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# SPATIAL AND TEMPORAL VARIATIONS IN THE GEOCHEMISTRY OF SUSPENDED PARTICULATE MATTER IN THE SHALLOW DELTAIC EMBAYMENT OF NORTHERN THERMAIKOS GULF, GREECE

Tsompanoglou K.[1], Tsirambides A.[1], Albanakis K.[1], Krasakopoulou E.[2],
Papageorgiou, A.[2], Anagnostou Ch.[2]

*[1] Department of Mineralogy-Petrology-Economic Geology, School of Geology, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece, ktsob@geo.auth.gr, ananias@geo.auth.gr, albanaki@geo.auth.gr*
*[2] Institute of Oceanography, Hellenic Centre for Marine Research, chanag@ath.hcmr.gr, ekras@ath.hcmr.gr, alkpa@ath.hcmr.gr*

**Abstract:** The chemical composition of Suspended Particulate Matter (SPM) in the northern Thermaikos Gulf was studied during a six month experiment, carried out from June 2004 to November 2004. Water samples were collected from three different depths (1 m bellow sea-surface, 10 m depth, 2 m above sea-bottom) and filtered to obtain SPM elemental and Particulate Organic Carbon (POC) concentrations. The geochemical properties of SPM were determined by thin-film X-ray Fluorescence spectrometry. SPM and POC concentrations exhibited strong spatial and temporal variations, related to the different environmental characteristics such as river discharge, wind/wave-induced resuspension of bottom sediment, biological productivity and anthropogenic interference. Correlation analysis showed that the elements Al, Si, Fe, Ti, K, Mg, V and Ba, have terrigenous origin, i.e. detrital aluminosilicates minerals. Chromium, Ni and Co, are of natural origin; they are derived from Axios and Aliakmon watersheds as mafic and ultramafic detrital material. Sulphur, Zn and Cu are derived from partly treated domestic and industrial effluents. The vertical distribution of POC implies higher biological activity at the upper layer of the water column. A part of Ca represents the autocthonous biogenic fraction i.e. biogenic carbonates. Phosphorus is mainly in the form of organic phosphate.

## 1. Introduction

The study area is the Northern part of Thermaikos Gulf, situated in the northwest Aegean Sea and consists of the Bay and Gulf of Thessaloniki (Fig. 1). This part of the Gulf is a shallow (<40 m), substantially tideless, semi-enclosed continental shelf. The geological structure of the coastal system is the result of active Quaternary delta progradation recording the imprint of river drainage basin weathering and denudation processes.

The northern Thermaikos Gulf receives freshwater inputs mainly from Axios, Aliakmon and Gallikos Rivers; their mean annual discharge is ca. 270 $m^3$ $s^{-1}$ (Poulos et al., 2000). During recent decades there has been significant reduction of freshwater inputs to the Gulf, as a result of canalizing river water to irrigation network, and also of a series of hydro-electric power dams on the Aliakmon watershed. Most of the particulate matter discharged from the rivers is deposited within the prodelta area and along the western coastline of the Gulf (Tsompanoglou et al., 2006). As regards the surface sediments of the study area, these are mainly silty; relict sands occur at the southeastern part of the Thessaloniki Gulf (Karageorgis and Anagnostou, 2001). The SE part of the study area is characterized by alternate erosional and depositional coastlines with the formation of marine terraces and lagoons respectively (Albanakis et al., 2005). Axios and Gallikos Rivers are comparatively the more polluted, as they receive fertilizers from agricultural effluents by Thessaloniki Deltaic plain (Karageorgis et al., 2005b; Skoulikidis, 1993).

The thermohaline circulation, mixing of different water masses and the prevailing wind regime, determines the movement of water over the study area. It has been observed that water masses consisting of saline and relatively dense waters enter from the SE, move towards the central and eastern areas, and finally enter the Thessaloniki Bay.

Freshwater inputs discharged from the Axios and Aliakmon Rivers, move south along the western part of the shelf (Hyder et al., 2002).

This northwestern part of Thermaikos Gulf receives the industrial and domestic sewage of the city of Thessaloniki. Recent studies in this part of the Thermaikos Gulf have shown that there are significant problems of eutrophication related to elevated loads of nutrients and trace elements in the water column (Pagou, 2000).

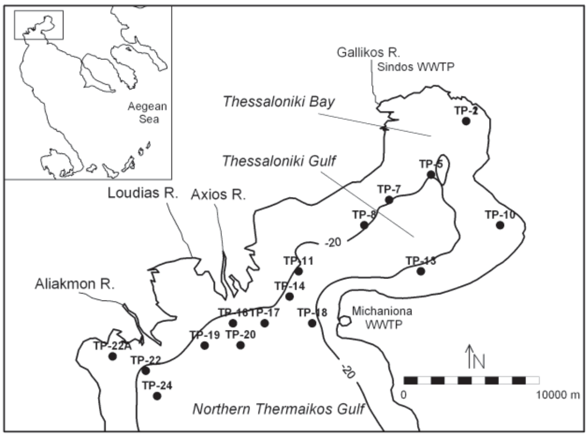

Fig. 1. Map of the study area showing the position of water sampling stations. The outfalls of Gallikos, Axios, Loudias and Aliakmon Rivers and the 20 m depth contour are also shown.

In coastal waters, POC is constituted by marine biological production and terrigenous mineral/organic material (Hedges et al., 1997). The former source represents living organisms (phytoplankton, zooplankton and bacteria), as well as their metabolic by-products and detritus of recently living organisms. The latter source is terrestrial inputs either by natural processes and/or by man-generated solid or liquid wastes. Organic matter plays a substantial role in the biogeochemical cycles of metals as it affects their partitioning and their bioavailability by forming either soluble complexes or insoluble flocks (Tankéré et al., 2000).

The aim of this work is to study the compositional variability of the SPM, during six-month period, in order to identify both spatial and temporal changes in SPM composition and concentration. We have investigated the distribution of particulate major and selected minor elements, as well as POC and Total Particulate Nitrogen ($PN_{tot}$) in the same waters. Data will be assessed to reveal the influence of river inputs, sediment resuspension and anthropogenic activities in the distribution of chemical elements in the Northern Thermaikos Gulf.

## 2. Sampling and analysis

Water samples were collected onboard a narrow hull fishing vessel, from 16 stations situated in the inner continental shelf of Thermaikos Gulf (Fig. 1). Most of sampling stations are located in the area of Axios and Aliakmon prodelta. Others are positioned around the Gulf of Thessaloniki to study the transport of water in Gulf of Thessaloniki. Station TP-5 is influenced by discharges of municipal Waste Water Treatment Plant (WWTP) of Sindos while station TP-18 is in the area where effluents from municipal WWTP of Nea Michaniona are discharged. Station TP-13 lies above an area of relict sands. Sampling was carried out at monthly intervals from June 2004 to November 2004.

Water was collected by using 10 l Niskin water bottles; these were deployed at 2 m above bottom (a.b.), at 10 m depth and 1 m below surface (b.s.). One aliquot of water of 2.0 l and two aliquots of 0.6 l were sampled from each Niskin bottle. The first was filtered onboard through polycarbonate membrane filters (nominal pore size 0.4 μm, diameter 47 mm); this was used in elemental analysis and in calculation of SPM concentration. The other two aliquots were filtered through GF/F filters (nominal pore size 0.7 μm, diameter 25 mm) which had been precombusted at $450^{o}$ C; these were used in POC and PNtot analysis. Particular attention was paid in rinsing the filters several times with filtered deionised and pH adjusted (8.2) water to remove sea salts. Samples were stored frozen in the dark; in the laboratory, they were defrozen and dried at $60^{o}$ C.

Elemental analysis was undertaken by thin-film X-ray spectrometry, following the method described by Price et al. (1999). Samples were analyzed by a Philips PW-2400 wavelength dispersive X-Ray spectrometer equipped with a Rh tube. In this method analysis, particulate matter contained on the filter is regarded as a thin film and, as a result, mass absorption correction was not required. Care was taken to achieve SPM loadings of ≈1 mg to fulfill the critical depth criterion.

POC and $PN_{tot}$ were determined by flash combustion analytical methods (Verardo et al., 1990) with an EA 1108 CHN Fisons Instruments analyser (instrument calibration by acetanilide). Organic carbon is determined after removing carbonate carbon; the filters were acidified with HCl 2 N. All measurements were corrected on the basis of blank filter measurements.

## 3. Results and Discussion

Spatial and temporal pattern of SPM concentration generally show high variability at the surface and at the bottom. At 10 m depth, SPM concentrations were always lower than the surface and the bottom. At the surface SPM concentration values varied between 0.2 and 11.6 mg/l, between 0.1 and 2.6 mg/l at 10 m depth and between 0.1 and 11.7 mg/l at 2 m above bottom (data presented at Tsompanoglou et al., 2006). At the surface, higher SPM values were observed in the area of Axios and Aliakmon prodelta creating the Surface Nepheloid Layer (SNL); lower values were observed in the SE part of Thessaloniki Gulf. The distribution of SPM at 2 m above bottom was various creating a Benthic Nepheloid layer in front of Axios and Ali-

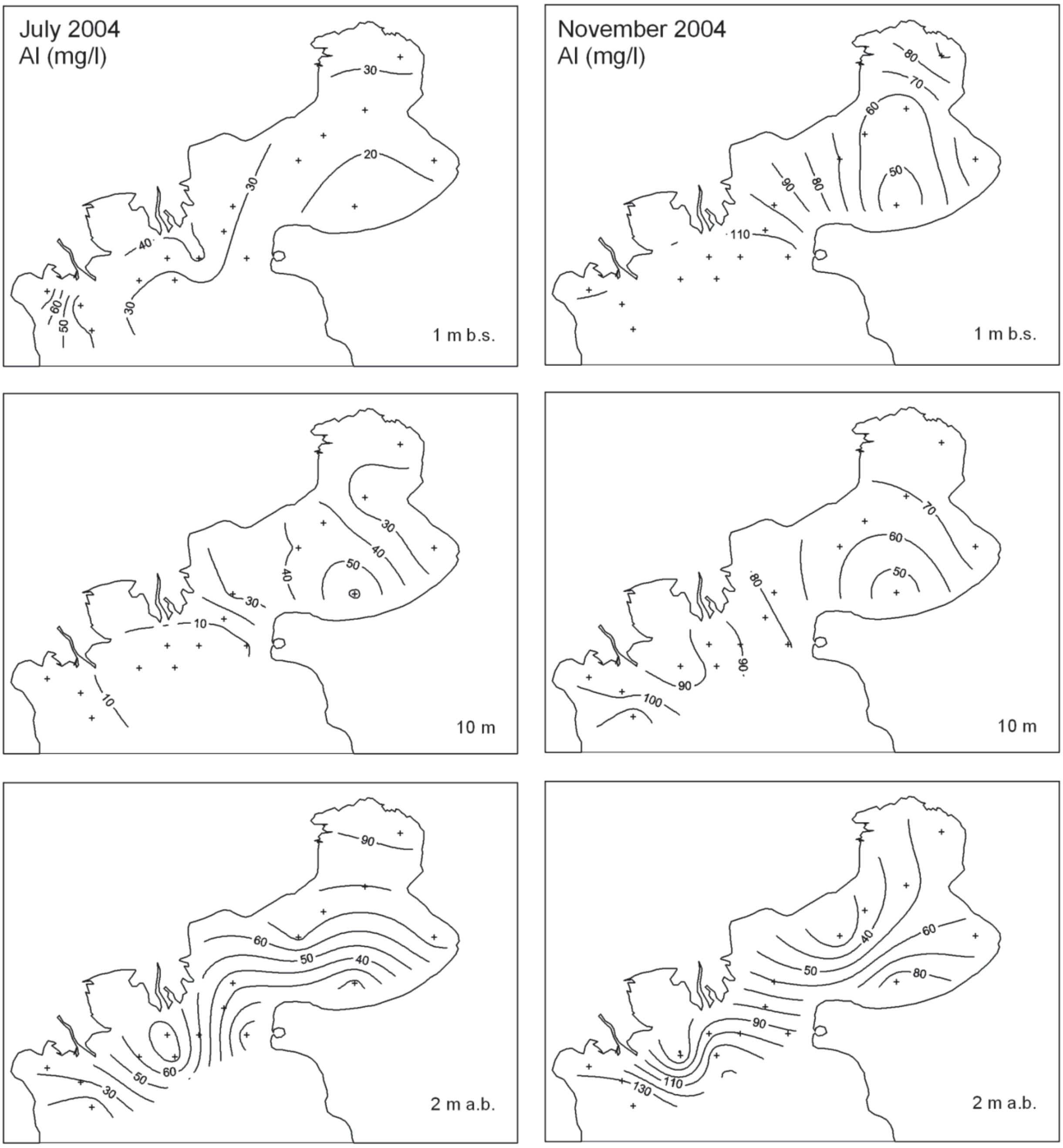

Fig. 2. The horizontal distribution of Al concentration (mg $l^{-1}$) at 1 m bellow sea-surface, at 10 m depth and at 2 m above sea-bottom on July and November sampling period.

akmon outfalls; these high SPM loads are attributed to resuspension of loosely deposited bottom sediment.

Here, we present concisely the distribution of Al and POC during July and November 2004 sampling periods (Fig. 2 and Fig. 3). It has been recognised that SPM elemental composition is controlled largely by the river inputs; these are being higher in November than in July. We also accept that in these shallower waters, SPM loads and composition can be variable over short time intervals, reflecting the regional impacts of wind/wave-induced resuspension, fluctuating riverine inputs and anthropogenic activities.

Aluminium has been used to define aluminosilicate concentration; its variation in water indicates the extent of bottom sediment resuspension and river input changes. Fig. 2 presents horizontal distributions of particulate Al at surface, at 10 m depth and at 2 m a.b. In July 2004, Al concentration values

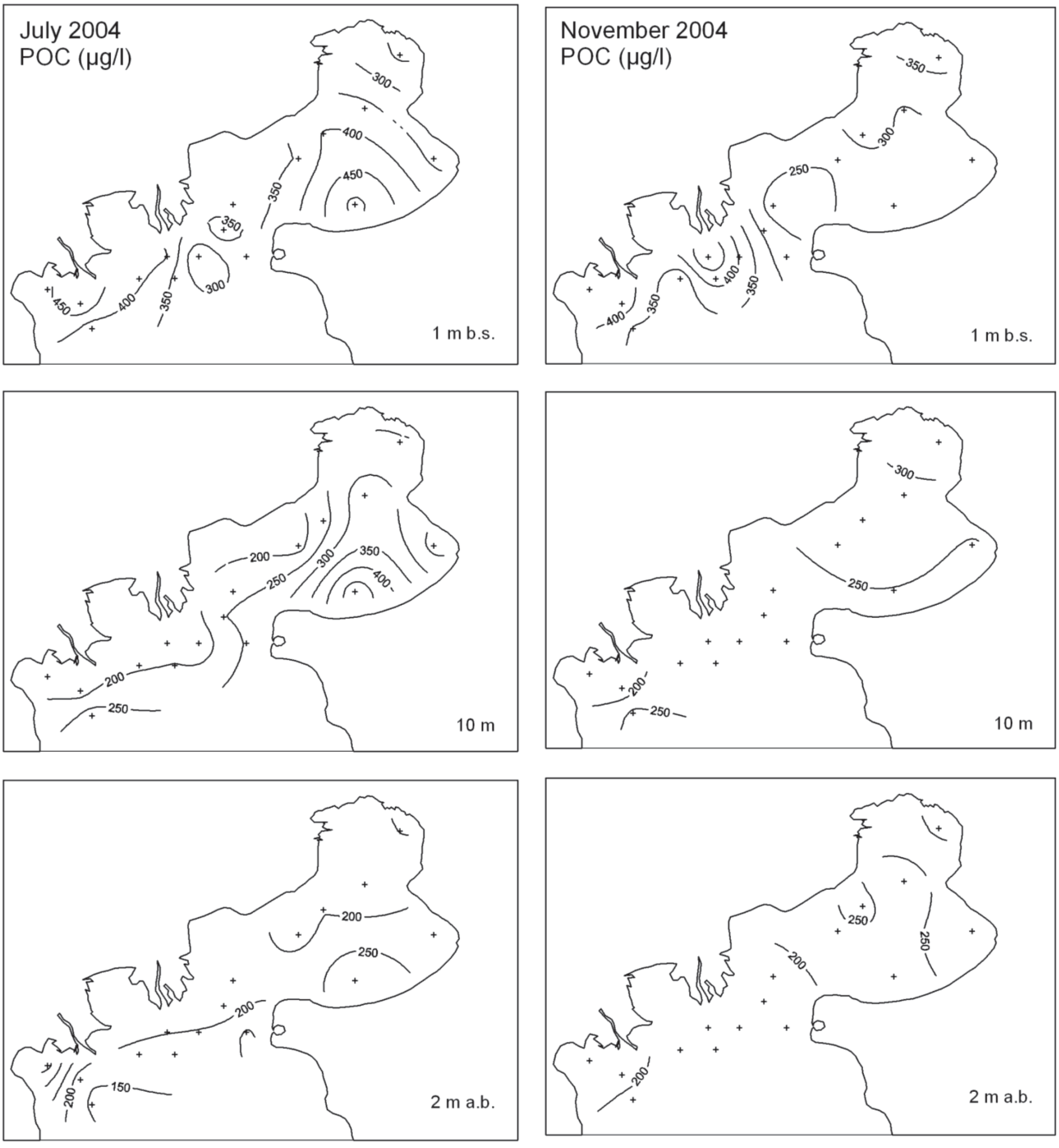

Fig. 3. The horizontal distribution of POC concentration (μg $l^{-1}$) at 1 m bellow surface, at 10 m depth and at 2 m above bottom on July and November sampling period.

varied between 3.37 (station TP17, 10 m depth) and 92.58 mg $l^{-1}$ (station TP2, 2 m a.b.). In November 2004, concentrations varied between 20.22 (station TP8, 2m ab.) and 155.60 mg $l^{-1}$ (station TP24, 2m ab.). The distribution of Al concentration at the bottom reflects different intensities of resuspension and the magnitude of Benthic Nepheloid Layer (BNL). The provenance of Al high values at the surface is the riverine inputs.

Elements Si, Fe, Ti, K, Mg, V and Ba show extremely strong correlations with Al (R>0.92, Tab 1). Their distributions in the waters of the Gulf are virtually the same as Al; they are predominantly held as aluminosilicates. There is no signal of marine barite formation.

The elements Fe and Mn are usually susceptible to re-distribution through redox cycling (Tankéré et al., 2000). Iron is associated closely with Al and is mainly lattice-bound in minerals. The uniform Fe/Al ratios throughout the water column implies the scarce occurrence of Fe oxyhydroxides even at the depth of 2 m a.b. Manganese appeared more reactive to redox cycling than Fe. We examined the distribution of the concentration of $Mn_{ex}$, which is the Mn held as oxyhydroxide coatings to mineral grains. $Mn_{ex}$ has been calculated from excess concentrations of Mn over those held with Al in aluminosilicates. It is the excess concentrations of Mn over the value Mn/Al = 0.01; this ratio is obtained from buried anoxic sediments of the Thermaikos Gulf (Karageorgis et al., 2005a) and is also similar to that of shale (Turekian and Wedepohl, 1961). The distribution of Ex. Mn/Al ratios in the water column did vary exhibiting higher values at the bottom layer.

The relationship between P and Fe is small while it shows good relationship with POC (R = 0.49); this suggests that the principal P species in the water column are organic phosphates originate from fertilizer treatment.

The vertical distribution of POC in the water column shows a decreasing trend towards the bottom; mean values lie at 323.78 μg $l^{-1}$ (n = 117) at the surface, 221.49 μg $l^{-1}$ (n = 105) at 10 m depth and 215.11 μg $l^{-1}$ (n = 113) at 2 a.b. The concentrations of POC were similar to anthropogenic affected systems (Krasakopoulou and Karageorgis, 2005). Higher POC concentrations in surface waters are associated with higher biological activity. $POC/PN_{tot}$ mass ratios unusually lie between 6 and 8 implying a combination of terrigenous inputs and also freshly produced or degraded autochthonous organic matter. POC concentrations do not correlate well with non element except P and S; these two elements interact with suspended organic matter. Sulphur is probably derived from partly treated domestic effluents. A poor positive correlation of Ca with POC implies that a substantial concentration of biogenic Ca is present in SPM. However the relationship of Ca with aluminosilicate detrital material implies that Ca predominantly originates from sediment resuspension.

Chromium, Ni and Co strongly correlate each

Table 1. R-Correlations between particulate major and minor elements (n = 281), POC (n = 259) and $PN_{tot}$ (n = 220).

| | *Si* | *Al* | *Fe* | *Ti* | *Ca* | *K* | *P* | *Mg* | *Na* | *Ba* | *Co* | *Cu* | *Mn* | *S* | *V* | *Zn* | *Cr* | *Ni* | *TC* | *POC* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 0,98 | 1,00 | | | | | | | | | | | | | | | | | | |
| Fe | 0,98 | 0,99 | 1,00 | | | | | | | | | | | | | | | | | |
| Ti | 0,97 | 0,99 | 0,99 | 1,00 | | | | | | | | | | | | | | | | |
| Ca | 0,63 | 0,62 | 0,63 | 0,63 | 1,00 | | | | | | | | | | | | | | | |
| K | 0,97 | 0,99 | 0,99 | 0,99 | 0,64 | 1,00 | | | | | | | | | | | | | | |
| P | 0,18 | 0,11 | 0,10 | 0,12 | 0,11 | 0,12 | 1,00 | | | | | | | | | | | | | |
| Mg | 0,92 | 0,92 | 0,93 | 0,89 | 0,57 | 0,91 | 0,08 | 1,00 | | | | | | | | | | | | |
| Na | 0,03 | 0,02 | 0,02 | 0,02 | 0,01 | 0,09 | 0,04 | 0,15 | 1,00 | | | | | | | | | | | |
| Ba | 0,94 | 0,96 | 0,95 | 0,96 | 0,60 | 0,95 | 0,16 | 0,85 | 0,04 | 1,00 | | | | | | | | | | |
| Co | 0,95 | 0,95 | 0,96 | 0,95 | 0,58 | 0,95 | 0,03 | 0,90 | 0,05 | 0,91 | 1,00 | | | | | | | | | |
| Cu | 0,20 | 0,21 | 0,22 | 0,23 | 0,16 | 0,22 | 0,19 | 0,14 | 0,01 | 0,25 | 0,16 | 1,00 | | | | | | | | |
| Mn | 0,62 | 0,62 | 0,61 | 0,61 | 0,43 | 0,62 | 0,23 | 0,58 | -0,01 | 0,58 | 0,58 | 0,18 | 1,00 | | | | | | | |
| S | 0,00 | -0,07 | -0,08 | -0,06 | 0,03 | -0,02 | 0,61 | -0,02 | 0,56 | -0,01 | -0,12 | 0,18 | 0,07 | 1,00 | | | | | | |
| V | 0,96 | 0,98 | 0,97 | 0,98 | 0,62 | 0,97 | 0,09 | 0,88 | 0,02 | 0,94 | 0,93 | 0,21 | 0,58 | -0,09 | 1,00 | | | | | |
| Zn | 0,33 | 0,34 | 0,33 | 0,35 | 0,29 | 0,34 | 0,26 | 0,23 | -0,02 | 0,38 | 0,28 | 0,70 | 0,24 | 0,18 | 0,32 | 1,00 | | | | |
| Cr | 0,46 | 0,48 | 0,54 | 0,51 | 0,33 | 0,49 | -0,03 | 0,43 | -0,06 | 0,48 | 0,51 | 0,30 | 0,23 | -0,09 | 0,47 | 0,23 | 1,00 | | | |
| Ni | 0,54 | 0,55 | 0,61 | 0,56 | 0,36 | 0,55 | -0,08 | 0,56 | -0,06 | 0,52 | 0,60 | 0,31 | 0,28 | -0,14 | 0,52 | 0,23 | 0,94 | 1,00 | | |
| TC | 0,02 | -0,05 | -0,06 | -0,08 | 0,08 | -0,06 | 0,48 | 0,05 | -0,01 | -0,06 | -0,09 | -0,04 | 0,00 | 0,55 | -0,09 | 0,12 | -0,17 | -0,14 | 1,00 | |
| POC | -0,02 | -0,07 | -0,08 | -0,09 | 0,05 | -0,07 | 0,49 | 0,02 | 0,00 | -0,08 | -0,10 | 0,01 | 0,02 | 0,54 | -0,09 | 0,12 | -0,13 | -0,10 | 0,96 | 1,00 |
| PN | 0,05 | -0,02 | -0,03 | -0,04 | 0,06 | -0,03 | 0,54 | 0,06 | -0,01 | -0,02 | -0,08 | -0,02 | 0,05 | 0,55 | -0,05 | 0,13 | -0,13 | -0,11 | 0,93 | 0,95 |

other. It is considered that they are weathering products of mafic and ultramafic rocks; ophiolites and peridotites cover parts of Axios watershed (Voutsinou-Taliadouri and Varnavas, 1995).

Zinc correlates well with Cu (R = 0.70); their distributions in the water column imply that riverine inputs are not their major provenance. Enhanced Zn and Cu concentrations appear at the Thessaloniki Bay area and also at the SW part of Thessaloniki Gulf. These elevated levels are attributes of anthropogenic activities carried out within the industrial part of Thessaloniki city, the by-products of which are actively transferred into the sea through atmospheric processes and influent discharge through outfalls.

## 4. Conclusions

The primary sources of particulate matter in the Northern Thermaikos Gulf are the river freshwater inputs, the primary production and the sewage outfall from the WWTP. The highest SPM concentrations were observed in the western part of the gulf, where Axios and Aliakmon Rivers outfall.

The fluvial transport is the major pathway for Al, Si, Fe, Ti, K, Mg, V and Ba that enter the sea as aluminosilicate particles; their concentrations are enhanced during the wet period (November), when fluvial discharge is maximized. These particles are also affected by bottom sediment resuspension; the distribution of particulate Al concentrations showed increased values in bottom waters over those measured at the surface.

Riverine freshwater inputs are also the sources of Fe and Mn although Mn distribution appears to be regulated by early diagenetic processes in the recently deposited sediment.

POC vertical distribution is generally characterized by higher values in surface waters that decrease gradually towards the sea-bottom. POC concentrations resemble those of eutrophic coastal areas. Organic matter is a mixture of marine primary production and terrigenous organic material.

Phosphate fertilizers are the source of particulate P in the water column, as revealed by its correlation with POC. Likewise, Zn, Cu and S concentrations seem to be anthropogenically enhanced.

Chromium, Ni and Co concentrations are of natural origin, derived from the weathering of mafic and ultramafic rocks of the Axios and Aliakmon drainage basins.

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