one northwestern nearshore sample of the study area.

Summarizing the above results, it is clear that there are two main factors that contribute to the degradation of sediment quality with respect to trace element contents: (i) port activities and (ii) the pollution load carried by the Evros River. The influence of port activities is restricted only in the close vicinity of this point source, whilst on the contrary, the influence of the Evros River is evident throughout a much wider area.

Acknowledgments

The authors are thankful to Mrs. Theodora Paramana for the critical reading of the manuscript and to both reviewers of the paper for their constructive comments.

Annex. Major and trace element concentrations

Station	Depth (m)	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	Ti (%)
38	2.0	6.06	2.37	2.47	1.91	0.73	2.46	0.074	0.37
41	2.5	6.31	2.82	3.03	1.74	0.89	2.32	0.103	0.46
43	2.5	6.12	2.57	2.49	1.80	0.84	2.35	0.090	0.36
33	2.5	6.55	2.09	1.86	2.03	0.74	2.72	0.054	0.25
19	2.5	7.15	2.09	2.47	2.19	0.97	2.79	0.040	0.26
26	2.6	7.01	1.82	1.62	2.23	0.69	2.90	0.035	0.18
13	2.9	4.08	10.04	3.00	0.80	0.93	1.14	0.027	0.14
51	3.0	6.65	3.66	4.57	1.63	1.15	2.39	0.166	0.76
42	3.9	6.33	1.97	1.65	2.00	0.66	2.60	0.045	0.22
40	4.6	7.10	1.78	2.49	2.33	0.94	2.45	0.046	0.27
39	5.1	10.77	1.67	4.45	2.56	1.56	1.87	0.065	0.45
34	5.1	7.01	1.91	1.90	2.31	0.80	2.74	0.039	0.22
20	5.1	6.98	2.40	2.83	2.16	1.06	2.47	0.047	0.30
27	5.3	7.11	1.83	1.82	2.10	0.77	2.88	0.033	0.20
14	5.4	4.71	6.68	2.45	1.18	0.86	1.65	0.034	0.18
56	6.0	6.95	2.62	2.62	2.07	0.95	2.55	0.072	0.34
35	7.0	7.22	2.87	2.51	1.89	1.06	2.48	0.095	0.36
1	7.3	4.51	9.00	3.35	1.14	1.47	1.32	0.035	0.17
28	8.7	6.76	2.63	2.76	2.06	0.97	2.75	0.080	0.39
36	9.9	7.02	2.47	3.43	2.18	1.19	2.31	0.066	0.38
29	10.0	10.85	2.01	4.35	2.20	1.54	2.10	0.062	0.44
15	10.1	6.98	2.31	3.08	2.20	1.10	2.59	0.061	0.34
22	11.0	7.09	2.47	2.72	2.01	0.99	2.62	0.070	0.34
53	11.0	7.22	2.20	2.71	2.32	1.01	2.62	0.051	0.29
9	11.6	6.64	4.15	3.51	1.99	1.35	3.29	0.059	0.30
30	14.6	11.86	2.30	4.55	2.48	1.59	2.16	0.065	0.43
10	14.9	7.78	2.36	3.62	2.28	1.31	2.17	0.062	0.37
37	15.0	9.73	1.91	4.53	2.30	1.51	2.12	0.069	0.42
4	15.0	6.96	3.03	3.75	1.98	1.27	2.19	0.059	0.35
23	15.0	7.17	2.11	3.53	2.27	1.25	2.45	0.060	0.36
16	15.2	7.30	2.03	3.63	2.26	1.29	2.21	0.060	0.36
11	17.7	7.52	2.17	3.88	2.34	1.40	2.12	0.054	0.37
24	19.3	10.71	2.08	4.48	2.36	1.59	2.26	0.064	0.42
5	19.8	7.65	2.19	3.99	2.28	1.45	2.32	0.062	0.39
31	19.9	11.02	2.10	4.65	2.44	1.63	2.24	0.066	0.42
12	20.5	10.57	2.08	4.41	2.30	1.59	2.07	0.064	0.40
50	21.0	10.94	1.96	4.62	2.34	1.68	2.63	0.071	0.42
54	25.0	9.99	2.03	4.41	2.50	1.60	2.02	0.065	0.41
21	29.0	6.81	2.41	2.48	2.08	0.93	2.86	0.064	0.32
12	29.4	7.04	3.29	3.81	2.17	1.37	2.23	0.053	0.33
18	29.5	6.09	6.67	3.40	1.68	1.15	1.78	0.048	0.29
32	29.7	11.67	2.15	4.84	2.45	1.74	2.61	0.070	0.44
25	30.0	10.56	1.94	4.80	2.34	1.67	2.35	0.069	0.43
6	31.4	11.00	2.42	4.58	2.33	1.71	2.37	0.065	0.41
45	34.5	4.73	13.70	1.50	1.34	0.88	1.87	0.028	0.15
47	34.5	4.55	14.67	1.56	1.30	0.93	1.78	0.027	0.14
46	35.0	5.28	7.35	2.09	1.63	0.82	1.94	0.034	0.19
48	36.0	5.22	9.21	1.95	1.61	0.84	1.78	0.033	0.19
55	36.0	6.18	7.82	2.50	1.77	1.00	1.92	0.041	0.23
44	36.5	5.00	7.64	1.28	1.78	0.60	1.91	0.026	0.12
49	39.0	8.74	1.90	4.46	2.30	1.60	2.53	0.058	0.40

Station	Depth (m)	Ba (ppm)	Be (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	La (ppm)	Mn (ppm)	Nb (ppm)	Ni (ppm)
38	2.0	571	2	9	51	4	56	705	8	19
41	2.5	512	2	10	64	4	84	804	10	19
43	2.5	521	2	8	50	3	41	665	8	19
33	2.5	639	2	8	30	4	23	471	6	18
19	2.5	618	2	11	36	11	15	595	7	29
26	2.6	662	2	9	23	6	14	400	6	20
13	2.9	195	0.5	12	64	14	14	658	3	33
51	3.0	479	2	12	190	13	128	1239	16	29
42	3.9	645	2	7	33	4	23	391	5	17
40	4.6	636	2	10	75	22	21	473	7	32
39	5.1	622	3	17	86	47	49	541	15	54
34	5.1	660	2	8	28	9	15	437	6	22
20	5.1	574	2	12	48	18	17	563	8	34
27	5.3	677	2	9	24	7	15	385	6	21
14	5.4	292	1	11	46	11	18	594	4	27
56	6.0	574	2	10	81	20	27	556	9	28

(continued on next page)

(continued)

Station	Depth (m)	Ba (ppm)	Be (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	La (ppm)	Mn (ppm)	Nb (ppm)	Ni (ppm)
35	7.0	578	2	9	48	6	48	610	8	22
1	7.3	274	1	16	113	15	19	656	4	47
28	8.7	588	2	10	52	12	38	625	10	27
36	9.9	558	3	14	66	33	25	687	11	42
29	10.0	505	3	15	79	36	49	589	13	53
15	10.1	750	2	12	60	26	23	557	9	36
22	11.0	595	2	10	46	15	29	541	9	28
53	11.0	599	2	11	53	17	18	478	8	30
9	11.6	403	2	15	84	36	22	1332	9	46
30	14.6	642	3	15	115	65	63	578	13	55
10	14.9	576	3	14	76	36	32	577	11	45
37	15.0	514	3	14	143	73	44	536	13	61
4	15.0	450	2	14	88	41	20	527	10	50
23	15.0	577	3	13	68	35	21	538	11	44
16	15.2	544	3	14	78	38	21	549	11	46
11	17.7	554	3	15	100	43	23	618	11	51
24	19.3	553	3	14	91	55	50	584	13	56
5	19.8	511	3	14	93	47	24	542	11	53
31	19.9	554	3	15	124	69	52	569	12	60
12	20.5	524	3	14	97	53	49	587	12	54
50	21.0	473	3	15	221	78	50	540	13	65
54	25.0	543	3	15	118	54	47	594	12	56
21	29.0	582	2	10	42	10	26	573	8	25
12	29.4	508	3	13	86	43	21	473	10	52
18	29.5	347	2	12	66	25	31	540	7	36
32	29.7	488	3	15	126	61	63	578	14	64
25	30.0	493	3	15	109	61	45	660	13	60
6	31.4	508	3	15	106	54	59	632	12	58
45	34.5	322	1	7	41	7	26	349	4	16
47	34.5	304	1	7	39	8	23	329	4	18
46	35.0	376	2	8	46	12	23	344	5	21
48	36.0	372	2	8	41	11	23	349	6	22
55	36.0	384	2	9	59	18	30	431	7	29
44	36.5	471	1	6	27	6	18	271	3	13
49	39.0	473	3	15	114	54	35	523	12	64

Station	Depth (m)	Pb (ppm)	Sc (ppm)	Sr (ppm)	Th (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
38	2.0	11	10	311	20	79	26	44	15
41	2.5	12	13	313	31	99	37	48	19
43	2.5	21	11	301	19	80	26	43	13
33	2.5	19	8	330	7	57	15	38	16
19	2.5	35	8	320	6	61	11	83	19
26	2.6	27	6	340	5	43	9	43	15
13	2.9	9	14	418	4	90	15	46	14
51	3.0	34	18	313	54	155	57	87	32
42	3.9	12	7	320	8	49	13	47	12
40	4.6	31	9	290	8	68	14	93	25
39	5.1	21	20	207	21	112	34	244	76
34	5.1	22	7	329	5	51	11	61	17
20	5.1	51	10	288	7	72	12	150	23
27	5.3	27	7	327	6	47	9	51	17
14	5.4	19	11	353	5	71	14	51	16
56	6.0	37	11	308	10	75	18	89	23
35	7.0	19	13	343	16	81	29	64	21
1	7.3	9	14	371	6	90	14	54	18
28	8.7	34	11	313	16	81	22	80	24
36	9.9	74	13	258	10	98	18	141	40
29	10.0	83	19	221	23	104	29	144	73
15	10.1	45	11	284	9	81	15	119	27
22	11.0	38	11	310	12	75	18	86	25
53	11.0	41	10	306	7	70	13	91	22
9	11.6	74	12	383	9	89	15	136	31
30	14.6	113	20	246	23	108	32	203	81
10	14.9	56	13	255	11	93	20	152	41
37	15.0	85	19	192	18	106	28	248	74
4	15.0	63	13	215	9	104	15	153	35
23	15.0	62	12	258	9	89	15	141	33
16	15.2	64	12	244	9	92	15	151	34
11	17.7	63	13	234	8	96	16	174	38
24	19.3	94	19	228	21	104	29	185	71
5	19.8	74	14	215	10	106	16	169	42
31	19.9	107	20	213	20	109	29	206	78
12	20.5	85	19	221	20	101	32	185	75

(continued)

Station	Depth (m)	Pb (ppm)	Sc (ppm)	Sr (ppm)	Th (ppm)	V (ppm)	Y (ppm)	Zn (ppm)	Zr (ppm)
50	21.0	92	20	187	20	110	31	245	84
54	25.0	87	18	217	17	105	25	184	71
21	29.0	30	10	315	10	71	17	66	19
12	29.4	72	13	260	9	100	15	144	39
18	29.5	46	11	622	9	87	17	111	33
32	29.7	99	22	210	25	113	34	196	105
25	30.0	95	20	193	20	110	26	198	79
6	31.4	95	21	229	25	110	33	188	81
45	34.5	30	6	1279	8	38	16	40	14
47	34.5	30	6	1458	7	38	15	44	16
46	35.0	31	8	680	7	53	14	63	23
48	36.0	31	7	769	6	49	15	60	21
55	36.0	36	9	642	10	61	16	81	27
44	36.5	33	5	774	4	30	11	37	13
49	39.0	95	16	184	14	112	21	171	67

References

Abdollahi, S., Raoufi, Z., Faghiri, I., Savari, A., Nikpour, Y., Mansouri, A., 2013. Contamination levels and spatial distributions of heavy metals and PAHs in surface sediment of Imam Khomeini Port, Persian Gulf, Iran. Mar. Pollut. Bull. 71 (1–2), 336–345.

Abrahim, G.M.S., Parker, R.J., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. Estuar. Coast. Shelf Sci. 136, 227–238.

Ackermann, F., 1980. A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. Environ. Technol. Lett. 1, 518–527.

Angelidis, M.O., Athanasiadis, A.I., 1995. Pollution mechanisms in a Ramsar wetland: delta of River Evros, Greece. Aquat. Sci. 57, 161–171.

Aptiz, S.E., Barbanti, A., Bocci, M., Carlin, A., Montobbio, L., Bernstein, A.G., 2007. The sediments of the Venice Lagoon (Italy) evaluated in a screening risk assessment approach: part I—application of international sediment quality guidelines. Integr. Environ. Assess. Manag. 3 (3), 393–414.

Atgin, R.S., El-Agha, O., Zararsız, A., Kocataş, A., Parlak, H., Tuncel, G., 2000. Investigation of the sediment pollution in Izmir Bay: trace elements. Spectrochim. Acta B 55, 1151–1164.

Bergin, F., Kucuksezgin, F., Uluturhan, E., Barut, I.F., Meric, E., Avsar, N., 2006. The response of benthic foraminifera and ostracoda to heavy metal pollution in Gulf of Izmir (Eastern Aegean Sea). Estuar. Coast. Shelf Sci. 66, 368–386.

Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010a. Dispersal of contaminant metals in the mining-affected Danube and Maritsa drainage basins, Bulgaria, Eastern Europe. Water Air Soil Pollut. 206, 105–127.

Bird, G., Brewer, P., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010b. Quantifying sediment-associated metal dispersal using Pb isotopes: application of binary and multivariate mixing models at the catchment-scale. Environ. Pollut. 158, 2158–2169.

Briant, N., Bancon-Montigny, C., Elbaz-Poulichet, F., Freydier, R., Delpoux, S., Cossa, D., 2013. Trace elements in the sediments of a large Mediterranean marina (Port Camargue, France): levels and contamination history. Mar. Pollut. Bull. 73 (1), 78–85.

Chapman, P.M., Allard, P.J., Vigers, G.A., 1999. Development of sediment quality values for Hong Kong Special Administrative Region: a possible model for other jurisdictions. Mar. Pollut. Bull. 38 (3), 161–169.

Chen, C.-W., Kao, C.-M., Chen, C.-F., Dong, C.-D., 2007. Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 88 (8), 1431–1440.

Christophoridis, C., Dedepsidis, D., Fytianos, K., 2009. Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessments using pollution indicators. J. Hazard. Mater. 168, 1082–1091.

Clark, R.B., 1993. Marine Pollution, 3rd ed. Oxford University Press, p. 172.

Comair, G.G., McKinney, D.C., Scoullos, M.J., Flinker, R.H., Espinoza, G.E., 2013. Transboundary cooperation in international basins: clarifications and experiences from the Orontes River Basin agreement: part 2. Environ. Sci. Policy 31, 141–148.

Cook, E.H., Johnson, D.P., Matii, C.J., Zemmels, I., 1975. Methods of sample preparation and X-Ray diffraction data analysis, D.S.D.P. Init. Rep. 28, 999–1007.

Covelli, S., Fontolan, G., Faganeli, J., Ogrinc, N., 2006. Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea). Mar. Geol. 230, 29–51.

Cukrov, N., Franc˘iškovic-Bilinski, S., Hlac, B., Barišic, D., 2011. A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia. Mar. Pollut. Bull. 62, 154–167.

De Lazzari, A., Rampazzo, G., Pavoni, B., 2004. Geochemistry of sediments in the Northern and Central Adriatic Sea. Estuar. Coast. Shelf Sci. 59, 429–440.

Diaz-de Alba, M., Galindo-Ria, M.D., Casanueva-Marenco, M.J., Garcia-Vargas, M., Kosore, C.M., 2011. Assessment of the metal pollution, potential toxicity and speciation of sediment from Algeciras Bay (South of Spain) using chemometric tools. J. Hazard. Mater. 190, 177–187.

Dimitriou, E., Mentzafou, A., Zogaris, S., Tzortziou, M., Gritzalis, K., Karaouzas, I., Nikolaidis, C., 2012. Assessing the environmental status and identifying the dominant pressures of a trans-boundary river catchment, to facilitate efficient management and mitigation practices. Environ. Earth Sci. 66, 1839–1852.

Gredilla, A., Ortiz, Fdez-, de Vallejuelo, S., de Diego, A., Arana, G., Madariaga, J.M., 2014. A new index to sort estuarine sediments according to their contaminant content. Ecol. Indic. 45, 364–370.

Guerra, R.M., Martın, R., Vila, J., Romo, J., 2000. Informe de Caracterització dels sediments en el Port de Barcelona. Servei de Medi Ambient de l'Autoritat Portuària de Barcelona.

Guerra, R., Pasteris, A., Ponti, M., 2009. Impacts of maintenance channel dredging in a northern Adriatic coastal lagoon. I: effects on sediment properties, contamination and toxicity. Estuar. Coast. Shelf Sci. 85, 135–142.

Hakanson, L., 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 14, 975–1001.

Hills, P., Zhang, L., Liu, J., 1998. Transboundary pollution between Guangdong Province and Hong Kong: threats to water quality in the Pearl River Estuary and their implications for environmental policy and planning. J. Environ. Plan. Manag. 41 (3), 375–396.

Huerta-Diaz, M.A., Munoz-Barbosa, A., Otero, X.L., Valdivieso-Ojeda, J., Amaro-Franco, E.C., 2014s. High variability in geochemical partitioning of iron, manganese and harmful trace metals in sediments of the mining port of Santa Rosalia, Baja California Sur, Mexico. J. Geochem. Explor. http://dx.doi.org/10.1016/j.gexplo.2014.05.014 (In Press).

Huntingford, E.J., Turner, A., 2011. Trace metals in harbour and slipway sediments from the island of Malta, central Mediterranean. Mar. Pollut. Bull. 62 (7), 1557–1561.

Ip., C.C.M., Li, X.D., Zhang, G., Wai, O.W.H., Li, Y.S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environ. Pollut. 147, 311–323.

Kalender, L., UÇar, S.C., 2013. Assessment of metal contamination in sediments in the tributaries of the Euphrates River, using pollution indices and the determination of the pollution source, Turkey. J. Geochem. Explor. 134, 73–84.

Kanellopoulos, T.D., Angelidis, M.O., Karageorgis, A.P., Kaberi, H., Kapsimalis, V., Anagnostou, C., 2006. Geochemical composition of the uppermost prodelta sediments of the Evros River, Northeastern Aegean Sea. J. Mar. Syst. 63, 63–78.

Kanellopoulos, T.D., Kapsimalis, V., Poulos, S.E., Angelidis, M.O., Karageorgis, A.P., Pavlopoulos, K., 2008. The influence of the Evros River on the recent sedimentation of the inner shelf of the NE Aegean Sea. Environ. Geol. 53, 1455–1466.

Karageorgis, A.P., Anagnostou, C.L., Kaberi, H., 2005. Geochemistry and mineralogy of the NW Aegean Sea surface sediments: implications for river runoff and anthropogenic impact. Appl. Geochem. 20, 69–88.

Karditsa, A., Poulos, S.E., 2013. Sedimentological investigations in a tideless river-influenced coastal embayment: the case of inner continental shelf of the NE Aegean Sea. Cont. Shelf Res. 55, 86–96.

Kouris, H., 1980. Sheet Mesi- Xylagani, Geologic Map of Greece, Scale 1:50.000, I.G.M.E., Athens.

Larner, B.L., Palmer, A.S., Seen, A.J., Townsend, A.T., 2008. A comparison of an optimised sequential extraction procedure and dilute acid leaching of elements in anoxic sediments, including the effects of oxidation on sediment metal partitioning. Anal. Chim. Acta. 608, 147–157.

Lekkas, Th., Kolokythas, G., Nikolaou, A., Kostopoulou, M., Kotrikla, A., Gatidou, G., Thomaidis, N.S., Golfinopoulos, S., Makri, Ch., Babos, D., Vagi, M., Stasinakis, A., Petsas, A., Lekkas, D.F., 2004. Evaluation of the pollution of the surface waters of Greece from the priority compounds of List II, 76/464/EEC Directive, and other toxic compounds. Environ. Int. 30, 995–1007. http://dx.doi.org/10.1016/j.envint.2004.04.001.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19 (1), 81–97.

Long, E.R., Field, L.J., MacDonald, D.D., 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ. Toxicol. Chem. 17 (4), 714–727.

Loring, D.H., 1990. Lithium — a new approach for the granulometric normalization of trace metal data. Mar. Chem. 29, 155–168.

Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. ICES J. Mar. Sci. 48, 101–115.

MacDonald, D.D., Carr, R.S., Calder, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5, 253–278.

Makhoukh, M., Sbaa, M., Berrahou, A., Vanclooster, M., 2011. Assessing water and sediment quality of the Moulouya River (East Morocco). Eur. J. Sci. Res. 61 (4), 508–523.

Marinos, G., Mariolakos, I., Sambo, V., 1976. Titanium magnetite sand deposit along the coast of Alexandroupolis (Thrace). Tech. Rep. Inst. Oceanogr. Fish. Athens 14, 46.

Martín, J., Sanchez-Cabeza, J.A., Eriksson, M., Levy, I., Miquel, J.C., 2009. Recent accumulation of trace metals in sediments at the DYFAMED site (Northwestern Mediterranean Sea). Mar. Pollut. Bull. 146–153.

McGlade, J.M., 2002. Governance of transboundary pollution in the Danube River. Aquat. Ecosyst. Health Manag. 5, 95–110.

Meinhold, G., Kostopoulos, D.K., 2013. The Circum-Rhodope Belt, northern Greece: age, provenance, and tectonic setting. Tectonophysics 595–596, 55–68.

Morillo, J., Usero, J., Gracia, I., 2007. Potential mobility of metals in polluted coastal sediments in two Bays of southern Spain. J. Coast. Res. 23 (2), 352–361.

Mylopoulos, Y.A., Kolokytha, E.G., 2008. Integrated water management in shared water resources: the EU Water Framework Directive implementation in Greece. Phys. Chem. Earth A/B/C 33 (5), 347–353 (Integrated Water Resources Management in a Changing World).

Olson, D.B., Kourafalou, V.H., Johns, W.E., Samuels, G., Veneziani, M., 2007. Aegean surface circulation from a satellite-tracked drifter array. J. Phys. Oceanogr. 37, 1898–1917.

Papadopoulos, P., 1982. Sheet Maronia, Geologic Map of Greece, Scale 1:50.000, I.G.M.E., Athens.

Pehlivanoglou, K., 1989. Evros delta: evolution of continental shelf sediments. Mar. Geol. 87, 27–29.

Pehlivanoglou, K., Tsirambides, A., Trontsios, G., 2000. Origin and distribution of clay minerals in the Alexandroupolis Gulf, Aegean Sea, Greece. Estuar. Coast. Shelf Sci. 51, 61–73.

Perrisoratis, C., Moorby, S.A., Papavasiliou, C., Cronan, D.S., Angelopoulos, I., Sakellariadou, F., Mitropoulos, D., 1987. The geology and geochemistry of the surficial sediments off Thraki, Northern Greece. Mar. Geol. 74, 209–224.

Poulos, S.E., Alexandrakis, G., Karditsa, A., Drakopoulos, P., 2007. Heavy metal investigation, as pollutant indicators, in the bottom sediments, in the Harbours Heraklion and Alexandroupolis (Aegean Sea, Greece). Proceedings of the 10th International Conference on Environmental Science and Technology, pp. B634–B641.

Puig, P., Palanques, A., Sanchez-Cabeza, J.A., Masqué, P., 1999. Heavy metals in particulate matter and sediments in the southern Barcelona sedimentation system (North-western Mediterranean). Mar. Chem. 63, 311–329.

Radakovitz, O., Roussiez, V., Ollivier, P., Ludwig, C., Grenz, C., Probst, J.-L., 2008. Input of particulate heavy metals from rivers and associated sedimentary deposits on the Gulf of Lion continental shelf. Estuar. Coast. Shelf Sci. 77, 285–295.

Reimann, C., Filzmoser, P., Garrett, R.G., 2002. Factor analysis applied to regional geochemical data: problems and possibilities. Appl. Geochem. 17, 185–206.

Romano, E., Ausili, A., Zharova, N., Celia, M.M., Pavoni, B., Gabellini, M., 2004. Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. Mar. Pollut. Bull. 49 (5–6), 487–495.

Roussiez, V., Ludwig, W., Monaco, A., Probst, J.L., Bouloubassi, I., Buscail, R., Saragoni, G., 2006. Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW Mediterranean Sea): a multi-tracer approach. Cont. Shelf Res. 26, 1843–1857.

Salomons, W., Forstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo 3540127550.

Sari, E., Çağatay, M.N., 2001. Distributions of heavy metals in the surface sediments of the Gulf of Saros, NE Aegean Sea. Environ. Int. 26, 169–173.

Schintu, M., Marras, B., Maccioni, A., Puddu, D., Meloni, P., Contu, A., 2009. Monitoring of trace metals in coastal sediments from sites around Sardinia, Western Mediterranean. Mar. Pollut. Bull. 58, 1577–1583.

Seshan, B.R.R., Natesan, U., Deepthi, K., 2010. Geochemical and statistical approach for evaluation of heavy metal pollution in core sediments in southeast coast of India. Int. J. Environ. Sci. Technol. 7 (2), 291–306.

Skias, S., Pliakas, F., Kallioras, A., 2013. Application of SWOT analysis for the management of transboundary River Evros (Bulgaria, Greece, Turkey). Int. J. Water 7, 104–121.

Skias, S., Kallioras, A., 2007. Cross border co-operation and the problem of flooding in the Evros Delta. In: Verwijmeren, J., Wiering, M. (Eds.), Many Rivers to Cross. Cross Border Co-operation in River Management. Eburon Academic Publishers, pp. 119–143.

Skias, S., Kallioras, A., Pliakas, F., 2008. Basic problems and prerequisites regarding the IWRM in SE Europe. The R. Evros case. IV International Symposium on Transboundary Waters Management, Thessaloniki, Greece, 15th–18th October 2008 (Published Abstract).

Skoulikidis, N.T., 2009. The environmental state of rivers in the Balkans — a review within the DPSIR framework. Sci. Total Environ. 407, 2501–2516.

Suleymanov, B., Ahmedov, M., Safarova, K., Steinnes, E., 2010. Metals in main rivers of Azerbaijan: influence of transboundary pollution. Water Air Soil Pollut. 213, 301–310.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39, 611–627.

Tanner, P.A., Leong, L.S., Pan, S.M., 2000. Contamination of heavy metals in marine sediment cores from Victoria Harbour, Hong Kong. Mar. Pollut. Bull. 40, 769–779.

Tessier, E., Garnier, C., Mullot, J.-U., Lenoble, V., Arnaud, M., Raynaud, M., Mounier, S., 2011. Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). Mar. Pollut. Bull. 62 (10), 2075–2086.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. 72, 175–192.

UN.ECE, 2011. Second assessment of transboundary rivers, lakes and groundwaters, chapter 6: drainage basin of the Mediterranean Sea United Nations Economic Commission for Europe. ECE/MP.WAT/34 United Nations Publication, pp. 288–292.

Van der Weijden, C.H., 2002. Pitfalls of normalization of marine geochemical data using a common divisor. Mar. Geol. 184, 167–187.

Voudouris, P., 2006. A comparative mineralogical study of Te-rich magmatic-hydrothermal systems in northeastern Greece. Mineral. Petrol. 87, 241–275.

Wiering, M., Verwijmeren, J., Lulofs, K., Feld, C., 2010. Experiences in regional cross border co-operation at the Dutch–German border. Water Resour. Manag. 24, 2647–2672.

Xeidakis, S.G., Delimani, P.K., Skias, S.G., 2006. Sea cliff erosion in the eastern part of the North Aegean coastline, Northern Greece. J. Environ. Sci. Health 41, 1989–2011.

Zhao, L., Qian, Y., Huang, R., Li, C., Xue, J., Hu, Y., 2012. Model of transfer tax on transboundary water pollution in China's river basin. Oper. Res. Lett. 40 (3), 218–222.

Zhuang, W., Gao, X., 2014. Surface sediments of the Laizhou Bay and the coastal waters of the Zhangi Island, China: comparison among typical marine sediment quality indices. PLoS ONE 9 (4), e94145. http://dx.doi.org/10.1371/journal.pone.0094145.