



Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay, Greece: Delineating the impact of inland waters and wastewaters

C. Violintzis, A. Arditoglou, D. Voutsas*

Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University of Thessaloniki, 54 124 Thessaloniki, Greece

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ABSTRACT

An integrate study on the occurrence of major, minor and trace elements in the coastal environment of Thermaikos Gulf, Northern Aegean Sea, was carried out. The elemental composition of marine sediments and suspended particulate matter from Thermaikos Bay as well as the composition of suspended particles from various inland water (3 rivers and 4 streams) and wastewater (4 types of municipal and industrial origin) end up to the gulf was investigated during the period 2005–2006. The elemental profiles and characteristics of particulate matter from the examined water-types were discussed. The pollution status of marine sediments was evaluated by employing enrichment factors and sediment quality guidelines (TEL/PEL, ERM/ERL). Zn, Cu, Pb, As and Ag were found to have significant contribution from anthropogenic sources. Sites located at the northern part of the bay exhibited higher pollution indices and can be considered of medium-high priority. Principal Component Analysis was employed to find out the factors affecting the composition of the sediments and suspended particulate matter and to elucidate similarities/dissimilarities in the elemental profiles between the different water-types.

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1. Introduction

The 2000/60/EC Directive in the field of the water policy aims at the maintenance and improvement of quality status of the aquatic environment in the Community by establishing a framework for the protection of inland surface waters, transitional waters, groundwaters and coastal waters in order to prevent further deterioration, protect and enhance their quality [1]. Metals are among the pollutants that must be monitored in order to obtain a coherent and comprehensive overview of the quality status of aquatic systems.

The occurrence and distribution of metals and other toxic elements in a coastal environment is of particular concern due to their environmental persistence, biogeochemical recycling and ecological risk. Chemical elements released to the environment through natural processes and/or human activities, may enter aquatic ecosystems and distributed between dissolved and particulate phase. The suspended particulate matter has been recognized both as carrier and as possible source of contaminants in aquatic systems affecting their transport, fate, biogeochemistry, bioavailability and toxicity. Variations in concentration and characteristics of particles along with possible physicochemical modifications play

an important role in estuarine biogeochemical cycles [2–4]. On the other hand, sediments provide a sink for contaminants accumulated over time. However, under certain environmental conditions, via chemical and biological processes, sediments may also act as source of chemicals to the aquatic environment and biota [5,6].

In this study the occurrence and distribution of elements in the coastal area of Thermaikos Gulf, located at the Northern Aegean Sea, Greece was investigated. Thermaikos Gulf is a complex system, being affecting by various factors:

- Three rivers (Aliakmon, Axios and Loudias) drain the hydrographical basin of Northern Greece and discharge to the Gulf. These rivers form a large deltaic complex designated as special protected area. The rivers through their route receive domestic and industrial wastewaters, animal husbandry, and agricultural runoff [7]. Moreover, small streams/canals receiving storm water and wastewaters end up to the Gulf.
- About 150,000 m³/d of effluents from the wastewater treatment plant are discharged to Thermaikos Gulf via a pipe. The plant treats sewage effluents mainly from the municipality of Thessaloniki and has also a small contribution (5–10%) from industry [8]. Moreover, ~60,000 of untreated or partially treated industrial wastes also end up to the coastal system [9].
- The surrounding coastal area is characterized by exponential increase of population associated with industrialization and

* Corresponding author. Tel.: +30 2310997858; fax: +30 2310 997747.
E-mail address: dvoutsas@chem.auth.gr (D. Voutsas).

- economic development. About one million of inhabitants live in the major area of Thessaloniki [9].
- (d) Various port and commercial activities are taking place in the Harbor of Thessaloniki (maritime traffic, ship discharge, bunkering, storage of hazardous cargo, dredging and disposal of dredged materials).
 - (e) Mussel farming activities are taking place in the coastal area. Mussel production reaches to 30,000 t/y, representing the 85% of the total Greek production [7].

The aim of this study was to thoroughly investigate the occurrence of major, minor and trace elements and their distribution in the area of Thermaikos Bay. For this purpose 27 elements were determined in suspended particulate matter and sediments from marine area. Moreover, particulate metals were determined in various surface waters and wastewater end up to the bay. The elemental profiles and characteristics of suspended matter were discussed. The pollution status of marine sediments was evaluated by employing enrichment factors and comparison with sediment quality guidelines. A chemometric approach was employed to elucidate similarities/dissimilarities between the elemental profiles.

2. Experimental

2.1. Study area

Thermaikos Gulf is located at the northwestern part of the Aegean Sea. The catchment area of the Gulf is ~40,000 km². Water depth in the inner bay is <30 m. The water mass circulation is predominately cyclonic. Aegean water masses enter the gulf from deeper layers along the eastern coastal land and move counter clockwise [7].

The eastern coastline consists mainly of MioPliocene lacustrine to terrestrial deposits, changing towards the south to marine deposits. The north/northwesterly coastline is formed by fluvial and deltaic deposits of Holocene age. The western shoreline is formed of recent Quaternary formations, consisting mainly of alluvial and fluvial deposits and finally the southernmost part of the western shoreline consists of limestone (mainly dolomite), marbles, gneisses, schists, amphibolites and metamorphic schist-chest formations of the Pelagonian zone of Triassic–Jurassic age [9].

2.2. Sampling

Samples were also collected from marine sites as well as from a wide range of inland water-types (rivers, streams, wastewaters) end up to Thermaikos Bay. The sampling sites are shown in Fig. 1. Seawater samples and sediments were collected from ten sites along the coastal area (T1–T10). The sampling sites cover the coastal line and are located away from obvious pollution sources in order to provide a representative coverage of the entire bay. The sites were 250–600 m away from the coastline and the depth ranged from 8 to 12 m (except site T6 that was in the middle of the bay about 2 km from the coast at a depth of 22 m). Seawater samples from 1 m depth were collected in amber glass bottles. Surficial sediments were sampled with an Eckman sampling device at the same sites and stored in amber glass jars. Samples kept cool in the field and transported within 4 h to the laboratory.

Samples were also collected from various inland water-types (Fig. 1): the rivers Aliakmon (R1), Axios (R2) and Loudias (R3), four streams/canals (S1–S4) and four industrial and municipal wastewaters (W1: treated sewage effluents, W2: treated industrial effluents, W3: domestic effluents and W4: tannery wastewaters). Water samples from rivers and streams were collected from well mixed areas

in the middle of their route away from point pollution sources and close to the mouth of river/stream.

Samples were collected during two sampling campaigns, September 2005 and March 2006, with average water temperatures 22 and 16 °C, respectively. Upon arrival at the laboratory, water/wastewater samples were filtrated through 0.45 μm membrane filters for separation of Total Suspended Solids (TSS). Loaded filters were dried at 105 °C and TSS was determined gravimetrically. The filters stored at 4 °C until elemental analysis. Marine sediments dried at 105 °C and sieved through stainless steel sieves of 2000 μm and 105 μm. Fine sediments were further used for elemental analysis.

2.3. Elemental analysis

Elements in suspended particulate matter and sediments were determined in a SPECTRO XEPOS bench-top XRF spectrometer (SPECTRO A.I., GmbH) with PD window X-ray tube. XRF analysis of TSS was carried out on a disc 32 mm diameter cut from each loaded filter. Sediments were first grounded to <40 μm in a mill (MM2). Approximately 3 g of pulverized material were palletized (2 mm thickness) in a 15-t press using SpectroBlend additive (77.1% C, 5.4% O, 12.8% N) as a binder. SPECTRO uses the TURBOQUANT calibration method that is able to analyse all elements from Na to U in completely unknown samples with accuracies between 10% and 20%. The calibration method induced 49 elements (Na–U) in pellets and 33 elements (Mg–Bi) in filter samples. The matrix effect of samples is detected by the Compton method. Values normalization and error correction is achieved by a specialized software program (SPECTRO X-LABPRO). Twenty seven elements (Mg–Pb) were quantifiable in samples.

Filter blanks and duplicate sample analyses were performed for about 10% of all samples according to standard operating procedures. Detection limits of individual elements ranged between 0.0003% and 0.15% in pellets and between 1 and 100 ng cm⁻² in filter samples. In addition, certified materials (SOIL-7, MESS-1, BCSS-1) were used for data validation. Precision for was ≤5% for K, V, Mn, Cu, As, Pb and ≤15% for Ca, Mg, Fe, Zn, Cr, Al, Si.

2.4. Determination of organic carbon

Suspended particulate matter, collected in precombusted at 450 °C GF/F filters, and sediments were analysed for organic carbon (POC and TOC, respectively). Organic carbon was measured by TOC-V_{SERIES} SSM-5000A Solid Sample Module for Total Carbon Analyzer (Shimadzu).

2.5. Determination of acid volatile sulfide

Acid Volatile Sulfide (AVS) was determined colorimetrically after treatment of sediments with hydrochloric acid and trap of produced H₂S to a zinc acetate solution [10].

2.6. Statistical analysis

Statistical treatment of the data was conducted using the SPSS 16.0 statistical software.

3. Results and discussion

3.1. Suspended particulate matter

3.1.1. Elemental concentrations

Suspended particulate matter has an important role in estuarine/marine biogeochemical cycles. The concentration and the elemental composition of TSS are controlled by their origin,

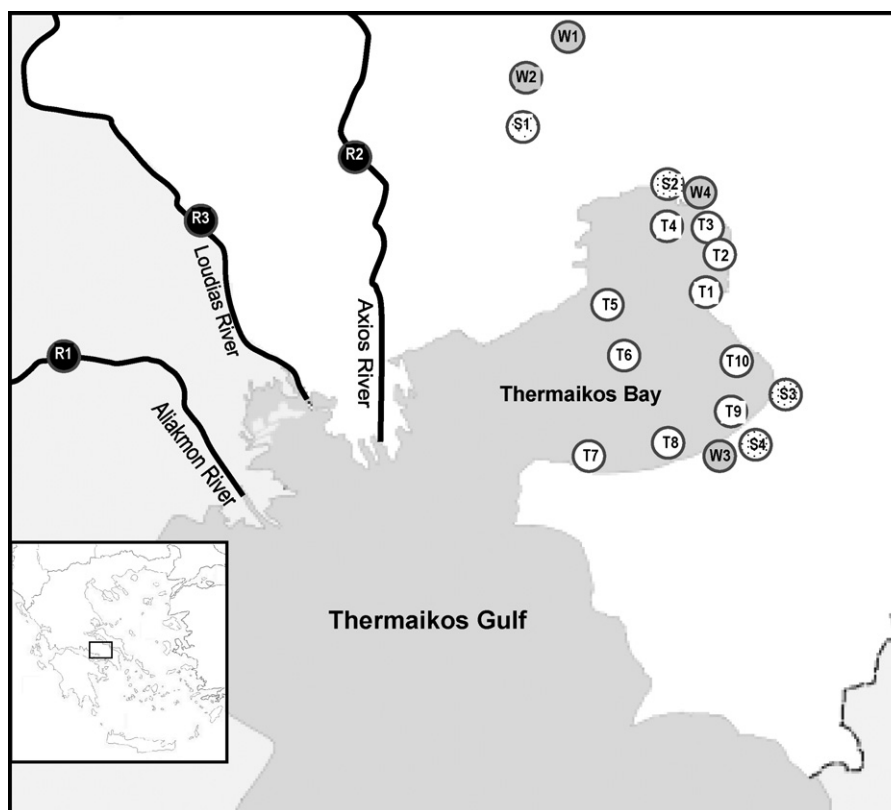


Fig. 1. Map of the study area. Sampling sites are illustrated (T1–T10: marine sites, R1–R3: rivers, S1–S4: streams, W1–W4: wastewaters).

the inputs from surface water/wastewater, the physicochemical processes occurred, the primary production and sediment resuspension, especially to the near bottom waters [4]. Changes in salinity, pH, redox conditions, dissolved and particulate organic matter could result in modification of chemical and particle reactivity [2,11].

The concentration of suspended particulate matter in seawater ranged from 17.3 to 32.3 mg/L. The organic content (POC) ranged from 2.3 to 6.9% (Table 1). Organic matter and hydrous oxides of Fe and Mn are considered as critical components of aquatic particles that can affect the sorptive removal of trace metals [11]. POC also plays an important role in biomediated cycling in the upper layer of the sea [12]. The concentrations of major, minor and trace elements in suspended particulate matter from seawater and from various inland waters-types (rivers, streams, wastewaters) are shown in Table 1. The marine particulates dominated (>10 mg/g) by Cl, Ca, K and Si. Mg, Al, Fe, Br, S and P exhibited concentrations ranged from 1 to 5 mg/g. Low concentrations (<0.1 mg/g) found for the metals Cr, Co, Ni, Cu, As, Cd and Pb.

Rivers exhibited higher particulate concentrations of almost all studied elements compared to marine particles; mainly of major elements Si, Al, Ca, K and Fe and minor/trace elements Mn, Pb, Ni, Co, Cr, As and Zn. Streams exhibited higher concentrations of particulate matter (37–113 mg/g) and organic content (8.2–47%) compared to rivers. Moreover, they also showed higher concentrations of Cl, S and P and lower concentrations of Al, Si, Fe, Mn and K, suggesting that these systems receive treated or/and partially treated wastewater besides storm water. Particularly the streams S1 and S2 located N/NW of the bay showed higher pollution levels. The concentration of elements in particulate matter from wastewaters showed wide variation due to the different origin of the wastewaters. In general, wastewaters exhibited low concentrations of lithogenic elements (Si, Al, Fe, Mn), relatively high concentrations of Cu and Zn, high

concentrations of P, S and Cl (maximum values were determined in urban W1 and industrial W2 wastewaters) and high concentrations of Cr (maximum values were found in tannery wastewaters W4).

Surface waters and wastewaters are considered as significant source of particles and metals to the coastal waters [3,13,14]. The occurrence of heavy metals in rivers has been previously investigated. Rivers exhibited relatively low concentrations of dissolved metals, usually lower than the proposed limits for drinking water and the protection of aquatic life [15,16]. Significant fraction of metals occurred in particulate phase. Fine grained fraction in Axios river (R2) contributed highly to the total metal content of sediments representing ~70% for Zn and >50% for Cd, As, Cu, Ti, V, Cr, Fe, Co and Ni [17]. It has been estimated that dissolved and particulate metal fluxes of Axios to the coastal environment are about 15 t/y for As, 5 t/y for Cd, 64 t/y for Cr, 37 t/y for Cu, 43 t/y for Ni 59 t/y for Pb and 142 t/y for Zn [18]. The suspended particulate matter in Aliakmon river (R1) contribute significantly to total metal content (from ~50% for Cd up to 90% for Mn) [15]. Soil leaching appeared to be the main source of most elements in rivers (Cu, Cr, Ni, Mn, Fe), whereas anthropogenic activities contribute highly to Pb, Zn and Cd concentrations [19]. As far as concerning wastewaters discharged to the coastal area they also considered as significant sources of metals. About ~150,000 m³/d treated domestic effluents from Thessaloniki (sample W1) end up to the Gulf at a site located at the middle of bay (close to the sampling site T6). It has been estimated that 47–63% of Cd, Cr, Pb, Fe, Ni and Zn remain in treated effluent and end up to the Gulf [8]. In the industrial area of Thessaloniki there are over 300 large or medium-sized industries (such as chemical plants, paper, metal, rubber plants, food products, breweries, etc.) that are also sources of metals. Most of the wastewaters are treated in a central plant and discharged to the gulf (sample W2). However, there are also partially treated or even untreated wastewaters that are discharged directly or through small streams to the gulf.

Table 1
Elemental concentrations in suspended particulate matter (mg/g dw).

	MARINE (n = 20)		RIVERS (n = 6)		STREAMS (n = 6)		WASTES (n = 7)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Mg	4.1	3.1–6.1	7.2	2.5–9.6	2.2	1.1–3.9	3.0	0.60–6.6
Al	4.6	2.1–12	22	11–34	7.6	4.4–16	7.6	1.1–21
Si	14	6.3–25	63	30–113	18	5.5–47	9.8	1.7–35
P	0.26	0.003–1.0	1.8	0.17–4.9	3.8	0.30–10	7.4	0.68–12
S	1.1	0.001–5.0	1.8	0.24–4.9	3.4	0.77–7.4	5.1	0.78–13
Cl	66	51–88	0.615	0.09–1.4	2.5	0.19–6.3	6.1	0.66–15
K	14	11–19	27	13–40	8.3	5.6–12	15	4.8–28
Ca	16	11–33	60	39–69	58	33–90	55	13–143
Ti	0.51	0.18–3.5	2.3	0.84–3.2	0.80	0.33–1.2	1.2	0.27–4.9
V ⁺	50	9–92	37	9–58	11	9–22	15	9–37
Cr ⁺	83	43–136	339	125–440	163	58–286	680	60–3770
Mn	0.29	0.15–0.47	3.2	0.41–10	0.24	0.11–0.39	0.38	0.06–1.8
Fe	3.4	1.5–7.5	30	12–38	7.2	2.8–13	9.7	2.4–35
Co ⁺	18	2–36	95	45–183	33	8–46	27	2–80
Ni ⁺	30	17–48	188	71–311	49	29–72	63	18–160
Cu ⁺	50	32–81	129	47–376	137	65–293	318	60–946
Zn ⁺	96	60–244	432	147–851	357	133–640	1210	223–5370
As ⁺	9	1–45	53	19–86	10	1–25	22	1–82
Se ⁺	8	3–16	4	2–9	8	2–21	13	2–31
Br	4.9	3.0–7.8	0.19	0.08–0.45	0.19	0.09–0.37	1.1	0.24–3.5
Sr	0.17	0.12–0.25	0.20	0.12–0.29	0.20	0.10–0.43	0.32	0.14–0.57
Cd ⁺	13	0.1–66	37	3–95	59	14–124	50	7–167
Sn ⁺	54	23–99	86	13–275	74	11–172	73	7–179
Sb ⁺	84	49–150	107	21–352	117	19–300	83	8–222
Te ⁺	88	41–153	125	21–479	120	12–252	110	5–461
Ba	0.28	0.18–0.42	0.46	0.15–1.3	0.33	0.09–0.63	0.31	0.04–0.77
Pb ⁺	86	38–223	153	55–348	70	30–115	99	47–270
POC ^{**}	4.3	2.3–6.9	9.6	0.6–20	26	8.2–47	24	12–37

⁺ μg/g; ^{**} %.

Moreover, until recently wastewater from small tanneries used to be discharged untreated to the gulf (sample W4).

Consequently, taking into account the high flow rates (20–86 m³/s) of rivers, these systems represent a significant source of particulate matter to the coastal environment. The mean annual solid discharge from rivers has been estimated to 0.628–25 × 10⁶ t/y [9,20]. Particulate matter from rivers can be considered as significant carrier of natural and anthropogenic derived metals to the sea. The rivers affect mainly the north-west open continental sector of Thermaikos Gulf, although there is a circulation in the inner part of the gulf [9,21]. The streams, although they present lower flow rates (~5000 m³/d for S1 and S2) along with the uncontrolled wastewater discharges may have a significant impact at the northern part of the bay where they end up.

3.1.2. Biogenic derived elements

The suspended particulate matter in a coastal environment is of terrigenous (sediment resuspension) and/or biogenic origin. Biogenic activity can affect the presence of elements such as P, N, Ba, Ca, Si in suspended particulate matter [4,22]. The ratio of Ca/Al in marine particulate matter is often used as an indication of biogenous occurrence of Ca. This ratio was 3.9 ± 1.5 in marine particulate matter and lower (1.3 ± 0.6) in sediments, suggesting that resuspension of sediments was not the main source of suspended particles and biogenic formation is possible. According to Price et al. ratio values ranged from 3 to 5 suggest a biogenic source of Ca probably due to calcareous organisms occurred in water column [22]. However, high ratios were also found in riverine particulate matter (2.0–4.5), in wastewaters (2.0–27) and in streams (2.4–17). Thus the biogenic formation of calcium cannot be distinguished from the impact of these inland sources.

Similarly, the Si/Al ratio is also considered as an indication of possible changes in Si occurrence from biogenic activity, although there are difficulties due to the predominance of this element associated with quartz and aluminosilicates materials [22]. The Si/Al

ratio was 3.2 ± 0.9 in marine particulate matter and 2.7 ± 0.3 in sediments. Inland waters/wastes exhibited similar values (1.2–3.4 in rivers, 1.2–3.4 in streams, 0.5–1.9 in wastes), consequently it is difficult to find out possible biogenic formation of Si.

The particulate phosphorus in seawater could also due to biological activity as well as to inputs from other sources. P in marine particulate matter was found at detectable concentrations only during second sampling campaign and the ratio P/Al was 0.187 ± 0.095. High ratio values ranged from 0.10 to 0.60 have been reported for upper waters in Thermaikos Gulf, suggesting in situ biological productivity or external P sources [22]. In current study inputs from inland water/wastewater showed also high ratios (0.009–0.225 in rivers, 0.057–2.246 in streams and 0.293–3.524 in wastewaters), thus the assessment of biogenic P is not possible.

3.2. Sediments

3.2.1. Sediment characteristics

Wide variation in textural composition observed in marine sediments. The sediments were predominately comprised with coarse fraction at all locations; fine fraction ranged from 6.5 to 45%. The concentrations of total organic carbon (TOC) and acid volatile sulfur (AVS) in marine sediments are shown in Table 2. TOC and AVS are significant parameters for the evaluation of toxicity of sediments since they play an important role in controlling the availability of inorganic and organic contaminants and the toxicity of sediments [23,24]. TOC concentrations ranged from 0.6 to 4.6%. Similar results (1.2–3% or even higher) have been previously reported for the same system [14,31]. The higher TOC values were observed at sites T1–T4 located at the inner part of the bay (Fig. 2). The preservation and accumulation of organic matter in these sites is enhanced by the anoxic conditions occurred in sediments. The black color and the unpleasant smell of the sediments is also an evidence of these conditions.

Table 2
Summary statistics of elemental concentrations in sediments from Thermaikos Bay (mg/g dw, grain fraction <105 µm, n = 20).

	Mean	SD	Median	25th	75th	Min	Max
Mg	20	1.4	20	19	21	16	22
Al	64	9	65	58	72	46	81
Si	168	14	169	156	179	147	189
P	1.2	0.2	1.1	1.0	1.2	0.9	1.6
S	5.2	2.0	5.2	4.6	6.0	2.0	9.5
Cl	15	11	11	9	16	7	54
K	28	4.4	28	25	32	22	36
Ca	77	24	72	62	96	46	130
Ti	4.5	0.62	4.4	4.0	5.2	3.7	5.7
V*	160	30	164	145	183	94	198
Cr*	294	60	311	253	335	21	470
Mn	0.77	0.09	0.79	0.72	0.84	0.59	0.89
Fe	46	7	47	41	51	32	57
Co*	33	8	34	30	37	15	50
Ni*	98	15	99	87	106	63	130
Cu*	72	30	61	56	89	32	130
Zn*	239	143	183	143	285	84	537
As*	19	7	19	15	23	9	30
Br	0.18	0.12	0.15	0.12	0.20	0.09	0.65
Sr	0.32	0.13	0.25	0.24	0.38	0.18	0.73
Ag*	3.1	2.9	3.2	0.4	4.8	0.4	9.3
Cd*	1.8	27	3.0	3.0	14	0.3	8.4
Sn*	11	4	12	79	14	6	16
Sb*	4.5	0.8	4.1	4.1	4.8	4.1	5.4
Te*	12	6	10	8	17	6	19
Ba	0.35	0.08	0.36	0.29	0.39	0.22	0.50
Pb*	87	45	67	57	106	38	190
TOC**	1.72	0.93	1.45	1.15	2.15	0.60	4.6
AVS**	0.80	0.57	0.57	0.40	1.16	0.15	2.1

* µg/g; **%.

AVS is operationally defined as the amount of sulphide that can be volatilized during a cold acid extraction [25]. The concentrations of AVS ranged from 0.15 to 2.1%. The higher concentrations were observed at the sites T2, T4 and T6 and the lower at T7 (Fig. 2). Relatively higher concentrations were found during the first sampling period (warm period), that is in consistent with the expected seasonal pattern under west-european climate conditions where the higher AVS concentrations occur in summer and the lower in late winter or early spring [23,25]. Under anoxic conditions, the availability of divalent metals to benthic organisms is related to AVS content in sediments. Cu, Cd, Pb, Ni and Zn can react with AVS to form insoluble metal sulfides. Therefore, AVS provides a mechanism of metal partitioning from pore water to solid phase, reducing their solubility and availability [23,25].

3.2.2. Elemental concentrations

The descriptive statistics (mean and median concentrations, standard deviation, minimum, maximum, 25th and 75th percentiles) of the studied elements in marine sediments are shown in Table 2. Concentrations lower than detection limits were considered as half of the limit. The most abundant elements in marine sediments were Si, Al, Fe and Ca at concentrations >30 mg/g. The concentrations of Mn, Zn, Cr and V ranged from 0.100 to 1 mg/g. Lower concentrations (0.01–0.1 mg/g) were observed for Pb, Ni, Cu, Co and As. The spatial distribution pattern of selected elements in marine sediments is illustrated in Fig. 2. There is a group of elements (i.e. Pb, Zn, Cu, As) that exhibit similar patterns with higher concentrations at sites T1–T4 suggesting common sources or similar geochemical behaviour of these elements. The other elements, although there are differences among the sampling sites, did not show a distinct spatial pattern.

3.2.3. Evaluation of pollution status

Two approaches are commonly used for assessing the pollution status of sediments: (a) comparison of concentrations in sediments with those of unimpacted sites or background concen-

trations expressed as enrichment factors and, (b) comparison with sediment quality guidelines for each contaminant and the cumulative effects of contaminants in sediments [26].

3.2.3.1. *Enrichment factors.* The enrichment of elements in sediments relative to a background-reference site is an indication of contribution from anthropogenic sources. The enrichment factor (EF) for the element M can be calculated according to the formula:

$$EF = \frac{([M]_s/[R]_s)}{([M]_{rf}/[R]_{rf})}$$

where $[M]_s$ and $[R]_s$ are the concentrations of the element M and the reference element R in sediments and $[M]_{rf}$ and $[R]_{rf}$ the concentrations in reference site. As reference element was selected Al because it can be considered as lithogenic component, whereas data from the upper crust were employed for the reference site [27]. If EF approaches unity, the earth's crust is considered as the predominant source.

The enrichment factors for sediments from Thermaikos Bay are shown in Fig. 3a. Most elements exhibited $EF > 1$ suggesting significant contribution from non-crustal sources.

However, the elemental composition of local geological substrate may be different from the upper crust thus, the best approach is to use local data [13]. In this case comparison with sediments of comparable grain size from unimpacted locations could be employed. Natural background data for sediments not subjected to any anthropogenic enrichment and derived only from land and biogenic sources are not available for the study area. For this reason, the elemental composition of sediments from sampling site T7 was used for comparison. This site located at the exit of Thessaloniki Bay exhibited the lower concentrations for almost all the studied elements, and although it cannot be considered as "background site" it is away from distinct pollution sources. The calculated EFs are shown in Fig. 3b, and present the enrichment of metals in sediments relative to reference site T7. Lower EF values were observed

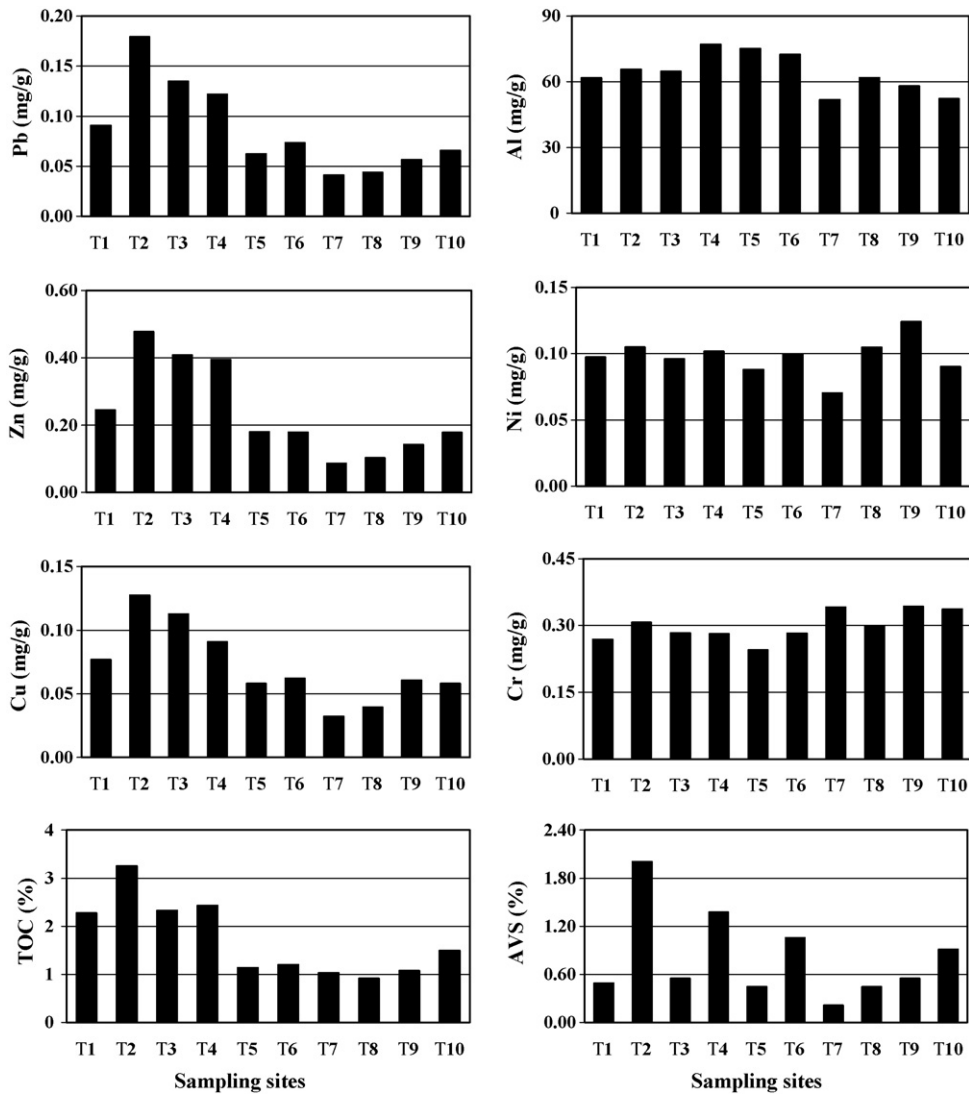


Fig. 2. Spatial distribution of selected elements, TOC and AVS in marine sediments.

for all elements. However significant enrichment still was found for Zn, Cu, Pb, As, Ag and Cd with maximum values observed at sites T1–T4 located at the inner part of the bay. The elements Cr, Co and Ni exhibited low EFs, contrary to the findings with respect to earth’s crust (Fig. 3a). These elements did not show significant spatial distribution and can be attributed to the local substrate. In the greater area of Northern Greece there are mafic/ultramafic and ophiolitic

geological formations [9,28,29]. These formations could be partially responsible for the occurrence of elements such as Fe, Cr, Ni, Co, Mn and Cd in marine sediments as previously reported by other investigators [7,30–32]. The occurrence of these elements in rivers has been also attributed to natural origin from soil leaching [19]. Thus, it seems that rivers affect significantly marine sediments. However streams and uncontrolled wastewaters discharges also have signif-

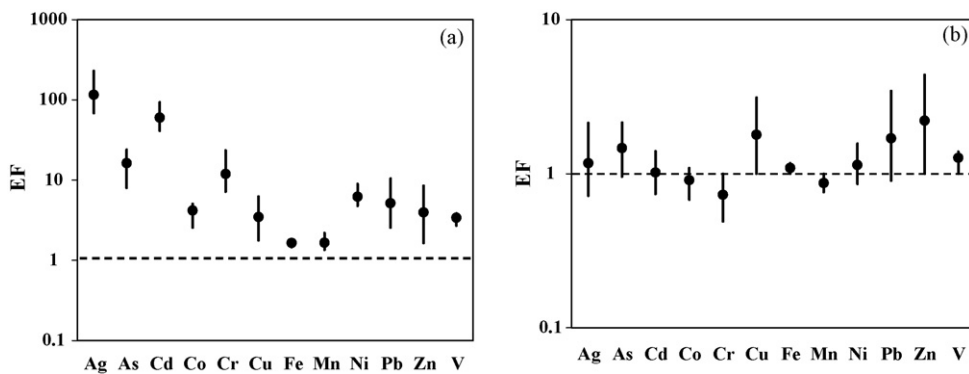


Fig. 3. Enrichment factors of metals in sediments with respect to earth’s crust (a) and reference site T7 (b) (minimum, maximum and mean values are shown).

icant impact, mainly at the northern part of the bay, resulting in enrichment of sediments with toxic elements (Zn, Cu, Pb, As, Ag, Cd).

3.2.3.2. Sediment quality guidelines. Sediment quality guidelines (SQGs) provide tolerable concentrations of sediments-bound contaminants in order to protect the organisms living in or near sediments. Large dataset combined chemical and toxicity data from various studies have been used to find out the relationships between the expected incidence of toxicity and the SQG values exceeded, although there are some limitations due to uncertainties associated with variations in characteristics of sediments and site specific field conditions [33]. The comparison of measured concentrations of various contaminants with SQGs is a common approach as first step to assess the quality of sediments. SQGs are used to rank and/or prioritise polluted areas and chemicals of concern for further investigation as well as to evaluate spatial patterns of sediment pollution [34–36]. Two sets of guidelines are commonly used, ERL/ERM and TEL/PEL approaches. Low range values (ERL or TEL) represent concentrations below which adverse effects upon sediment dwelling fauna would be expected infrequently. Upper range values (ERM or PEL) represent concentrations above which adverse effects are likely to occur [34,37]. The main difference is that the set TEL/PEL incorporates effects plus no effects data whereas the ERM/ERL set is based on effects data only [26].

Sediment quality criteria have been proposed for nine metals (Table 3) as well as for other organic pollutants. Each set of guidelines delineate three ranges in chemical concentrations where adverse effects are observed rarely (<ERL or <TEL), occasionally (ERL-ERM or TEL-PEL) and frequently (>ERM or >PEL). The distribution of metals in these ranges is shown in Fig. 4. Significant percentage of sediments exhibited concentrations of Ni, Cr, Cu, As, Pb, Zn and Ag that often exceeded the ERL or TEL values consequently, adverse effects to marine organisms are expected occasionally or frequently. The comparison with ERL/ERM guidelines showed that As, Cr, Cu and Pb displayed similar distribution with the majority of samples (>50%) in the middle range where, occasional adverse biological effects are predicted. Ni exhibited concentrations >ERM, lying in the probable effect range. Most samples (>70%) exhibited Cd concentrations <ERL indicating minimal effect. Similar conclusions derived from TEL/PEL set, although due to the lower proposed guidelines, these criteria were more frequently exceeded.

In order to obtain a more realistic measure of predicted toxicity than simply summing the numbers of ERMs/PELs exceeded, mean ERM or PEL quotients (ERM_Q, PEL_Q) were calculated as follows:

$$\text{ERM}_Q \text{ or } \text{PEL}_Q = \frac{\sum [C_i / (\text{ERM}_i \text{ or } \text{PEL}_i)]}{n}$$

where C_i is the concentration of element i in sediments, ERM_i , PEL_i the guideline values for the element i and n is the number of metals.

Table 3
Sediment quality guidelines ($\mu\text{g/g dw}$).

	ERL	ERM	TEL	PEL
As	8.2	70	7.24	41.6
Cr	81	370	52.3	160
Ni	20.9	51.6	15.9	42.8
Cu	34	270	18.7	108
Zn	150	410	124	271
Ag	1	3.7	0.73	1.77
Cd	1.2	9.6	0.68	4.21
Hg	0.15	0.71	0.13	0.7
Pb	46.7	218	30.2	112

ERL: effects range low; ERM: effects range median.
TEL: threshold effect level; PEL: probable effect level.

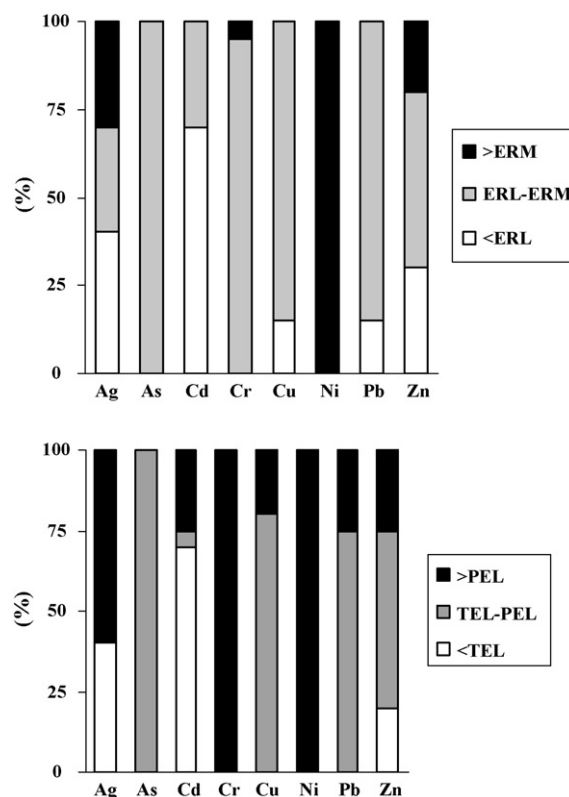


Fig. 4. Distribution of sediments with respect to ERM/ERL and TEL/PEL guidelines (ERL/ERM: effects range low/median, TEL/PEL: threshold/probable effect level).

Mean quotients are considered as useful tools for reducing a large amount of contaminants into a single number. By calculating mean quotients it is assumed that adverse effects to marine organisms caused by individual chemicals are additive, rather than synergistic or antagonistic. An additional limitation is that this approach does not consider all the chemicals present in sediments but only those include in the SQG list [28].

Mean quotients can be used to identify, delineate and prioritize areas of potential concern with respect to quality of sediments [39]. ERM_Q values of <0.1, 0.11–0.5, 0.51–1.5 and >1.5 related to 12%, 30%, 46% and 74% likelihood, respectively, that sediments present toxicity in amphipod survival bioassays. Similarly, PEL_Q values of <0.1, 0.11–1.5, 1.51–2.3 and >2.3 coincide with 10%, 25%, 50% and 76% likelihood of toxicity, respectively [34,35,38]. Consequently, four relative levels of priority (high, medium-high, medium-low and low) have been proposed. The mean ERM and PEL quotients calculated for the sampling sites in Thermaikos Bay (based on metals Ag, As, Cd, Cr, Cu, Ni, Pb and Zn) are shown in Fig. 5. These sites distributed among the classes of medium-low and medium-high priority. Particularly, sediments from sites T2, T3, T4 (Fig. 1) exhibited the highest quotients and eventually they present significant risk to the biota.

3.2.4. Comparative data

Comparative data of metal concentrations in sediments of Thermaikos Gulf during the last 30 years are shown in Table 4. It is difficult to compare results among various studies, even for the same coastal system, because there are differences in the actual grain size used, the analytical method employed and the location of sampling sites.

Data in Table 4 can provide a wide comparison for the range of metal concentrations in Thermaikos Gulf. The concentrations of heavy metals in this study are similar to data provided by Anagnostou et al., 10 years ago [40]. Both studies referred to total

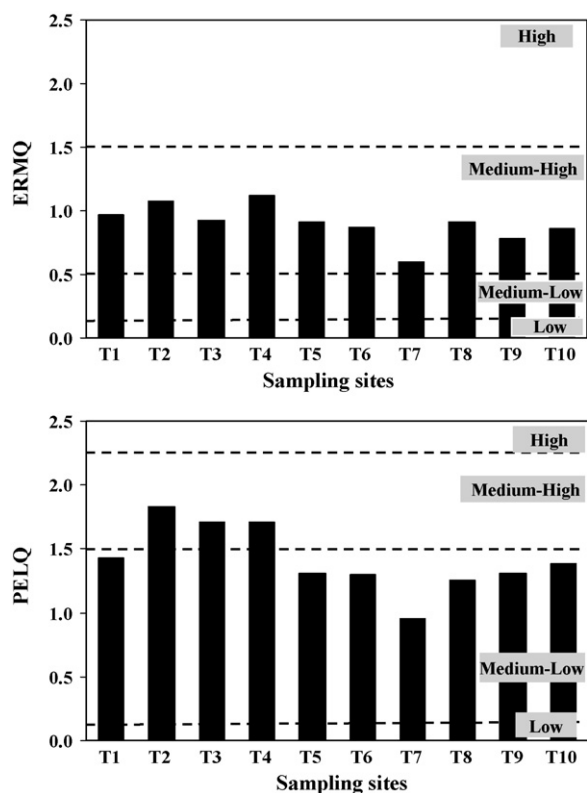


Fig. 5. Characterization of marine sites with respect to mean ERM and PEL quotients.

concentrations of metals in fine sediments from the inner part of Thermaikos Bay. A comparison with elemental concentrations almost 20 years ago reported by Voutsinou-Taliadouri and Varnavas [31] was attempted, although these data referred to acid available metal concentrations in bulk sediments from the entire area of Thermaikos Gulf whereas, in current study total concentrations in fine sediments from the inner part of the bay, that are usually more enriched in heavy metals, were determined. It seems that there is a relative reduction in concentrations of metals, mainly for Pb and Zn. This is in consistent with the expected reduction of metal fluxes to the gulf due to the operation of two plants for the treatment of municipal and industrial wastewaters. It has been reported that

during treatment of municipal wastewaters a ~50% reduction of daily inputs for Cr, Pb, Ni, Cd and Zn is accomplished [8].

4. Statistical treatment

Datasets from environmental studies usually contain a large number of samples analyzed for many parameters. Multivariate approaches are considered as valuable tools for the interpretation of these complex data matrices [19,41–45]. Principal Component Analysis (PCA) is often employed in environmental datasets in order to understand the distribution modes of contaminants, find out similarities/dissimilarities between parameters and samples and elucidate possible sources. The objective of PCA is to derive a reduced number of new variables as linear combinations of the original variables. This provides a description of the structure of the data with the minimum loss of information [19,45].

PCA was performed on normalized elemental concentration data. To compensate for strongly skewed distribution and/or to avoid that high concentration dominates the mathematical model, all data were log-transformed. The results of the PCA after varimax rotation are shown in Table 5. Three factors were found to explain 81.87% of the total variance. The first factor (PC1) accounted for 32.13% of the total variance, exhibited high loadings with Pb, Zn, Cu, As, TOC and AVS. The second factor (PC2) accounted for 31.52% of the variance, associated positively with major elements Al, Si, Fe, Mn. The third factor (PC3) showed high loading with Ni, Mg, V and AVS and explained 18.22% of the variance. The interpretation of each factor is not easy due to the complexity of the studied area. The factor PC1 could be related to sulphide materials occurred in sediments. Moreover, correlation of metals, TOC and AVS with the same factor present a strong evidence of possible impacts from wastewaters/streams that also exhibited high organic and sulfur content and heavy metals. The factor PC2 represents silicate mineralogy of lithogenic materials revealing their natural origin. The factor PC3 could be related to weathering from rocks occurred in the catchments of the rivers. The correlation of Ni and V with the same factor PC3 could also imply pollution by hydrocarbon spills and/or shipyard and industrial activities where metals extensively used in alloys and metallurgical materials [42,46]. The distribution of the samples between the first two factors is illustrated in Fig. 6. Samples are clustered into three groups: (a) sites T1, T2, T3 located at the inner part of the Thermaikos Bay presented high scores with PC1, (b) a second group of sites T5, T6 located at the western part

Table 4
Comparative data on elemental concentrations in sediments from Thermaikos Gulf ($\mu\text{g/g dw}$).

		Pb	Cd	Zn	Cu	Mn	Ni	Cr	Method	Grain size	Reference
2005/06	Min	38	0.3	84	32	590	63	21	XRF	<105 μm	This study
	Max	190	8.4	537	130	890	130	470			
	Mean	87	1.8	239	72	770	98	284			
2000	Min	3.1	0.17	28	2	81	17	18	$\text{HNO}_3\text{-HCl}$, AAS	<2000 μm	[47]
	Max	86	6.3	1014	119	239	42	148			
2000	Min	0.64	0.13	12	0.5	47	6.8	2.8	0.5N HCl, AAS	<2000 μm	[47]
	Max	17	6.3	914	76	121	22	21			
1997/98	Min	17	–	33	4	286	35	39	XRF	<2000 μm	[14]
	Max	265	–	429	108	4336	407	458			
	Mean	52	–	120	34	1378	146	222			
1995	Min	46	0.55	193	57	535	76	196	$\text{HNO}_3\text{-HF-HCl-HClO}_4$, AAS	<63 μm	[40]
	Max	113	4.59	549	162	1322	115	265			
	Mean	64	1.33	296	79	826	95	221			
1985	Min	11	0.3	4	7	206	29	39	50% HCl, AAS	Bulk	[31]
	Max	334	8.7	2600	200	1451	143	386			
	Mean	126	1.3	410	64	690	105	191			
1981/82	Min	20.9	0.87	12.1	0.6	52	6.8	–	$\text{HClO}_4\text{-HNO}_3$, AAS	<63 μm	[48]
	Max	27.8	1.08	28.2	2.3	64.8	9.1	–			

Table 5
Factor analysis on elemental composition of marine sediments.^{a,b}

	PC1	PC2	PC3
Al		0.846	0.433
Si		0.871	
Fe	0.480	0.695	0.487
Mn		0.787	
Ca		-0.848	
Mg		0.555	0.772
Pb	0.957		
Zn	0.948		
Cu	0.930		
Ni			0.897
Cr		-0.699	
As	0.816	0.450	
Co		0.590	
V	0.448	0.586	0.618
TOC	0.870		
AVS	0.560		0.598
Variance (%)	32.13	31.52	18.22

^a Extraction method: Principal Component Analysis; Rotation method: Varimax with Kaiser Normalization.

^b Factor loadings <0.300 are not reported.

of the Bay exhibited high scores with PC2 and, (c) a third group of sites T9, T10, T7, T8 located at the eastern part of the Bay with low scores for both factors.

Principal Component Analysis was also performed on the dataset of log-transformed elemental concentrations in suspended particulate matter from different water-types (marine, rivers, streams, wastewaters). Three factors describe over 80.77% of the variance in this dataset (Table 6): (a) the first factor associated with the lithogenic elemental group (Si, Al, Mn, Ni, Fe and Mg) and explained 36.29% of the total variance (b) the second factor associated with Zn, Ca, Cu, Cr and POC accounted for 33% of total the variance and, (c) the third factor exhibited high loadings with Cd and Pb and explained 11.48% of the total variance. Estimated factor scores showed different environmental status based on the prevalence of certain factors at each site. The first factor showed high positive scores with rivers R1, R2 and R3. The second factor exhibited high positive scores with wastewaters (W1–W4), streams (S1, S2) and rivers (R2, R3). The third factor also showed high positive scores with wastewaters, streams and rivers.

To gather additional information regarding similarities/dissimilarities of compositional patterns of suspended particulate matter from different water-types (marine, rivers, streams, wastewater) and marine sediments, PCA was employed on the whole dataset.

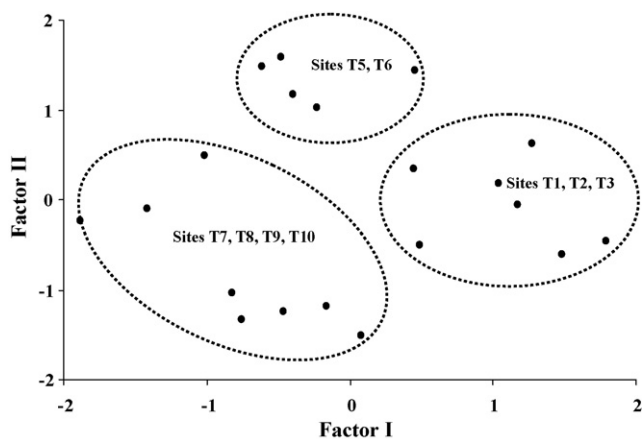


Fig. 6. Scores for the main two factors extracted by factor analysis to the dataset of marine sediments.

Table 6
Factor analysis of suspended particulates from different water-types.^{a,b}

	PC1	PC2	PC3
Al	0.840	0.326	
Si	0.933		
Fe	0.774	0.471	
Mn	0.860		
Ca	0.395	0.825	
Mg	0.771	-0.349	0.338
Pb			0.610
Cd			0.877
Zn		0.949	
Cu		0.795	
Ni	0.788	0.519	
Cr	0.385	0.717	
POC	-0.436	0.762	
Variance (%)	36.29	33.00	11.48

^a Extraction method: Principal Component Analysis; Rotation method: Varimax with Kaiser Normalization.

^b Factor loadings <0.300 are not reported.

The score plot in Fig. 7 presents the distribution of samples between “lithogenic factor I” (Al, Si, Fe, Mg, Mn, Ni) and “pollution factor II” (Zn, Cu, TOC). Samples are clustered into three groups: a homogenous group of marine particulate matter, a second group of river particulate matter and marine sediments and a third group of streams and wastewaters, that present relatively high inhomogeneity. Suspended particulate matter from marine sites represented a group that is different from the other water-types (rivers, streams, wastewaters) as well as from the marine sediments. Thus, the composition of particulate matter did not coincide to that of inland sources. Moreover, the differences in composition between marine particulate matter and sediments suggest that resuspension was not the main mechanism for the occurrence of particulate matter. It is more possible detrital and partly living algal biomass domain the particulate matter in the upper seawater. Similarly findings about the origin of particulate matter in seawater have been reported by other investigators [4,12]. Suspended particulate matter from the rivers Axios and Aliakmon and marine sediments are clustered in the same group. These samples showed similar compositional patterns, revealing the impact of rivers in marine sediments. This is in consistent with findings reported that modern sedimentation patterns of Thermaikos Gulf, yielding >500 t/km² per year, are due to terrigenous fine grained sediments from rivers [9]. Moreover, modeling the transport of particles in Thermaikos Gulf by Krestenitis et al., showed that Axios river is the major sediment supplier of Thermaikos Bay [21].

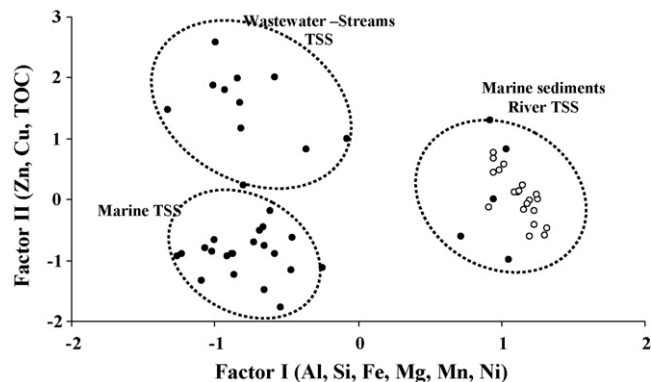


Fig. 7. Scores for the main two factors extracted by factor analysis to the dataset of marine sediments and suspended particulate matter from different water-types (closed circles: suspended particulate matter, open circles: sediments).

5. Conclusions

This paper investigated the occurrence of 27 major, minor and trace elements in suspended particulate matter and sediments in Thermaikos Bay, Northern Aegean Sea, Greece. Moreover the compositional profiles of suspended matter from various inland water (3 rivers and 4 streams) and wastewater (municipal, industrial, and effluents from tanneries) end up to the sea were also examined. The particulate matter from rivers dominated by aluminosilicate, calcium and iron materials. Wastewaters exhibited lower lithogenic content and are characterized by the presence of P, S, Cl, Cu, Zn, Cd and Cr. Marine sediments have been evaluated with respect to their pollution status by employing enrichment factors and comparison with sediment quality guidelines. Zn, Cu, Pb, As and Ag were found to have significant contribution from anthropogenic sources particularly at the inner part of the Bay. Most metals were found at concentrations that could adversely affect marine biota and the sites could be considered of medium-low and medium-high priority with respect to the likelihood of toxicity. Principal Component Analysis showed that marine particulate matter exhibited different compositional pattern from sediments suggesting that originate mainly from primary production rather than resuspension of sediments. Rivers have a significant impact on marine sediments.

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