

SIZE-FRACTIONATED PARTICULATE ORGANIC CARBON (POC) EXPORT FLUXES ESTIMATED USING ^{234}Th - ^{238}U DISEQUILIBRIA IN THE SARONIKOS GULF (GREECE) DURING WINTER BLOOM

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ABSTRACT

Activity concentrations of the naturally occurring, short-lived and highly particle-reactive radionuclide tracer ^{234}Th in the dissolved and particulate phase were determined at 3 shallow-water stations (maximum depths: 65 (S.3), 97 (S.5) and 220 m (S.7)) of the Saronikos Gulf (central Aegean Sea, Greece – Eastern Mediterranean) during winter 2010 to assess the time scales of the dynamics and the depositional fate of particulate matter (POC, particulate ^{234}Th). For that reason, the method of in situ pumping was performed previously used by many researchers.

The fluxes of POC were estimated using radionuclides' disequilibrium. Specifically, the natural radionuclide ^{234}Th has been used as an indicator for export flux of particulate species from the euphotic zone. Its particle reactive and short half-life ($t_{1/2}=24.1$ d) nature, in contrast to the conservative and long ($t_{1/2}=4.5 \times 10^9$ y) ones of its parent ^{238}U can be used to trace processes occurring over short time-scales. Despite the wide application of ^{234}Th , studies using $^{234}\text{Th}/^{238}\text{U}$ disequilibrium on export fluxes are still very limited, largely because of the demanding sampling and analyses.

From the data obtained, the average activity concentrations of particulate and dissolved ^{234}Th were 5.4 ± 0.8 and 18.4 ± 7.4 Bq m^{-3} , respectively. Regarding the vertical profiles of ^{234}Th in comparison to the mother radionuclide ^{238}U , a strong deficit of ^{234}Th was observed and as a result, rapid export of POC was estimated. The cumulative export fluxes of particulate ^{234}Th (after integration over the total depth of the stations) were estimated to be 52 ± 7 in S.3, 180 ± 19 in S.5 and 400 ± 46 Bq $\text{m}^{-2} \text{d}^{-1}$ in S.7. The respective cumulative scavenging rates of dissolved ^{234}Th onto particles were estimated to be 23 ± 3 in S.3, 86 ± 8 in S.5 and 172 ± 19 Bq $\text{m}^{-2} \text{d}^{-1}$ in S.7. Finally, the cumulative export fluxes of POC in the 3 stations examined were found 375 ± 38 , 311 ± 34 and 300 ± 33 Bq $\text{m}^{-2} \text{d}^{-1}$, respectively.

Large export fluxes of POC were observed here, over one order of magnitude compared to other areas of the Mediterranean Sea, attributed to the enhanced biological activity due to phytoplankton bloom in conjunction with the large amounts of organics that the gulf accepts for a long time period. At the stations S.5 and S.7 fine particles were found to sink rapidly in all depths examined except the bottom nepheloid layer. This is a result of aggregation processes due to the shallow depths of the sampling area or due to the instability of large aggregates during sampling that might induce uncertainty in particle sampling. Larger particles ($> 25 \mu\text{m}$) of ^{234}Th were found increased at the surface, whereas smaller ones ($0.6 - 25 \mu\text{m}$) increased or remained the same near the seabed. Increase of large ^{234}Th particles at the surface certifies the origin of surface ^{234}Th linked with the land-based atmospheric deposition and/or surface advective movements. The distribution of particulate ^{234}Th in both fractions is controlled by SPM, (SPM versus particulate ^{234}Th : $R^2 > 0.6$), whereas POC follows a different trend attributed to the fact that POC is carried in the volume of a particle, whereas ^{234}Th sorbs to the surface. It is essential to mention that the Saronikos Gulf is still affected by the wide carbon discharges (domestic, industrial etc.) prior and after the construction of Psitalia WWTP as it is characterized by late renewal times of its waters.

KEYWORDS: POC; Particle Size; ^{234}Th - ^{238}U Disequilibrium Approach; Export Flux; Scavenging Rate, Saronikos Gulf.

1. INTRODUCTION

The production and flux of biogenic particles in the ocean controls the distribution of many elements [1]. Some elements are actively taken up by phytoplankton and play important physiological roles [2, 3]. Others become intimately associated with the flux of biogenic material through processes of elemental substitution [3], bioaccumulation [4], chemical scavenging [5], mineral precipitation in parti-

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cle interstices, such as barite, and on particle surfaces (e.g. Mn, aggregation during zooplankton grazing) [4], and particle adherence to organic surfaces [6]. The export of biogenic particles to deeper waters leaves surface waters depleted in nutrient and particle-reactive elements [1], often limiting marine productivity but also effectively cleansing the surface marine systems of airborne mineral dusts and pollutants.

Specifically, the particle flux of organic carbon is one of the largest sinks of atmospheric carbon dioxide. Nowadays, an attempt has been made to increase primary production by iron-fertilization, where iron is added at the surface of seawater, although the implications for carbon export to the marine interior have been less clear. Considering that a lot of discussion has been made for global warming and climate change, it remains a challenge to accurately estimate this important component of the global carbon cycle. Knowing the mechanisms that lead the flux of carbon to the deep sea is an important demand for understanding the marine carbon cycle and thus the potential impacts of rising atmospheric CO₂ concentrations. Processes that occur in coastal environments, such as decomposition of organic matter, mineral formation, and denitrification affect the pelagic balances of many elements. Because of the proximity of sediments to the euphotic zone, these environments are unique in the sense that sedimentary processes can influence pelagic systems [7].

Over the past 20 years, the deficit of the natural radionuclide ²³⁴Th (half-life 24.1 d) with respect to its parent ²³⁸U in the upper water column has increasingly been used to determine the export of particulate organic carbon (POC) from the euphotic zone (see references there in). This approach is based on the scavenging of particle-reactive ²³⁴Th onto biogenic particles in the upper 100 – 200 m of the oceanic water column, followed by export of the ²³⁴Th as the particles sink. The method usually involves measurement of particulate and dissolved ²³⁴Th profiles in the water column. The flux of ²³⁴Th required to support the deficit of this radionuclide in the water column is converted to a POC flux by multiplying the ²³⁴Th flux by the POC/²³⁴Th ratio on the sinking particles.

POC is carried in the volume of a particle, whereas ²³⁴Th sorbs to the surface. The calculation of ²³⁴Th-based POC export flux depends on measurement of the POC/²³⁴Th ratio of sinking particles, which has been found to vary with both particle size and depth [9-12]. POC/²³⁴Th ratios have been observed to decrease with particle size, due to the preferential assimilation and/or degradation of carbon [8]. Burd *et al.* [13] showed that aggregation and adsorption of ²³⁴Th alone might account for particles < 10 µm. A decrease in POC/²³⁴Th ratios with depth could be attributed to preferential remineralization of POC and retention of ²³⁴Th onto particles as they sink through the water column [9, 12-14]. An understanding of the mechanisms controlling the variability in the POC/²³⁴Th ratio is needed for accurate estimates of export fluxes of POC using ²³⁴Th as a proxy; however, there are only few published studies

of the size distribution of POC/²³⁴Th ratios on multiple particle size fractions.

In the present paper, we examine the POC export fluxes estimated using ²³⁴Th – ²³⁸U disequilibrium approach in Eastern Saronikos Gulf, a populated area located in the Eastern Mediterranean Sea. Moreover, the depth profiles of size-fractionated POC and ²³⁴Th in two particle fractions (0.6 – 25 µm and > 25 µm) are used to (a) assess factors controlling the depth and size distribution of POC and particulate ²³⁴Th and (b) evaluate if POC and ²³⁴Th are removed from surface seawater by the same sinking particles. This analysis allows for an assessment of the levels and the accuracy of ²³⁴Th-based POC export fluxes in the Mediterranean Sea, a region for which relatively few ²³⁴Th-based POC fluxes have been reported.

2. THE AREA OF INTEREST

The present study was carried out at the eastern region of the Saronikos Gulf (Greece) (Fig.1). The eastern section of Saronikos, characterized by the Athens metropolitan area, has relatively uniform depth topography, with a maximum depth of 200 m to the south-east of Aegina to 90 m between Aegina and coastal suburbs of Athens. The main body of the eastern basin has depths between 70 and 90 m. The western part of Saronikos is deeper. At the north end of the gulf lies the Elefsis Bay with maximum depth of about 30 m. The bay is joined to the gulf by two narrow and shallow channels. The eastern connection, with a dredged channel 11 m deep, communicates with the Keratsini Bay and Eastern Saronikos. Piraeus Port, which is one of the largest in Mediterranean, is located about 1 km southern of the eastern channel.

The Saronikos Gulf is mainly polluted from the Wastewater Treatment Plant of Psitalia (WWTP), located in a small island near the Piraeus harbour and the Keratsini Bay, which discharges pre-treated domestic wastes of Athens (whose population reaches over 5,000,000 inhabitants). An approximate 800,000 m³ d⁻¹ of treated waste is discharged, carrying 100 x 10⁶ g C d⁻¹ (or 96 mol C s⁻¹; 8.3 x 10⁶ mol C d⁻¹) of dissolved organic carbon [15]. Significant amounts of nutrients are also introduced in the form of industrial effluents directly into Elefsis Bay as along the bay more than 30 industries are located (oil refineries, steel mills, shipyards, etc.) [16]. In the main Saronikos Gulf the effect of WWTP outflows is evident, as a plume of nutrient-rich water extends about 20 km south of Salamis Island [17].

Hopkins and Coachman [18] reported that the renewal times of Saronikos Gulf waters from Aegean Sea occur with currents entering from south-eastern, following the east coastline up to Aegina Isl. and outflowing from the western part. The renewal times of surface waters in eastern and western Saronikos are within 1-2 months; however, in greater depths they decrease to 2.1 up to 8.1 years [18].

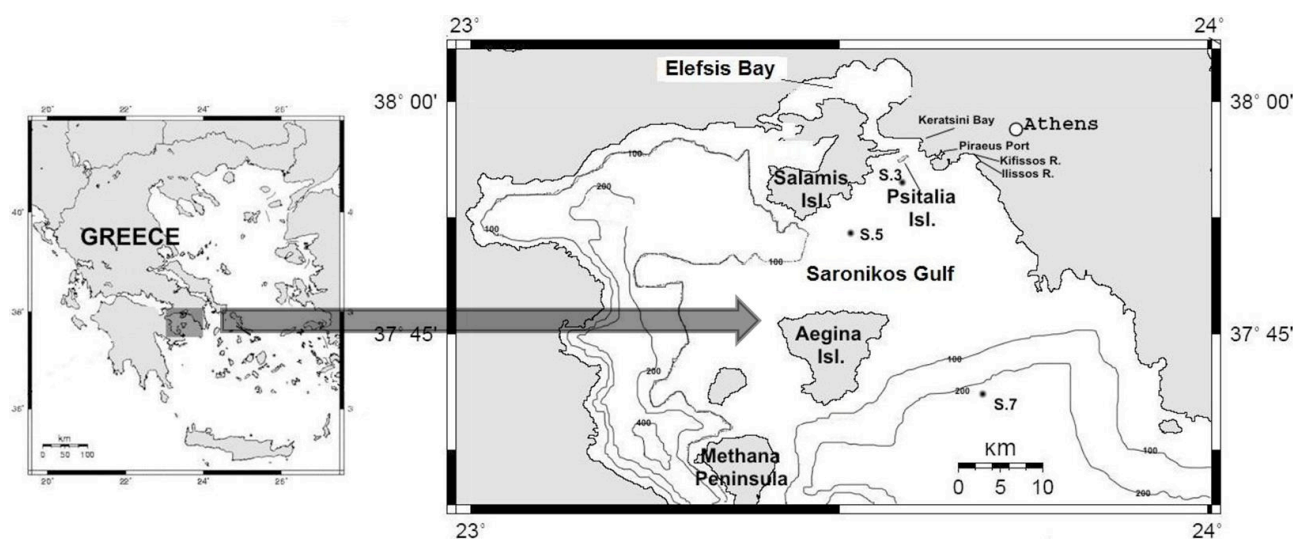


FIGURE 1 – The area of sampling with the selected sampling stations (Saronikos Gulf, Greece).

3. MATERIALS AND METHODS

The method used for ^{234}Th determination is based on in situ filtration (using Challenger Oceanic Systems & Services' pumps) via GF/A disc prefilters to scavenge particulate fraction of ^{234}Th and via impregnated cartridges (with MnO_2) to adsorb dissolved one. After sampling, the filters were transferred back to the laboratory for physical treatment and the final products were measured with gamma spectrometry. ^{238}U was calculated via its proportionality with salinity. The method is described in detail by Bueseler et al. [10] and Evangelidou et al. [19]. Samples were collected during bloom evolution of winter 2010 from the eastern part of the Saronikos Gulf, at stations S.3, S.5 and S.7 with maximum depths of 65, 97 and 220 m, respectively (Fig. 1). Temperature, salinity and pH were determined by an in situ CTD, model YSI 53 in the 3 stations.

3.1 Sampling of particulate and dissolved ^{234}Th via in situ filtration

A high volume in situ pump (manufactured by Challenger Oceanic Systems and Services, UK) was deployed in every selected depth of the stations. Seawater was directly pumped through a manifold consisting of two disc prefilter (for the examination of two fractions of particles) and two MnO_2 -impregnated cartridges (see next chapter 3.2) connected in series and finally through an impeller-based flow-meter to record the volume of the water filtered. Sample volumes of 500 – 1000 L were processed at flow-rates of 0.3 – 1.0 $\text{m}^3 \text{h}^{-1}$ and the respective accuracy of the flow-meter was $\pm 2\%$, operating in a range of 22.7 to 2730 L h^{-1} [20].

The in situ pumps separated dissolved and suspended particulate phases via filtration through two pre-cleaned, pre-combusted 142 mm Whatman GF/A disc filters, one of pore-size of 25 μm to scavenge "coarse" particle frac-

tion of > 25 μm and a second one of 0.6 μm for the separation of the "fine" fraction in the range of 0.6-25 μm .

3.2 Impregnation procedure of cartridges with MnO_2 in the laboratory prior to sampling

Cotton wound cartridge filters (25 cm long and 1 μm pore-size) were used in the impregnation procedure. It has been found that these filters are easy to handle and they have a high loading capacity and a very low radionuclide blank [21, 22]. Impregnation was obtained by circulating water suspension of KMnO_4 and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a closed loop, employing a small pump and the filter to be impregnated. The filters collected the green-brown slurry formed. When the circulating solution was clear, the impregnated filters were removed from the loop, they were dried in an oven at 60-80 $^\circ\text{C}$ for 24 h and packed for the sampling [21, 22].

3.3 Physical treatment and gamma spectrometry measurements in the laboratory

After sampling, the filters were transferred to the laboratory. The disc filters were rinsed with distilled water to remove the residual salts, air-dried and directly measured with gamma spectrometry after transfer to a calibrated measurement pot (radius 7.1 cm and height 1.0 cm). The cartridges were dried and ashed in ovens at 350 $^\circ\text{C}$. The remaining ash was transferred into special measurement pots (radius 3.4 cm and height 2.0 cm) for gamma – spectrometry measurements.

The measurements were carried out in a gamma – spectrometry system comprised of a high-purity Germanium detector (Canberra Coaxial HPGe Detector System) with a relative efficiency of 90% and resolution of 2.1 keV (at 1.33 MeV photopeak of ^{60}Co). The HPGe detector was connected to a multi-channel analyzer and the whole system was controlled by Canberra Genie 2000 software. The duration of each measurement was at least 7×10^4 s usually overnight.

The energy calibration was performed using standard active sources of ^{241}Am and ^{60}Co in a range of 2000 keV in 8000 channels (0.25 keV/ch). The detector's efficiency was calculated (in connection with energy) using a mixed standard solution of ^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{137}Cs , ^{203}Hg , ^{113}Sn , ^{85}Sr , ^{88}Y of total activity of 5202 Bq. The mixed standard solution produced more photopeaks in lower energies of the spectrum where ^{234}Th emits. As low energy gamma rays are attenuated quite easily by self absorption, careful attention must be paid to sample geometry in order to maximize overall detection efficiency and to ensure reproducibility. Buessler et al. [23] reported that the smaller the sample volume, the greater the detection efficiency. In this study, the geometries used were of small volume (radius 7.1 cm and height 1.0 cm – radius 3.4 cm and height 2.0 cm) and efficiency calibration was performed using the same geometry; thus self-absorption assumed negligible.

Once the seawater sample was filtered to separate the particle fractions, it was passed sequentially through 2 cartridge filters that have been impregnated with MnO_2 (see chapter 3.2). It has been previously shown that dissolved thorium is efficiently extracted from seawater by these cartridges [22]. The collection efficiency of each sample was calculated from the pair of MnO_2 cartridges by the following equation:

$$A(^{234}\text{Th}) = \frac{A_1}{E} = \frac{A_1}{1 - \frac{A_2}{A_1}} \quad (1)$$

where A_1 and A_2 are the ^{234}Th activities (corrected for physical decay to the date of sampling) of the first and second MnO_2 cartridge, respectively and E is the collection efficiency. The collection efficiencies (E) of the cartridges used were kept around 90 % (average: 90 ± 3 %) indicating high quality of the data. Previous studies have shown that collection efficiencies below 50 % usually result in ^{234}Th : ^{238}U ratios larger than 1, attributed to the lateral advection of ^{234}Th in coastal regions. The uncertainties of ^{234}Th activities in the first and the second filter (A_1 , A_2) were 1σ values derived from counting statistics (Typical counting statistic error: 0.26 ± 0.01 %). The final uncertainty of $A(^{234}\text{Th})$ was estimated by propagation.

3.4 Determining Uranium-238 activity concentrations from salinity

Uranium-238 was calculated via its proportionality with salinity. Typically, the relationship derived by Chen et al. [24] is used in open ocean studies. However, Mediterranean waters are generally of higher salinity than the open Atlantic and Pacific waters for which this relationship was obtained. It has been found that ^{238}U concentrations in the Mediterranean are enhanced relative to the U-salinity relationship of Chen et al. [24], due to phosphate fertiliser run-off into this enclosed basin [25]. However, a recent work has compared the Mediterranean with Atlantic and Pacific waters, finding no significant difference in their U-salinity relationship [26]. Although U can deviate

from conservative behaviour in some coastal areas [27, 28], this deviation occurs usually where either freshwater or reducing conditions dominate. The salinity range observed in the present study (33.5 psu in 60 m depth at S.3 and 38.3 psu at the surface of S.7) indicates that freshwater has no significant influence in salinity, although there are some fresh-water inputs in the system. Therefore, ^{238}U concentrations were derived from the following equation [26].

$$\text{U-238 (dpm L}^{-1}\text{)} = (0.07065 \pm 0.00146) \times \text{salinity (psu)}$$

or (2)

$$\text{U-238 (Bq m}^{-3}\text{)} = (1.1775 \pm 0.0243) \times \text{salinity (psu)}$$

3.5 Analysis of Suspended Particulate Matter (SPM) and Particulate Organic Carbon (POC)

After gamma spectrometry analysis of the filters and prior to the POC analysis, the same pre-weighted disc filters (Whatman GF/A of pore size 0.6 μm and 25 μm and diameter of 142 mm) weighed in a microbalance Sartorius BP 211 D to obtain the SPM concentration. The percentage uncertainty of the microbalance was less than 1.

The same filters were then treated for POC analysis. Carbonates were eliminated from the filter before analysis by fuming the filter with 10 % HCl. The filters were then analyzed with TruSpec CHN Leco analyzer. The advantage of this apparatus is the fact that high amount of the filter could be loaded into (50 – 1500 mg) and thus no further aliquots or subsamples need to be produced. The range of TruSpec CHN Leco analyzer for carbon was 0.002 – 100 %. The LOD was calculated to be 1 $\mu\text{mol L}^{-1}$.

4. RESULTS AND DISCUSSION

4.1 Hydrographic features of Saronikos Gulf, SPM and POC distribution during bloom evolution

Temperature, salinity, pH and density ($\sigma\text{-t}$) profiles are illustrated in Fig. 2, for winter 2010 at the three stations. At S.3 located next to the pipeline of the Psitalia WWTP, a sharp halocline can be observed, although sampling took place in winter, as a result of the low dense waters that outflow at 65 m depth and primarily dominate the deeper layers before mixing. At the deepest S.5 and S.7 stations, which they are located at 7 and 28 nautical miles away from the WWTP, a complete mixing layer can be observed as no significant impact from washout processes and low dense outflows can be recorded.

SPM concentrations ranged from 0.11 to 0.30 mg L^{-1} at S.3, which is in the lowest lever considering that the Psitalia WWTP pipelines outflow next to that station. SPM was relatively high (0.51 mg L^{-1}) near the seabed of S.5, attributed to the bloom of phytoplankton during primary productivity that accumulates biogenic particles in the bottom nepheloid layer. Regarding S.7, higher concentrations were observed at the surface (0.82 mg L^{-1}), as a result of the bloom of phytoplankton. Phytoplankton develops in Mediterranean during winter [8] producing

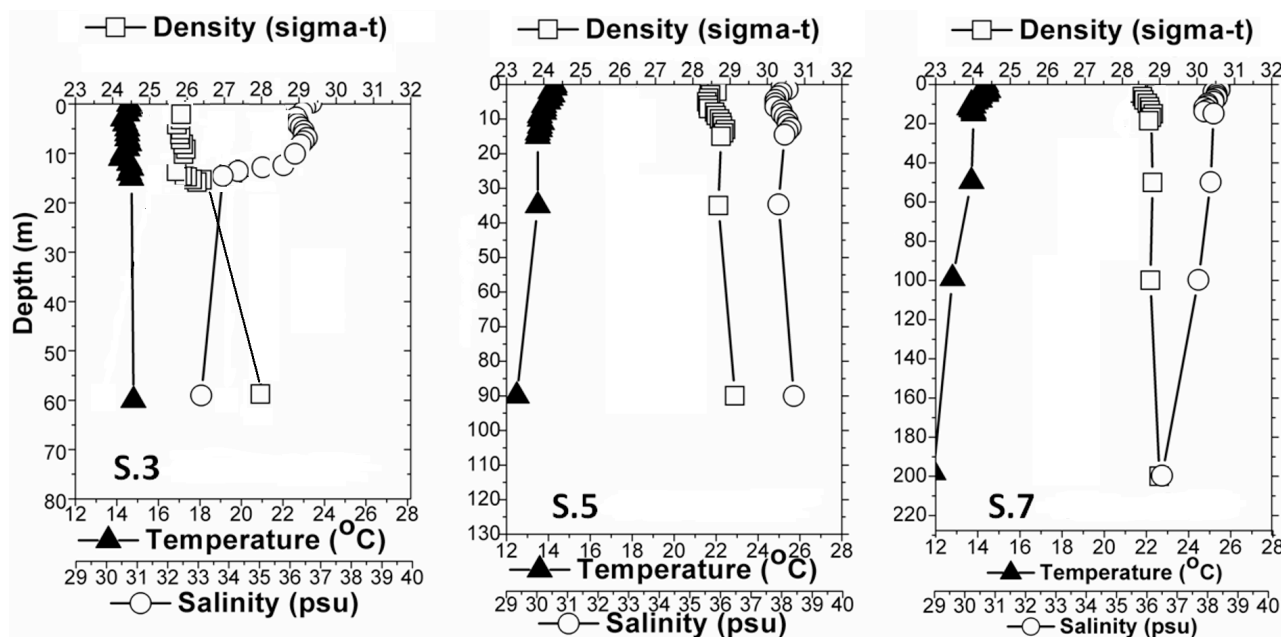


FIGURE 2 – Salinity, temperature and density vertical profiles at the stations (S.3, S.5 and S.7) in the Eastern Saronikos Gulf

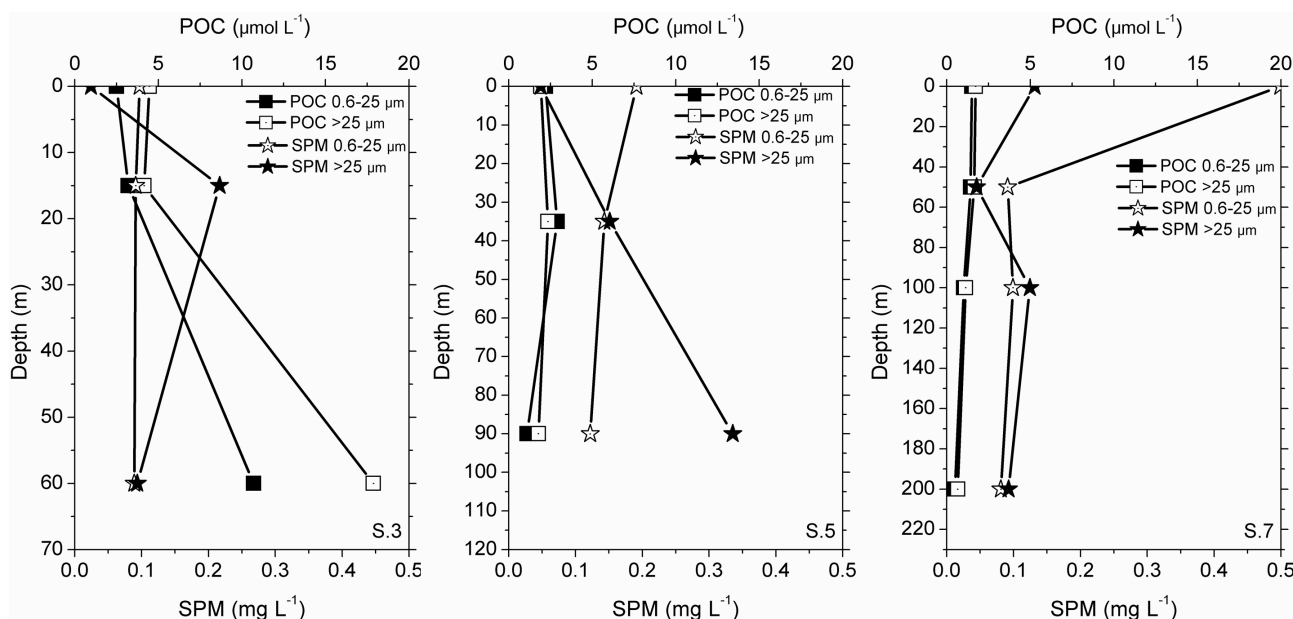


FIGURE 3 – Vertical profiles of SPM and POC in two fractions (0.6 – 25 and > 25 µm) at the stations of the Saronikos Gulf.

biogenic particles at the surface that gradually sink to the sediment. Nevertheless, one can note that the generally low SPM values certify the imperceptible washout and erosion processes that characterize the area.

Vertical profiles of POC and SPM are depicted in Fig. 3 for two particulate fractions (0.6 – 25 and > 25 µm). During winter bloom, POC ranged between 7.5 and 10.9 µmol C L⁻¹ at S.3 located near the Psitalia WWTP with the maximum being at 60 m depth. At S.5 and S.7 POC

concentrations were considerably lower (S.5: 1.5 – 4.3 µmol C L⁻¹, S.7: 1.3 – 3.1 µmol C L⁻¹). Azetsu-Scott and Johnson [29] reported that during bloom evolution POC concentrations are high in the surface water and low in the middle and deep water. In the present study this not apparent due to the domestic impact in carbon charges (i.e. WWTP of Psitalia) that affects the bottom of S.3 and via current movements it is dispersed to the wider Saronikos Gulf (S.5 and S.7).

The same workers also reported that at the beginning of a bloom, particulate species in the surface waters are composed of particles of sizes up to 40 μm , and usually no aggregates are observed below the thermocline. In the present study larger particles ($> 25 \mu\text{m}$) dominate the medium and bottom layers, whereas smaller ones (0.6 – 25 μm) the surface (Fig. 3). It seems that during their sinking, small particles are aggregated producing larger ones certifying the importance of the Saronikos Gulf marine environment. In contrast with the surface water, particles in the bottom water changed from smaller and more degraded particles to large biogenic particles, including faecal pellets as the bottom nepheloid layer became thicker and stronger. Large aggregates in the water column are very fragile and tend to disaggregate during sampling [30], and, consequently, observations of particles are not always representative of their size or shape.. However,

aggregates in the bottom nepheloid layer that settle during or immediately after the surface bloom may be more robust and harder to disaggregate than those found later in the season.

4.2 Activity concentrations of ^{234}Th and ^{238}U and flux estimates

The activity concentrations of ^{234}Th relative to ^{238}U are illustrated in Fig. 4. Specifically, the particulate, as well as the dissolved and total ^{234}Th is shown in the same figure with the salinity-based mother ^{238}U . From the figure, one can observe large disequilibrium between ^{234}Th and ^{238}U resulting in high export fluxes of particles associated with ^{234}Th . More specifically, ^{234}Th was found 25 – 50 % far from equilibrium in S.3, around 30 % in S.5 and between 30 – 75 % in S.7.

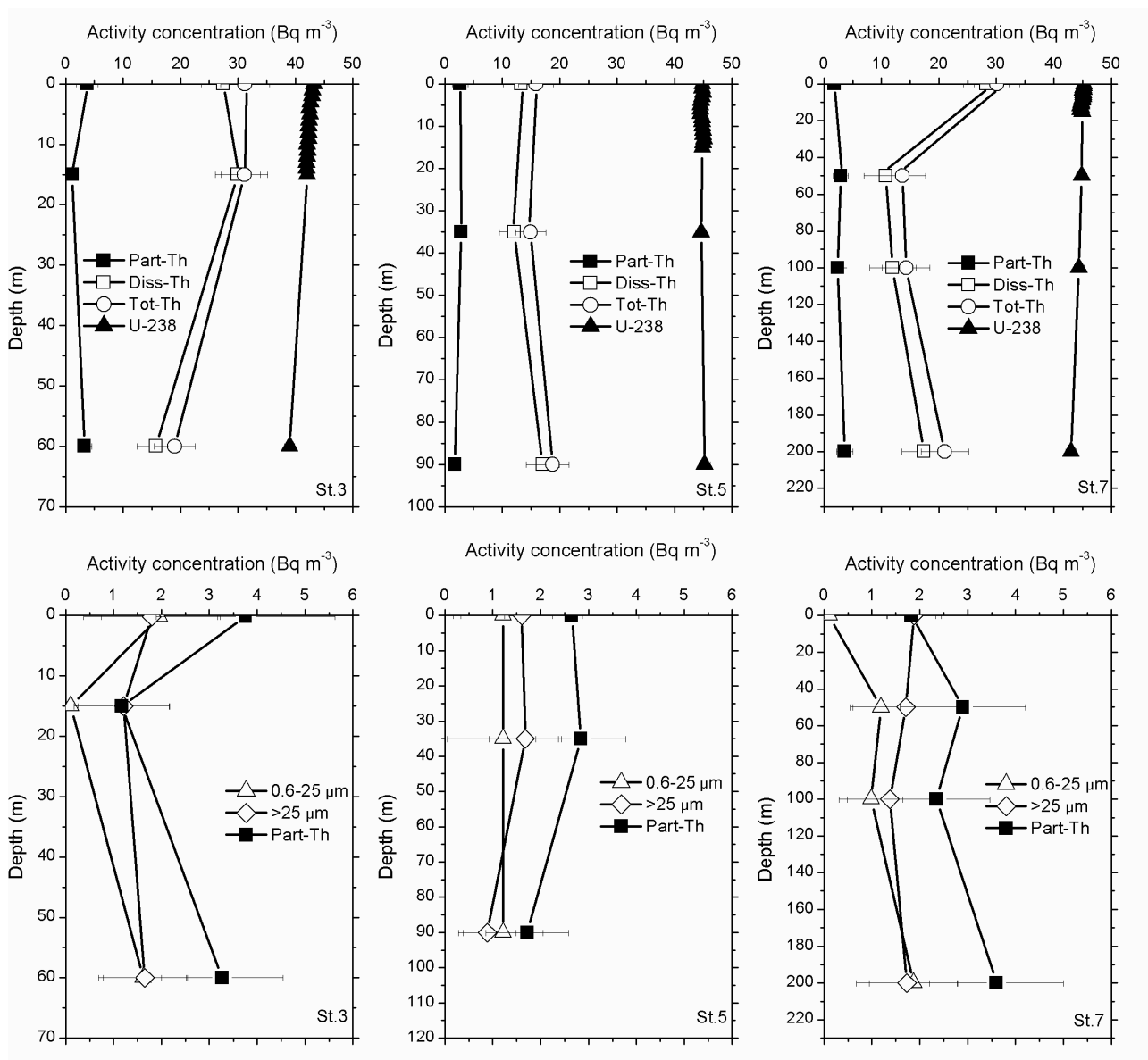


FIGURE 4 – Particulate, dissolved and total ^{234}Th profiles relative to ^{238}U at stations S.3, S.5 and S.7. Profiles of particulate ^{234}Th fractions (0.6 – 25, $> 25 \mu\text{m}$ and total).

As regards particle speciation, depth profiles indicate that the fraction of large particulate ($> 25 \mu\text{m}$) ^{234}Th was found increased at the surface of the stations. On the other hand, smaller particles ($0.6 - 25 \mu\text{m}$) associated with ^{234}Th increased or remained at the same level near the seabed (Fig. 4). Nevertheless, POC and particulate ^{234}Th in the two fractions examined here ($0.6 - 25$ and $> 25 \mu\text{m}$) showed extremely weak correlation ($R^2 < 0.06$), though the distribution of both POC and ^{234}Th varied in a different manner. Thus, at each depth, POC and ^{234}Th showed non-identical distribution among the sampled particle size fractions (Fig. 3 and Fig.4) and thus it is not controlled by the same particles. Furthermore, increase of large particles of ^{234}Th at the surface testifies the origin of surface ^{234}Th . It has been found [18] in the same area that surface ^{234}Th sometimes exceeds equilibrium with ^{238}U as a result of land-based atmospheric deposition or advective movements. It would be essential to note that the distribution of particulate ^{234}Th in both fractions is clearly controlled by SPM; they follow the same distribution pattern and also significant correlation was achieved ($R^2 > 0.6$).

In order to calculate the fluxes of particulate ^{234}Th and the scavenging rates of dissolved ^{234}Th , the One dimensional Box Model described by Coale and Bruland [31, 32] was applied. The general formulation of ^{234}Th activity in the model is the result of a balance between continuous production from ^{238}U , radioactive decay of ^{234}Th , removal onto rapidly sinking particles and transport into or out of the box by advection and diffusion. The temporal change in total ^{234}Th is expressed by:

$$\frac{\partial A_{Th}^t}{\partial t} = \lambda_{Th} A_U - \lambda_{Th} A_{Th} - P_{Th} + V \quad (3)$$

where A_U and A_{Th} are the ^{238}U and the total ^{234}Th activities (expressed in Bq m^{-3}), respectively, λ_{Th} is the decay constant of ^{234}Th ($= 0.02876 \text{ d}^{-1}$), P_{Th} (expressed in $\text{Bq m}^{-2} \text{ d}^{-1}$) is the removal flux of particulate ^{234}Th , and V is the sum of the advective and diffusive processes.

The key assumptions of this model are that: (i) steady-state conditions prevail, which means that ^{234}Th activities and removal rates (J_{Th} and P_{Th}) are essentially constant with respect to the ^{234}Th decay constant; (ii) horizontal and vertical advection and diffusion of ^{234}Th are negligible; and (iii) scavenging is irreversible. The assumptions are usually fulfilled in that restricted region (see: Evangeliou et al. [18]); thus Eq. 3 is simplified to:

$$P_{Th} = \lambda_{Th} (A_U - A_{Th})$$

or (4)

$$P_{Th}^i = \lambda_{Th} \int_{z_0}^{z_i} (A_U - A_{Th}) dz + P_{Th}^{i-1}$$

if one integrates over the depth. P_{Th}^{i-1} represents the flux of the particles sinking from the above layer (i-1) and equals to 0 in the surface layer. This formulation of ^{234}Th

flux (Eq. 3 and 4) is by far the most commonly used model in ^{234}Th export studies, due to its simplicity and ease of application (only total ^{234}Th need to be measured).

Since the supply of ^{234}Th is through the decay of ^{238}U , then the removal from the dissolved phase is via either scavenging onto particles or radioactive decay:

$$J_{Th} = A_U \lambda_{Th} - A_{Th}^d \lambda_{Th}$$

or

(5)

$$J_{Th}^i = \lambda_{Th} \int_{z_0}^{z_i} (A_U - A_{Th}^d) dz$$

if one integrates over the depth. J_{Th}^i is the rate of scavenging of dissolved ^{234}Th onto the particulate phase and A_{Th}^d is the activity of dissolved ^{234}Th .

Moran et al. [33] demonstrated mathematically that this empirical method is based on the key assumptions that the particle size distributions of POC and ^{234}Th and the sinking rates of particles that transport POC and ^{234}Th from surface waters are equivalent. However, because POC is carried in the volume of a particle and ^{234}Th sorbs to the surface, it has been suggested that the distribution of ^{234}Th is skewed towards smaller particles because of the decreasing surface area to volume ratio with increasing particle size. Furthermore, ^{234}Th may be scavenged by inorganic particles such as carbonate, opal, or lithogenic material, all of which are characterized by particle densities that exceed the density of organic matter. Further mathematical evaluation of the ^{234}Th method by Smith et al. [34] indicates that if POC and ^{234}Th are not removed from surface waters by the same particles. A particle-fractionated study was attempted here.

As mentioned previously, the calculation of POC export fluxes also depends critically on measurement of the POC/ ^{234}Th ratio of sinking particles, which has been found to vary with both particle size and depth. Any decrease in POC/ ^{234}Th ratios with depth has been attributed to remineralization of POC and retention of ^{234}Th on particles as they sink through the water column. POC/ ^{234}Th ratios are shown in Fig. 5. POC/ ^{234}Th ratios ranged between 1.9 ± 0.7 and $8.7 \pm 1.2 \text{ mmol Bq}^{-1}$ at S.3, around 1.6 mmol Bq^{-1} at S.5 and between 0.3 ± 0.1 and $1.4 \pm 0.2 \text{ mmol Bq}^{-1}$ at S.7.

A rapid decrease with the depth was observed at the bottom of station S.5. This decrease is clearly attributed to the remineralisation of POC. Although station S.5 is inside the mooring area of the vessels to the Piraeus Port, it seems that vessels' anchors have not caused resuspension, which would result in excess of ^{234}Th relative to ^{238}U . It is likely that suspended particles present within the interface between water and sediment could desorb scavenged ^{234}Th back to the water column increasing dissolved ^{234}Th activity concentrations. In fact, this is apparent if one observes the slight increase of dissolved ^{234}Th at the bottom of S.5 in Fig. 4.

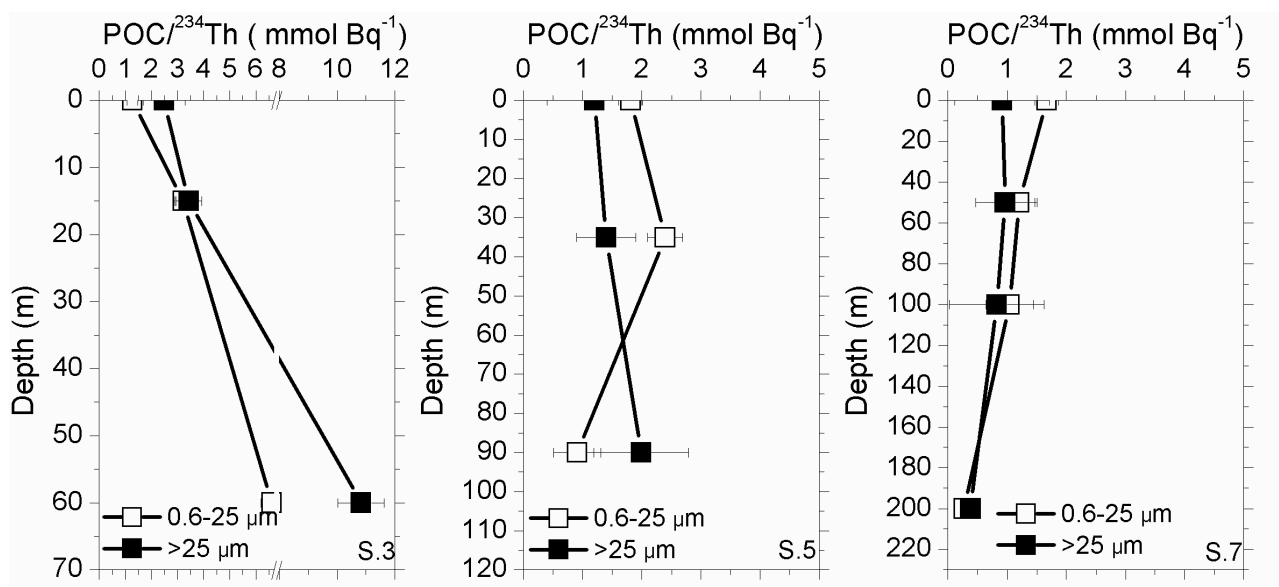


FIGURE 5 – Profiles of POC/²³⁴Th ratios in two fractions (0.6 – 25 μm and >25 μm) at stations S.3, S.5 and S.7 of the Saronikos Gulf. Axis – x breaks where extreme values were observed.

4.2 Size-fractionated export fluxes of POC

The ²³⁴Th-based POC export flux (P_{POC}^i , mmol m⁻² d⁻¹) is defined as the product of the flux of ²³⁴Th (P_{Th}^i , Bq m⁻² d⁻¹), which is measured as the depth-integrated deficit of ²³⁴Th relative to its conservative parent ²³⁸U and the POC/ A_{Th}^p ratio of sinking particles:

$$P_{POC}^i = \frac{POC}{A_{Th}^p} P_{Th}^i \quad (6)$$

where POC and A_{Th}^p represent the concentration of organic C (μmol L⁻¹) and activity concentration of ²³⁴Th (Bq m⁻³) on sinking particles, P_{Th}^i is the flux of particulate ²³⁴Th (Bq m⁻² d⁻¹) from the highest to the lowest boundary of the depth integration. The main assumption is that the POC/ A_{Th}^p ratio sampled is representative of the entire sinking flux, though it is more often derived from some type of filtration process of suspended material, rather

than from a direct measurement on sinking particles. The obtained results are shown in Table 1 and Fig. 6.

From the calculated fluxes one might observe that larger particles sink more rapidly at S.3 (Fig. 6). Large POC fluxes at the bottom of S.3 were likely caused by the extreme concentrations of POC due to WWTP outflows, rather than primary productivity. It is noteworthy that in the other two stations (S.5 and S.7) the opposite phenomenon was observed in all depths examined except the bottom nepheloid layer. We conclude that insignificant aggregation processes occurred due to the shallow depths of the sampling area and therefore small particles submerged rapidly. An additional explanation could be in terms of the instability of large aggregates during sampling previously mentioned in the paper. On the other hand, the higher fluxes of large particles appeared at the bottom nepheloid layer of the stations are owed to the thickness of the layer during phytoplankton bloom.

TABLE 1 - Fluxes of particulate ²³⁴Th (Bq m⁻² d⁻¹) and POC (mmol m⁻² d⁻¹) in the Saronikos Gulf. POC fluxes were calculated from ²³⁴Th/²³⁴U disequilibria using the POC/²³⁴Th ratio of each particle size fraction (see: Speicher et al. [8]). The final uncertainties were calculated by propagation of the uncertainties in the ratio and in the particulate ²³⁴Th flux.

Station	Depth integral (m)	²³⁴ Th flux (Bq m ⁻² d ⁻¹)	POC flux (mmol m ⁻² d ⁻¹)		
			0.6-25 μm	>25 μm	Total
S.3	0-15	5 ± 2	7 ± 3	13 ± 5	10 ± 4
	15-60	19 ± 3	62 ± 10	66 ± 10	64 ± 10
	60-70	28 ± 4	184 ± 26	302 ± 43	244 ± 35
S.5	0-35	28 ± 4	50 ± 7	33 ± 5	40 ± 6
	35-90	74 ± 8	178 ± 19	104 ± 11	135 ± 15
	90-97	78 ± 8	71 ± 7	156 ± 16	107 ± 11
S.7	0-50	22 ± 4	36 ± 7	20 ± 4	25 ± 5
	50-100	67 ± 8	80 ± 10	64 ± 8	71 ± 8
	100-200	153 ± 16	160 ± 17	127 ± 13	140 ± 15
	200-220	158 ± 17	42 ± 5	60 ± 6	51 ± 5

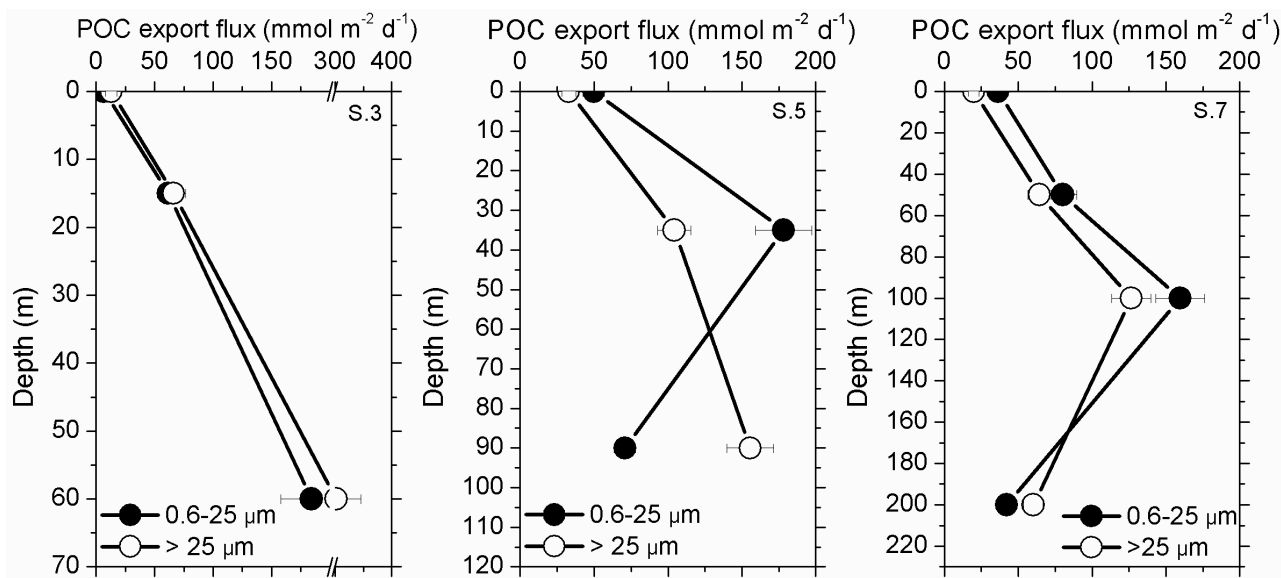


FIGURE 6 – Size-fractionated POC fluxes at S.3, S.5 and S.7 stations of the Saronikos Gulf during winter bloom evolution.

The fluxes of POC calculated in the present study were 1- 2 orders of magnitude higher than those observed in the open Aegean Sea ($0.9 \pm 0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ [8]) and over 1 than those reported in the western Mediterranean ($10.4 - 14.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ [8]). This trend can be attributed to the increase of primary production since sampling took place during phytoplankton bloom. Primary productivity caused increase of biogenic particles in the surface layers of the stations that rapidly submerge into deeper layers. Another explanation could be in terms that Saronikos accepts high amount of organics due to anthropogenic and industrial activities for a long time period [15, 35, 36]. For that reason, it makes sense that large fluxes are expected throughout the water column.

5. CONCLUSIONS

The export fluxes of POC, as well as the respective fluxes of size-fractionated particles in the water column of the Saronikos Gulf estimated using $^{234}\text{Th}/^{238}\text{U}$ disequilibrium approach are evaluated in the present study. Extremely high export fluxes of POC were observed here, over one order of magnitude compared to other areas of Mediterranean Sea. This is attributed to the enhanced biological activity due to phytoplankton bloom in conjunction with the large amounts of organics that the gulf accepts for a long time period. It is noteworthy that at S.5 and S.7 smaller particles showed larger fluxes in all depths except near the seabed. It is attributed to the insignificant aggregation processes that might have occurred due to the shallow depths of the area or the instability of large aggregates during sampling. In conjunction, the higher fluxes of large particles observed within the bottom nepheloid layer could be a result of the thickness of the layer during phy-

toplankton bloom. Larger particles ($> 25 \mu\text{m}$) of ^{234}Th were found increased at the surface, whereas smaller ones ($0.6 - 25 \mu\text{m}$) increased or remained at the same level near the seabed. Increase of large ^{234}Th particles at the surface certifies the origin of surface ^{234}Th linked to land-based atmospheric deposition or surface advective movements. The distribution of particulate ^{234}Th in both fractions is controlled by SPM, (SPM versus particulate ^{234}Th : $R^2 > 0.6$), whereas POC follows a different trend attributed to the fact that POC is carried in the volume of a particle, whereas ^{234}Th sorbs to the surface. It is essential to mention that the area of Saronikos is still affected by the wide carbon discharges (domestic, industrial etc.) prior and after the construction of Psitalia WWTP as it is characterized by late renewal times of its waters.

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