

# Evaluation of processes occurring in the bottom nepheloid layer (BNL) of an eastern Mediterranean area using $^{234}\text{Th}/^{238}\text{U}$ disequilibria

Nikolaos Evangeliou · Heleny Florou

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**Abstract** Particle-reactive radionuclide  $^{234}\text{Th}$  and its ratios with the conservative  $^{238}\text{U}$  were used to trace the marine processes occurring over short timescales in the bottom nepheloid layer (BNL) of seven stations in the Saronikos Gulf and the Elefsis Bay (Greece) during three seasons (summer 2008, autumn 2008 and winter 2009). Summer was considered as a steady season where low physical processes occur and stratification is well established, autumn as a commutative period and winter as period of extensive trawling and physical activities. The obtained ratio profiles showed excess of  $^{234}\text{Th}$  relative to  $^{238}\text{U}$  in the BNL of the sampling area during summer, caused by the dissolved fraction of  $^{234}\text{Th}$ . During autumn, the situation was different with large  $^{234}\text{Th}$  deficit throughout the water column leading to large export fluxes of particles from the water column. Finally, during winter the ratios showed that predominant phenomenon in the area was likely resuspension of bottom sediments. The resuspension signature was additionally evaluated by total suspended matter (TSM) inventories in the BNL. Despite the intense resuspension, small scavenging of dissolved  $^{234}\text{Th}$  was recorded in the BNL resulting in high residence times of dissolved  $^{234}\text{Th}$ . A 1 order of

magnitude difference between dissolved and particulate  $^{234}\text{Th}$  residence times was observed indicating that scavenging from dissolved to particulate  $^{234}\text{Th}$  could be highly variable and, as a result, the Saronikos Gulf is a highly dynamic environment, in terms of temporal and spatial particle uptake and removal. Comparing these values to literature ones consistent results were obtained. The possibility of sediment resuspension in the BNL during winter was amplified by the bloom of phytoplankton resulting in even decreased residence times of particulate  $^{234}\text{Th}$  (average values). In contrast, the respective residence times of the dissolved fraction of  $^{234}\text{Th}$  in the BNL were higher showing a maximum in winter at the stations where resuspension concluded. Nevertheless,  $^{234}\text{Th}$  cycling in the area is not controlled by TSM, probably due to the presence of colloids, which could play an essential role in  $^{234}\text{Th}$  scavenging.

**Keywords** Disequilibrium · Residence times · Bottom nepheloid layer (BNL) · Saronikos · Resuspension

## Introduction

Studies on particle fluxes and removal rates in coastal waters of the Greek marine environment are limited, even though there are many records on conservative pollution inventory. However, enclosed areas such as the Saronikos Gulf and the Elefsis Bay present great interest, since water currents are low, waters are

N. Evangeliou (✉) · H. Florou  
NCSR ‘Demokritos’, Institute of Nuclear  
Technology-Radiation Protection,  
Environmental Radioactivity Laboratory,  
15310 Agia Paraskevi,  
Athens, Greece  
e-mail: nevag@ipta.demokritos.gr

naturally oligotrophic, nutrients and organic carbon are enhanced and resuspension of bottom sediments is relatively limited (Friligos 1982). Resuspension of bottom sediments is an important mechanism in removing particle-reactive substances from the water column, as well as restore them and thus reveals biological and chemical activity in the water column. There is a general need to estimate the removal rates of reactive compounds over shallow waters where the bottom nepheloid layers (BNL) are dominated by resuspended matter. It is difficult to define or measure which particles are resuspended or produced in the water column and this fact is a major problem in such studies.

On the other hand, exchange between dissolved and particulate species of particle-reactive types, such as nutrients or pollutants, is enhanced as a result of the large surface area available for reaction (Rutgers van der Loeff and Boudreau 1997). Thereby, it is not sufficient to simply know the concentration of the species of interest in the dissolved and particulate phases; rather, it is important to know the rate of removal of dissolved species onto particulate material via scavenging reactions. In order to establish these kinetic parameters, it is necessary to determine all the supply and removal processes involved, which is often difficult.

Particle-reactive radioisotopes characterized by short half-lives and continuous production from a long-live parent are useful markers for the determination of particle dynamics in the marine environment and provide insight into different types of particles. The most commonly used particle-reactive radionuclide is  $^{234}\text{Th}$  ( $t_{1/2}=24.1$  days), which is produced from the alpha decay of the long-lived conservative  $^{238}\text{U}$  ( $t_{1/2}=4.47\times 10^9$  a) in the marine environment and it has been used in a large number of studies after 2000 (Amiel et al. 2002; Baskaran et al. 2003; Buesseler et al. 2006; Burd et al. 2000; Charette et al. 2001; Chen et al. 2002; Coppola et al. 2002; Dai and Benitez-Nelson 2001; Demopoulos et al. 2003; Foster and Shimmield 2002; Green et al. 2002 and many others). In a closed system, long-live mother and short-live daughter radionuclides reach secular equilibrium whereas, in a natural open system, reactivity, transport, selective bioaccumulation, etc., cause a disagreement between them. The extent of the resulting disequilibrium may be used to identify and assess the processes responsible for the difference (Rutgers van der Loeff

2001). The larger the depth-integrated deficit of  $^{234}\text{Th}$  with respect to  $^{238}\text{U}$ , the greater the particle flux necessary to maintain the observed water column activity balance (Cochran et al. 2000; Benitez-Nelson et al. 2001; Rutgers van der Loeff et al. 2002a). In contrast, whenever excess of  $^{234}\text{Th}/^{238}\text{U}$  ratio is observed, resuspension and potentially remineralization could be concluded. In the present work, the vertical profiles of  $^{234}\text{Th}$  are assessed and the  $^{234}\text{Th}/^{238}\text{U}$  ratios are used to verify resuspension and/or remineralization processes in the BNL. These data are linked with the physicochemical parameters obtained from the area of study, as well as the general characteristic in order to justify the proposed resuspension and/or remineralization. Finally, the calculated export fluxes and residence times of  $^{234}\text{Th}$  within the BNL are evaluated.

## Study area

The present study was carried out in eastern Mediterranean, specifically at a west-central region of the Aegean Sea (Saronikos Gulf and Elefsis Bay, Greece) (Fig. 1). The Saronikos Gulf is a typical semi-enclosed area directly linked (Fig. 1) with the Athens metropolitan area. It comprises two main sections, the eastern and the western ones, separated by the Aegina Island (Fig. 1). The eastern section has relatively uniform depth topography, with a maximum depth of 200. The main body of the eastern basin has depths between 70 and 90 m. The western part of Saronikos is deeper (maximum depth of over 400 m). At the north of the Gulf lies the Elefsis Bay with a maximum depth of about 30 m. The Bay is joined to the gulf by two narrow and shallow channels. The Piraeus Port, which is one of the greatest in the Mediterranean Sea, is located about 1 km southern of the eastern channel. The Saronikos Gulf is mainly influenced by the Wastewater Treatment Plant of Psitalia (WWTP) located in the Psitalia Island, near the Piraeus harbour and the Keratsini Bay, which discharges approximately  $800\text{ m}^3\text{ day}^{-1}$  pre-treated domestic wastes of Athens (Zeri et al. 2009). Significant amounts of nutrients also outflow directly into the Elefsis Bay, as along the bay more than 30 industries are located (oil refineries, steel mills, shipyards, etc.) (Voutsinou-Taliadouri 1981; Dassenakis et al. 2004). In the main Saronikos Gulf, the effect of WWTP discharges is evident, as a plume of nutrient-rich waters (Friligos 1982). Fishery and trawling activities are also important in the



2006), Murray et al. (1996) and Rutgers van der Loeff et al. (2006). Temperature, salinity and pH were determined by an in situ CTD probe (YSI 53).

#### Sampling of particulate and dissolved $^{234}\text{Th}$

Three high volume in situ pumps, one manufactured by Challenger Oceanic Systems and Services, UK, and two by McLane Laboratories, USA, borrowed by the IAEA, were deployed in the water column of the stations. Seawater was directly pumped through a manifold consisting of one disc pre-filter and two  $\text{MnO}_2$ -impregnated cartridges (see section “[Impregnation of  \$\text{MnO}\_2\$  cartridges](#)”) connected in series and finally through an impeller-based flow-meter to record the volume of the water filtered. Sample volumes of 500–1,000 l were processed at flow-rates of 0.3–1.0  $\text{m}^3\text{h}^{-1}$ . The accuracy of the flow-meter was  $\pm 2\%$ , operating in a range of 22.7–2,730  $\text{lh}^{-1}$  (Simpson 1997; Trull and Armand 2001).

The in situ pumps separated dissolved and suspended particulate phases via filtration through a pre-cleaned, pre-combusted Whatman GF/A disc filter (pore size of 0.6  $\mu\text{m}$ , diameter of 142 mm). It has been found that these filters are easy to handle and they have a high loading capacity and a very low radionuclide blank (Mann et al. 1984; Livingston and Cochran 1987).

#### Impregnation of $\text{MnO}_2$ cartridges

Cotton wound cartridge filters (25 cm long and 1  $\mu\text{m}$  pore size) were used for the impregnation. Impregnation was performed at the laboratory by circulating water suspension of  $\text{KMnO}_4$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in a closed loop, employing a small peristaltic pump and the filter to be impregnated. The filters collected the green-brown precipitate 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 (Mann et al. 1984; Livingston and Cochran 1987).

#### Thorium-234 treatment and analysis

After sampling, the filters were transferred to the laboratory. The disc filters were air-dried, rinsed with

distilled water to remove the residual salts and directly measured by gamma spectrometry after transfer into a calibrated measurement pot (radius 7.1 cm and height 1.0 cm). The cartridges were dried and ashed in an oven at 350  $^\circ\text{C}$ . The remaining ash was transferred into calibrated measurement pots (radius 3.4 cm and height 1.5 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  $^{60}\text{Co}$ ). The HPGe detector was connected to a multi-channel analyzer and the whole system was controlled using Canberra Genie 2000 software. The duration of each measurement was over  $7 \times 10^4$  s usually overnight.

The energy calibration was performed using standard active sources of  $^{241}\text{Am}$  and  $^{60}\text{Co}$  in a range of 2,000 keV in 8,000 channels (0.25 keV/ch). The detector's efficiency was calculated (in connection with energy) using a mixed-standard solution of  $^{241}\text{Am}$ ,  $^{109}\text{Cd}$ ,  $^{139}\text{Ce}$ ,  $^{57}\text{Co}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{203}\text{Hg}$ ,  $^{113}\text{Sn}$ ,  $^{85}\text{Sr}$ ,  $^{88}\text{Y}$  of total activity of 5,202 Bq. The mixed-standard solution produced photopeaks in the lower energies of the spectrum (specifically  $^{241}\text{Am}$  in 59.5 keV and  $^{109}\text{Cd}$  in 88.0 keV). This was necessary because the photopeaks that  $^{234}\text{Th}$  emits and used in the present calculations were 63.3 and 92.6 keV. As low-energy gamma rays are attenuated quite easily by self-absorption, careful attention must be paid to sample geometry in order to maximize the overall detection efficiency and to ensure reproducibility. Buessler et al. (1992) reported that the smaller the sample volume, the higher the detection efficiency. In the present 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. For justification, the self absorption of the samples was checked using Monte Carlo efficiency transfer, code DETEFF, and it was found insignificant. The quality assurance was checked by participating in proficiency tests (IAEA-CRP1471-01 proficiency test and EC inter-laboratory comparison JRC-IRMM).

Once the seawater sample was filtered, it was passed sequentially through two cartridge filters that

have been impregnated with MnO<sub>2</sub> (see section “Impregnation of MnO<sub>2</sub> cartridges”) (Livingston and Cochran 1987). The collection efficiency for each sample was calculated from the pair of MnO<sub>2</sub> cartridges by the equation:

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

where *A*<sub>1</sub> and *A*<sub>2</sub> are the <sup>234</sup>Th activities (decay corrected to the date of sampling) of the first and second MnO<sub>2</sub> cartridge, respectively, and *E* is the collection efficiency (Roos et al. 1994).

The collection efficiencies (*E*) of the cartridges used are shown in Table 1. Efficiencies ranged from 81±8 % to 95±3 % (average: 90±3 %). Previous studies have shown that collection efficiencies below

50 % usually result in <sup>234</sup>Th/<sup>238</sup>U ratios larger than 1, attributed to the lateral advection of <sup>234</sup>Th in coastal regions. However, this is not present in this study, since the efficiencies of the cartridge filters were kept at 90 %. The uncertainties for <sup>234</sup>Th activities in the first and the second filters (*A*<sub>1</sub>, *A*<sub>2</sub>) were 1σ values derived from counting statistics (Typical counting statistic error: 8 %). The final uncertainty of *A*(<sup>234</sup>Th) was estimated by propagation.

#### Uranium-238 estimations

Uranium-238 was calculated via its proportionality with salinity. Typically, the relationship derived by Chen et al. (1986) is used in open ocean studies. However, Mediterranean waters are generally of higher salinity than the open Atlantic and Pacific

**Table 1** Estimated collection efficiencies (*E*) of the cartridges used in each station during sampling

Station number		Summer 2008 <i>E</i> % (±uncert)	Autumn 2008 <i>E</i> % (±uncert)	Winter 2009 <i>E</i> % (±uncert)
S.1	0 m	89±5	81±8	85±8
	15 m	91±4	89±8	91±7
	25 m	90±4	91±6	92±6
S.2	0 m	85±5	88±7	82±7
	15 m	92±6	90±5	94±7
	25 m	89±3	89±4	91±9
S.3	0 m	90±2	91±5	89±4
	15 m	95±2	93±6	90±3
	60 m	94±3	93±7	88±5
S.4	0 m	90±3	89±6	93±6
	50 m	95±4	94±8	90±4
	100 m	90±2	91±9	90±3
	200 m	90±2	89±8	89±6
S.5	0 m	88±3	88±9	93±8
	35 m	89±2	90±8	95±3
	90 m	88±4	88±7	93±3
S.6	0 m	85±5	85±8	90±8
	35 m	91±6	88±6	94±4
	100 m	92±6	90±5	92±2
S.7	0 m	86±5	87±7	88±6
	50 m	87±7	90±5	93±9
	100 m	93±8	93±9	89±6
	200 m	93±9	93±9	90±9
Mean ± SD		90±3	90±3	90±3

waters, for which this relationship was obtained. It has been suggested that  $^{238}\text{U}$  concentrations in the Mediterranean are enhanced, comparing to the U–salinity relationship of Chen et al. (1986), due to phosphate fertiliser run-off (Schmidt and Reyss 1991). However, a recent work has compared the Mediterranean with Atlantic and Pacific waters, finding no significant difference in their U–salinity relationship (Delanghe et al. 2002). Although Uranium can deviate from conservative behavior in some coastal areas (Carroll and Moore 1993; Kersten et al. 1998; McKee et al. 1987), this deviation usually occurs where either freshwater or reducing conditions dominate. A more accurate estimation is the equation proposed by Pates and Muir (2007) obtained by analyzing samples from many Mediterranean regions including Greece. Specifically, among others, they analyzed samples from the Thermaikos Gulf, an area completely similar to the Saronikos Gulf. Therefore,  $^{238}\text{U}$  concentrations were derived from the following equations (Pates and Muir 2007).

$$\text{U-238 (dpm l}^{-1}\text{)} = (0.0931 \pm 0.0016) \times \text{salinity (psu)} \quad (2)$$

or

$$\text{U-238 (Bq m}^{-3}\text{)} = (1.552 \pm 0.0266) \times \text{salinity (psu)} \quad (3)$$

#### Total suspended matter (TSM)

Samples for the determination of the TSM were collected after the deployment of the large volume pumps. The same pre-weighted disc filters used to remove particulate  $^{234}\text{Th}$  (Whatman GF/A filter with pore size of 0.6  $\mu\text{m}$  and diameter of 142 mm) were subsequently rinsed with distilled water to remove residual salts, they were air dried, and then weighed in a microbalance Sartorius BP 211 D. The percentage uncertainty of the microbalance is less than 1. In order to define the BNL of the stations, seawater from large depths (just above the sediment) was pumped using impeller based pumps through plastic pipelines and filtered on board using the same pre-weighted disc filters and recording the volume of the water each time. The filters were treated as mentioned previously for TSM. At stations S.1, S.2, S.3, S.5 and S.6, TSM

was obtained at every 2.5 m of the last 10 m above the sediment, whereas at S.4 and S.7 at every 5 m of the last 15 m above the sediment.

## Results

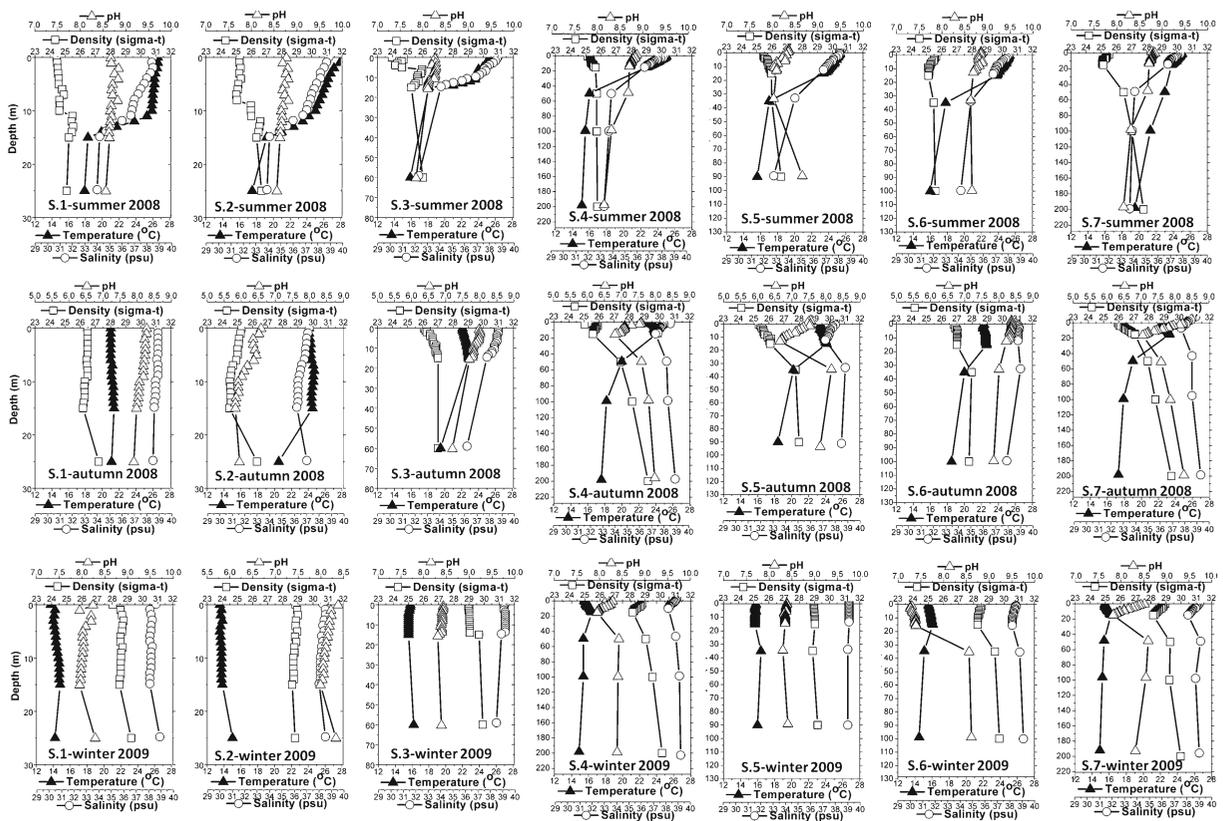
### Physicochemical characteristics

Temperature, salinity, pH and calculated density ( $\sigma\text{-t}$ ) profiles of every selected station of the study areas are illustrated in Fig. 2 for all sampling seasons (summer 2008, autumn 2008 and winter 2009). These data are of great interest since they define the characteristics of seawater (thermocline, pycnocline), in order to predict if there are additional processes that might influence particle dynamics.

Seawater temperature and salinity showed large seasonal fluctuation (14–32 °C and 32.5–39.5 psu, respectively) since the area is impacted by weather processes, such as evaporation (mean maximum temperature during summer was over 28 °C and minimum in winter below 10 °C) and rainfalls (mean annual rainfall in the area of Saronikos was 365 mm for 2008) (HNMS 2008). Data of pH ranged from 5.5 to 8.5 in all seasons and sampling depths. Low pH values might be attributed to external parameters such as ephemeral waste inputs from small industries, vessels or domestic areas that are not controlled by the WWTP of Psitalia (e.g., pH was below 7 at 10–15 m of S.5 in autumn).

### $^{234}\text{Th}/^{238}\text{U}$ ratio profiles and residence time estimates

Figure 3 shows the detailed vertical profiles of particulate, dissolved and total  $^{234}\text{Th}/^{238}\text{U}$  ratios for summer 2008, autumn 2008 and winter 2009. The dashed line indicates the ratio of 1 (secular equilibrium). Vertical profiles of TSM concentrations ( $\text{mg l}^{-1}$ ) are also plotted in the same illustrations (continuous black line). The presence of the BNL was checked at 10 m above sediment at stations S.1, S.2, S.3, S.5 and S.6, as well as at 15 m above the final depth at stations S.4 and S.7. As one can observe, the presence of the BNL in these depths was apparent and included the deepest sampling point of all stations. This was crucial in order to verify the possible mechanisms that dominate the BNL.



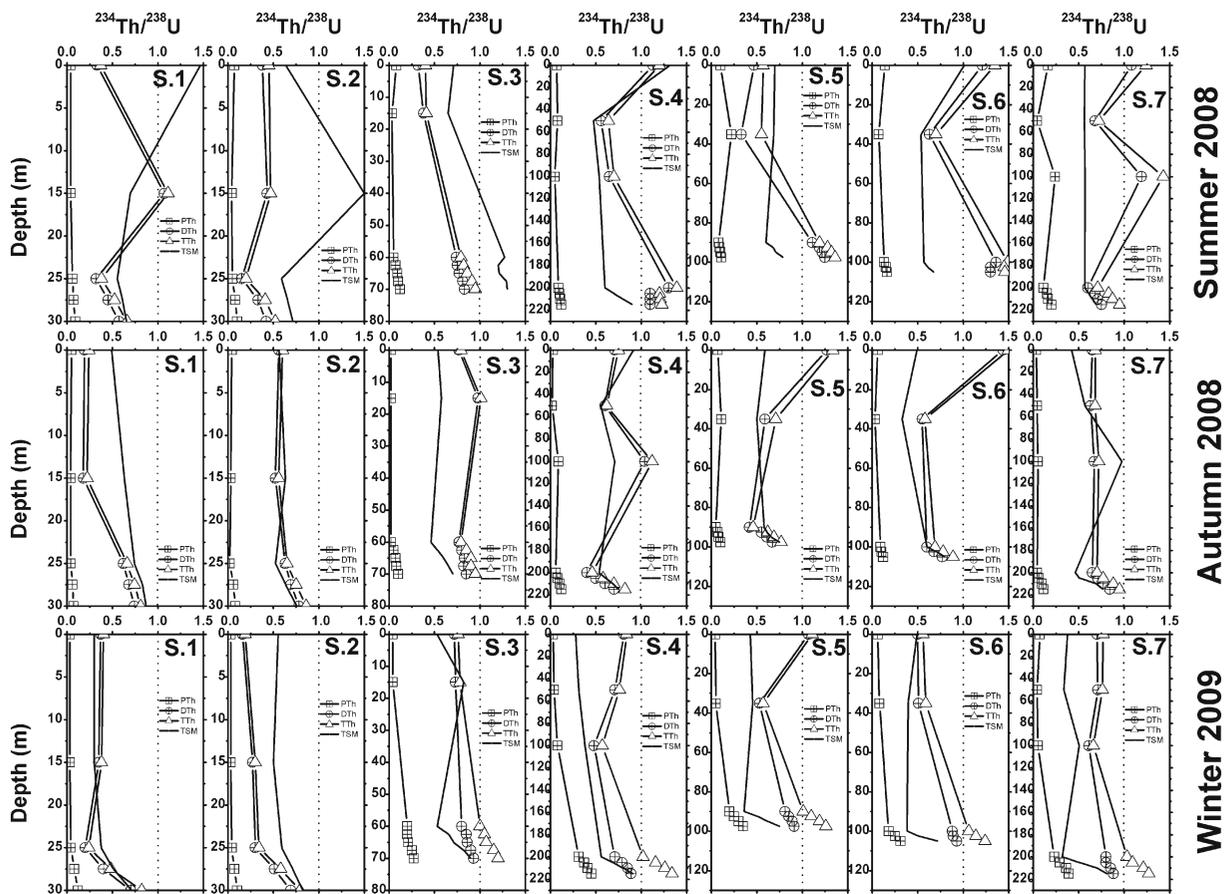
**Fig. 2** Temperature, salinity, density and pH data in the selected sampling stations (S.1–S.7) during summer 2008, autumn 2008 and winter 2009 cruises

In Table 2, the respective inventories of particulate, dissolved and total  $^{234}\text{Th}$  and  $^{238}\text{U}$  for summer 2008, autumn 2008 and winter 2009 are shown integrated within the BNL together with the respective residence times of  $^{234}\text{Th}$ . In order to calculate the residence times, the One Dimensional Box Model reported by Coale and Bruland (1985, 1987) was applied. The general formulation of  $^{234}\text{Th}$  activity in the model is the result of a balance between continuous production from  $^{238}\text{U}$ , radioactive decay of  $^{234}\text{Th}$ , removal onto rapidly sinking particles and transport into or out of the box by advection and diffusion. The temporal change in total  $^{234}\text{Th}$  is expressed by:

$$\frac{\partial A_{\text{Th}}'}{\partial t} = \lambda_{\text{Th}} A_{\text{U}} - \lambda_{\text{Th}} A_{\text{Th}} - P_{\text{Th}} + V \quad (4)$$

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

The key assumptions of this model are that: (1) steady-state conditions prevail, which means that  $^{234}\text{Th}$  activities and removal rates ( $J_{\text{Th}}^i$  and  $P_{\text{Th}}^i$ ) are constant, with respect to the  $^{234}\text{Th}$  decay constant; (2) horizontal and vertical advection and diffusion of  $^{234}\text{Th}$  are negligible; and (3) scavenging is irreversible. Muir et al. (2005) reported that the assumptions are fulfilled in (more or less stable) enclosed systems stating the aforementioned equation the most frequently used in particle kinetic studies. However, attention must be paid to horizontal advection in the area. Following that, the circulation patterns in the Saronikos Gulf correspond to domination of wind-driven currents (Laskaratos and Kaltsounidis 1989) with velocities ranging from 0.45 up to  $7 \text{ cms}^{-1}$  (Krasakopoulou and Karageorgis 2005). Therefore, steady state conditions could be assumed since the net effect of advective and diffusive transports of  $^{234}\text{Th}$  are small compared to uptake of  $^{234}\text{Th}$  on particles and radioactive decay. Thus, Eq. 2 is simplified into:



**Fig. 3** Vertical profiles of particulate (PTh, plus symbol enclosed by a square), dissolved (DTh, plus symbol enclosed by a circle) and total (TTh, empty triangle)  $^{234}\text{Th}/^{238}\text{U}$  ratios for

summer 2008, autumn 2008 and winter 2009. The dashed line indicates the ratio of 1 (secular equilibrium). TSM concentrations ( $\text{mg l}^{-1}$ ) are also plotted on the x-axis (—)

$$P_{\text{Th}} = \lambda_{\text{Th}}(A_{\text{U}} - A_{\text{Th}}) \quad (5)$$

If one integrates over a layer designated by depths  $z_0$  and  $z_i$  (e.g., BNL), Eq. 5 becomes:

$$P_{\text{Th}}^i = \lambda_{\text{Th}} \int_{z_0}^{z_i} (A_{\text{U}} - A_{\text{Th}}) dz + P_{\text{Th}}^{i-1} \quad (6)$$

where  $P_{\text{Th}}^{i-1}$  represents the flux of particles sinking from the above layer ( $i-1$ ).  $P_{\text{Th}}^{i-1}$  equals to 0 at the surface layer. Since the supply of  $^{234}\text{Th}$  is through the decay of  $^{238}\text{U}$ , then the removal from the dissolved phase is via either scavenging onto particles or radioactive decay and thus:

$$J_{\text{Th}} = A_{\text{U}} \lambda_{\text{Th}} - A_{\text{Th}}^{\text{d}} \lambda_{\text{Th}} \quad (7)$$

or

$$J_{\text{Th}}^i = \lambda_{\text{Th}} \int_{z_0}^{z_i} (A_{\text{U}} - A_{\text{Th}}^{\text{d}}) dz \quad (8)$$

if one integrates between two depths in order to define a layer. In that case, no additional term is needed, since we assumed that horizontal and vertical advection and diffusion are negligible. In Eq. 8,  $J_{\text{Th}}$  is the rate of scavenging of dissolved  $^{234}\text{Th}$  onto the particulate phase (expressed in  $\text{Bq m}^{-2} \text{day}^{-1}$ );  $A_{\text{U}}$  is the activity of  $^{238}\text{U}$ ;  $\lambda_{\text{Th}}$  is the decay constant for  $^{234}\text{Th}$ ; and  $A_{\text{Th}}^{\text{d}}$  is the activity of dissolved  $^{234}\text{Th}$ . Since  $J_{\text{Th}}^i$  and  $P_{\text{Th}}^i$  represent the non-radioactive removal rates for dissolved and particulate  $^{234}\text{Th}$ , mean residence times can be defined for both the dissolved ( $T_{\text{d}}^i$ ) and particulate ( $T_{\text{p}}^i$ ) phases:

**Table 2** Particulate, dissolved and total <sup>234</sup>Th, <sup>238</sup>U and TSM inventories, particle export fluxes of <sup>234</sup>Th ( $P_{Th}^i$ ), scavenging rates of dissolved <sup>234</sup>Th ( $J_{Th}^i$ ) and respective calculated residence times integrated within the BNL

Station	Depth interval (m)	TSM (gm <sup>-2</sup> )	U-238 (Bqm <sup>-2</sup> )	PTh-234 (Bqm <sup>-2</sup> )	DTh-234 (Bqm <sup>-2</sup> )	TTh-234 (Bqm <sup>-2</sup> )	$P_{Th}^i$ (Bqm <sup>-2</sup> day <sup>-1</sup> )	$J_{Th}^i$ (Bqm <sup>-2</sup> day <sup>-1</sup> )	$T_p^i$ (d)	$T_d^i$ (day)
<i>Summer 2008</i>										
S.1	5	2.8	200±4	12±5	64±15	76±18	15.9±3.9	3.9±1.1	0.8±0.2	16±3
S.2	5	2.9	199±4	10±4	30±9	40±9	21.9±1.1	2.0±0.9	0.4±0.2	6±1
S.3	10	12.7	380±8	15±99	142±13	157±52	44.5±1.9	2.8±1.7	0.2±0.1	102±10
S.4	15	12.0	784±16	68±18	1020±52	1088±196	44.5±1.9	<0	1.2±0.3	<0
S.5	7	4.9	193±4	16±5	213±14	229±37	48.4±2.9	<0	0.5±0.2	<0
S.6	10	2.8	201±4	25±5	274±19	299±30	23.0±3.3	<0	2.2±0.4	<0
S.7	15	11.3	794±16	88±20	476±50	564±88	19.4±2.4	4.6±2.7	4.5±0.9	52±7
<i>Autumn 2008</i>										
S.1	5	3.7	226±4	8±2	141±15	149±15	22.3±1.1	2.5±1.1	0.4±0.1	57±6
S.2	5	2.6	261±4	5±2	138±9	143±14	16.7±2.1	0.9±0.2	0.3±0.1	60±6
S.3	10	4.6	426±9	9±5	326±23	335±24	6.8±1.9	2.9±2.7	0.7±0.2	114±12
S.4	15	10.7	916±18	56±16	364±62	420±64	48.0±5.2	8.0±2.8	1.2±0.4	23±2
S.5	7	2.9	226±4	10±4	94±17	104±18	28.3±3.9	7.6±3.0	0.5±0.1	25±2
S.6	10	3.0	229±5	21±11	222±10	243±15	38.4±2.3	2.6±0.4	1.0±0.2	52±6
S.7	15	9.2	926±20	40±18	606±64	646±66	82.8±3.8	4.6±2.7	0.5±0.1	66±8
<i>Winter 2009</i>										
S.1	5	3.9	229±4	9±5	45±9	54±11	20.7±2.4	5.3±2.1	0.4±0.1	8±1
S.2	5	3.0	226±4	10±5	69±18	79±18	31.0±3.1	1.8±1.6	0.3±0.1	15±2
S.3	10	14.8	453±9	30±13	428±27	458±30	19.8±4.1	2.6±2.2	0.8±0.2	138±12
S.4	15	13.2	924±20	74±24	868±112	942±114	83.4±3.7	3.8±2.7	0.9±0.2	86±9
S.5	7	5.8	229±4	15±9	218±11	233±15	31.0±4.2	2.6±1.7	0.7±0.2	144±14
S.6	10	2.9	229±5	21±11	222±10	243±15	55.4±2.1	4.7±1.2	0.7±0.2	107±10
S.7	15	11.4	918±18	78±22	868±90	946±92	76.1±7.4	2.7±1.6	1.0±0.2	135±14

The final uncertainties were calculated by propagation

$$\tau_p^i = \frac{A_{Th}^p}{P_{Th}^i} \tag{9}$$

and

$$\tau_d^i = \frac{A_{Th}^d}{J_{Th}^i} \tag{10}$$

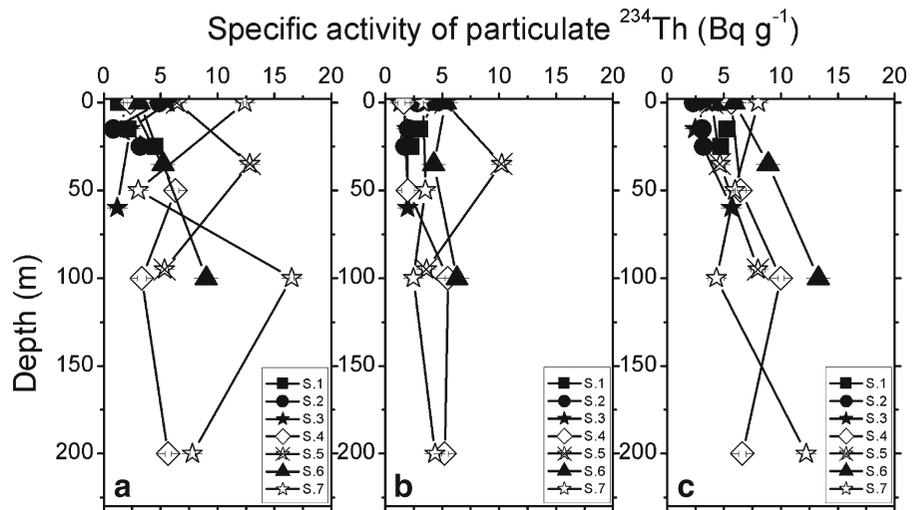
where  $T_d^i$  represents the average time it takes for a dissolved <sup>234</sup>Th atom to be transferred into the particulate phase within a layer and  $T_p^i$  the time of particle-associated <sup>234</sup>Th being present in a given water layer before its export from that layer.

Specific activities of <sup>234</sup>Th

An outstanding point of the present work was to examine which processes are dominant in the BNL.

For that reason we checked direct resuspension of bottom sediments using the excess of total <sup>234</sup>Th relative to its parent <sup>238</sup>U. However, another significant process in the BNL might be remineralization of the scavenged <sup>234</sup>Th. In order to verify if remineralization is apparent in the BNL, vertical profiles of specific activity (=activity of <sup>234</sup>Th per gram of particulate matter) of <sup>234</sup>Th in the water column of the stations are given in Fig. 4. Trimble and Baskaran (2005) reported that a rapid decrease in specific activity in the water column is likely attributed to remineralization of particulate matter. A potential problem is the fact that remineralization of <sup>234</sup>Th contradicts with the assumption of irreversible scavenging of <sup>234</sup>Th onto suspended particles. However, it is used in the present chapter in order to record the residence times. At a first glance, one might note that a conflict might occur

**Fig. 4** Vertical profiles of specific activities (activity of  $^{234}\text{Th}$  per gram of particulate matter) of  $^{234}\text{Th}$  in summer 2008 (a), autumn 2008 (b) and winter 2009 (c)



during summer, as the large decreases of specific activity in the BNL of the stations S.3, S.5 and S.7 might imply remineralization of  $^{234}\text{Th}$ . From these stations, only at S.5 it seems that remineralization might occur, since there was excess of  $^{234}\text{Th}$  relative to  $^{238}\text{U}$  in the BNL caused by the dissolved fraction and also the specific activity of  $^{234}\text{Th}$  decreased (Fig. 4a). During autumn specific activities of  $^{234}\text{Th}$  were similar throughout the water column suggesting no remineralization (Fig. 4b) and, finally, in winter they were slightly increased in the BNL (Fig. 4c), as a result of the tiny scavenging of the dissolved fraction of  $^{234}\text{Th}$  onto the suspended particles.

It is noteworthy to pay attention to the BNL of the station S.5 in summer (Fig. 4a), where the conflict of reversible scavenging occurred and the model seems to be inappropriate. It concerns a localised event and if one examines the characteristics of that area, useful findings can be obtained. Station S.5 is located approximately 2 nautical miles south-eastern of Salamis Island (see Fig. 1). A motivation of choosing that station was the fact that it is located inside the anchorage area of the Piraeus Port, where many commercial vessels moor for long time period before they enter Piraeus Port. It was a great challenge for us to examine if the continuous mixing of the sediments affects the behaviour of several particle-reactive species. Consequently, it seems that continuous sediment mixing in S.5 caused remineralization of  $^{234}\text{Th}$  back to the dissolved form.

## Discussion

### Seasonal stratification

As one can observe, during summer 2008 a sharp thermocline was developed in the water column of the seven selected stations. Specifically, in the stations located in the Elefsis Bay (S.1 in the central part and S.2 in the western basin) thermocline was found at about 15 m depth. Regarding the Saronikos Gulf, at station S.3, thermocline was found at 15 m depth, at S.5 and S.6 intense stratified layer was observed with thermocline existing at 35 m and at about 50 m for the deepest stations S.4 and S.7. The existence of stratification was amplified with an observed halocline near the same depths at all stations of the study areas (Fig. 2).

During autumn 2008 an almost homogenous layer was observed in the stations of the Elefsis Bay (S.1 and S.2), due to the shallow depths of the stations (~30 m) that assisted the collapse of stratification. At S.3 a mild pycnocline was observed at 15 m depth attributed to the fresh water outflows from the WWTP of Psitalia through two pipelines near S.3 (Fig. 1). As large amounts of pre-treated wastes are discharged at about 63 m depth, they occupy mostly the bottom layers of the column, resulting in an extension of stratification. The lower density of water in the deeper layer of that station causes a continuous mixing of the water column since dense shallow waters continuously sinks below more buoyant ones. At stations S.4–S.7, the situation was clear. Thermocline started breaking

down at the end of summer and the denser surface waters submerged at higher depths (Fig. 2).

Finally, during winter 2009 the water column of the seven stations was completely mixed due to the advective and weather processes. Even at S.3, which accepts effluents throughout the year, the column was found homogenous in winter. At the deepest stations (S.4, S.6 and S.7), elevated density was calculated near the seabed indicating the complete breakdown of thermocline, as well as the low intensity of the existing currents that did not impact deeper waters with WWTP waters (Fig. 2).

Use of  $^{234}\text{Th}/^{238}\text{U}$  ratios as a qualitative tool in the BNL

The general pattern of  $^{234}\text{Th}/^{238}\text{U}$  ratios obtained for summer 2008 is that in many stations  $^{234}\text{Th}$  exceeded secular equilibrium with  $^{238}\text{U}$  (ratio >1). Specifically, at station S.1 located in the Elefsis Bay dissolved and total  $^{234}\text{Th}$  activity concentration at 15 m depth were higher than  $^{238}\text{U}$  one (Fig. 3). However, since specific activity did not show rapid decrease (Fig. 4a) and this excess could not be attributed to remineralization of dissolved  $^{234}\text{Th}$ . A possible explanation could be that near the thermocline dissolved metals are generally accumulated (Dassenakis et al. 1994; Scoullou et al. 2004a). Stations S.2 and S.3 showed  $^{234}\text{Th}$  depletion being 20–96 % of  $^{238}\text{U}$  activity (Fig. 3).  $^{234}\text{Th}$  depletion is a measure of the deficit in  $^{234}\text{Th}$ , relative to its supply by  $^{238}\text{U}$  and it is indicative of rapid scavenging and particulate removal processes that influence the system. Muir et al. (2005) reported that whenever dissolved  $^{234}\text{Th}$  activity decreases with increasing depth, such as at stations S.1 and S.2, dissolved  $^{234}\text{Th}$  might be scavenged at the BNL. Since the specific activity of  $^{234}\text{Th}$  increased in the BNL one could note that scavenging of dissolved  $^{234}\text{Th}$  by suspended particles is likely (Fig. 4a). At S.4, increased  $^{234}\text{Th}$  activities with respect to  $^{238}\text{U}$  were found at the surface and the bottom layer, and the excess was obviously caused by the dissolved fraction of  $^{234}\text{Th}$ . However, remineralization could not be assumed, since specific activity of  $^{234}\text{Th}$  tended to increase in the BNL (Fig. 4a). Stations S.5 and S.6 showed the same results, with ratios overlapping secular equilibrium at the surface (S.6) and bottom layers (both stations) caused by dissolved fractions. Finally, at S.7  $^{234}\text{Th}/^{238}\text{U}$  ratio was over 1 at the surface area

and at 100 m depth. The excess of  $^{234}\text{Th}$  at the surface could be attributed to the impact from the vessel mobility, as the station is next to the ship traffic of the Piraeus Port. However, this approach needs further research. A noteworthy point of the sampling during summer is the likely remineralization of  $^{234}\text{Th}$  in the BNL of station S.5, since the specific activity of  $^{234}\text{Th}$  showed a rapid decrease there (Fig. 4a) in connection with the continuous sediment mixing caused by the anchors of the mooring vessels. The export fluxes of particulate  $^{234}\text{Th}$  integrated within the BNL ranged between  $15.9 \pm 3.9$  and  $48.4 \pm 2.9$   $\text{Bqm}^{-2}\text{day}^{-1}$  (average:  $31.1 \pm 4.5$   $\text{Bqm}^{-2}\text{day}^{-1}$ ), whereas the scavenging rates of dissolved  $^{234}\text{Th}$  onto particles between negative and  $4.6 \pm 2.7$   $\text{Bqm}^{-2}\text{day}^{-1}$  (average:  $1.9 \pm 0.4$   $\text{Bqm}^{-2}\text{day}^{-1}$ ) (Table 2). It is noteworthy that  $J_{\text{Th}}$  was found to be negative in the BNL of the stations S.4–S.6 during summer 2008 causing negative values for the respective residence times ( $T_d$ ). This was caused by the excess of dissolved  $^{234}\text{Th}$  relative to  $^{238}\text{U}$  in the BNL of these stations.

During autumn 2008,  $^{234}\text{Th}$  depletion dominated the water column in most of the sampling stations (S.1, S.2, S.3 and S.7).  $^{234}\text{Th}$  depletion in autumn fluctuated between 25 % and 90 % and this prompted large export fluxes of particulate  $^{234}\text{Th}$  (Fig. 3 and Table 2). At stations S.5 and S.6 enhanced activity concentrations of dissolved  $^{234}\text{Th}$  in the surface layers could be attributed to ephemeral storm events occurring during autumn in the Saronikos Gulf (Fig. 3). The rapid decrease of the dissolved  $^{234}\text{Th}$  activity with the depth in connection to the slight increase of specific activity of  $^{234}\text{Th}$  at the BNL of stations S.3–S.6 (Fig. 4b) could be attributed to scavenging of dissolved  $^{234}\text{Th}$  by the particles that dominate the BNL. Indeed, this is obvious by our calculations, since in these stations the scavenging rates of  $^{234}\text{Th}$  were found maximum (Table 2). The particle export fluxes of  $^{234}\text{Th}$  in the BNL fluctuated between  $6.8 \pm 1.9$  and  $82.8 \pm 3.8$   $\text{Bqm}^{-2}\text{day}^{-1}$  (average:  $34.8 \pm 4.7$   $\text{Bqm}^{-2}\text{day}^{-1}$ ) and the respective scavenging rates between  $0.9 \pm 0.2$  and  $8.0 \pm 2.8$   $\text{Bqm}^{-2}\text{day}^{-1}$  (average:  $4.2 \pm 1.7$   $\text{Bqm}^{-2}\text{day}^{-1}$ ) (Table 2).

The profiles of  $^{234}\text{Th}$  ratios and TSM showed distinct resuspension of bottom sediments in the BNL of many stations during winter 2009 (Fig. 3). In the stations located inside the Elefsis Bay (S.1 and S.2),  $^{234}\text{Th}$  was not in secular equilibrium with  $^{238}\text{U}$  ( $^{234}\text{Th}$  deficit between 25 % and 40 %), indicating that export

flux of particulate  $^{234}\text{Th}$  occurred during winter 2009. At stations S.3–S.7 located in Saronikos  $^{234}\text{Th}$  activity concentrations exceeded  $^{238}\text{U}$  in the BNL. This phenomenon was clearly induced by the elevated particulate  $^{234}\text{Th}$  levels in these depths (Fig. 3). Several authors (Rutgers van der Loeff and Boudreau 1997; Muir et al. 2005) have reported that the overlap of total  $^{234}\text{Th}$  comparing to  $^{238}\text{U}$  in the bottom layers indicates resuspension of sediments. However, it is difficult to define what caused this resuspension. Evangelioiu et al. (2010) proposed at a previous study that at S.5 the resuspension is attributed to the vessel anchors, as the station is located in the mooring area of the Piraeus Port. Moreover, trawling activities that are onset during this period (winter) in the inner Saronikos Gulf could be another reason for this resuspension that caused high TSM and particulate  $^{234}\text{Th}$  concentrations this period. Although BNL is apparent in winter period (increased TSM values), small scavenging was recorded there (average:  $3.4 \pm 0.7 \text{ Bq m}^{-2} \text{ day}^{-1}$ ) (Table 2) explaining why dissolved  $^{234}\text{Th}$  slightly increased in the BNL (Fig. 4c). Another reason of the increase of dissolved  $^{234}\text{Th}$  observed in the BNL of many stations could be caused by the disaggregation of particulate  $^{234}\text{Th}$ , as a result of mixing processes, releasing dissolved  $^{234}\text{Th}$  into the water column. A further explanation could be that dissolved  $^{234}\text{Th}$  had insufficient time to adsorb to particulate matter after that localised resuspension event.

Another process that is present during winter is the bloom of phytoplankton, which it has been found extensive in Mediterranean during cold seasons; thus, more particles were created at the surface submerging rapidly in deeper waters and causing particle ingrowths in bottom layers (Bosc et al. 2004; Fowler et al. 1991; Schmidt et al. 2002). Moreover, the particulate fraction was found to increase in the BNL, if compared to the bottom layer  $^{234}\text{Th}$  activities obtained during previous seasons. Except for the resuspension event examined in the previous paragraph, the increase of particulate  $^{234}\text{Th}$  in combination with the BNL particle export maximum obtained for winter (average:  $45.3 \pm 5.7 \text{ Bq m}^{-2} \text{ day}^{-1}$ ) (Table 2) clearly indicates the seasonality caused by the bloom that creates biogenic particles at the surface that rapidly sink to the sediments. However, in the relevant literature a rapid removal of  $^{234}\text{Th}$  with sinking particles during a bloom has never been found to cause excess of  $^{234}\text{Th}$  relative to  $^{238}\text{U}$  in the BNL.

Stations S.1 and S.7 in summer and S.4 in autumn display relatively high contents of total  $^{234}\text{Th}$  in medium depths caused by the dissolved fractions of  $^{234}\text{Th}$ , although this phenomenon is usually apparent in the open ocean. These high activities suggest that these stations have received an additional dissolved input, however, no evidence for that input could be found. Given that in the area not important amount of fresh water inputs in the surface seawater have been recorded, therefore, the surface increase of dissolved  $^{234}\text{Th}$  cannot be attributed to washout processes. Sahara dust events are usual during summer and autumn carrying particles from long distances.  $^{234}\text{Th}$  concentrations up to  $8.1 \text{ mBq m}^{-3}$  have been found during summer in the atmospheric aerosol (Eleftheriadis et al. 2010) and this may induce an additional source of  $^{234}\text{Th}$  in the area. However, this hypothesis needs further research.

#### Residence times of dissolved and particulate $^{234}\text{Th}$ in the BNL

Table 2 shows the residence times of particulate and dissolved  $^{234}\text{Th}$  estimated after integration within the BNL. During summer dissolved and particulate  $^{234}\text{Th}$  ranged between negative and  $102 \pm 10$  days (average:  $25 \pm 5$  days) and  $0.2 \pm 0.1$  and  $4.5 \pm 0.9$  days (average:  $1.8 \pm 0.4$  days), respectively. During autumn, the residence times of dissolved  $^{234}\text{Th}$  fluctuated between  $23 \pm 2$  and  $114 \pm 12$  days (average:  $57 \pm 7$  days) and between  $0.4 \pm 0.1$  and  $1.2 \pm 0.4$  days (average:  $0.9 \pm 0.3$  days) of particulate one. Finally, during winter, the residence times varied between  $8 \pm 1$  and  $138 \pm 12$  days (average:  $95 \pm 11$  days) for dissolved  $^{234}\text{Th}$  and between  $0.3 \pm 0.1$  and  $1.0 \pm 0.2$  days (average:  $0.6 \pm 0.2$  days) for particulate one. The 1 order of magnitude difference between dissolved and particulate  $^{234}\text{Th}$  residence times indicates that scavenging from dissolved to particulate  $^{234}\text{Th}$  is highly variable, within sampling periods; this suggests that the Saronikos Gulf is a highly dynamic environment, in terms of temporal and spatial particle uptake and removal.

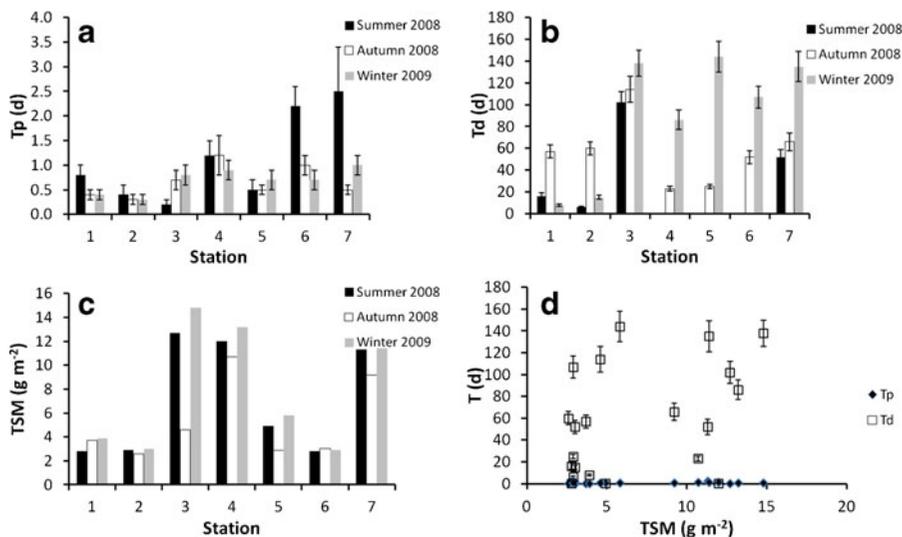
Comparing these values to reported ones from the relevant literature for similar environment and similar depth integrals, such as Bacon and Rutgers van der Loeff (1989) for NW Atlantic ( $T_p = 25$  days), Kersten et al. (1998 for the Baltic Sea ( $T_p = 1.2\text{--}20.1$  days,  $T_d = 1.2\text{--}9.7$  days), Santschi et al. (1999) for continental

margin waters Middle Atlantic Bight ( $T_p=5-20$  days,  $T_d=30-200$  days), Guo et al. (2002) for the Gulf of Mexico ( $T_p=2-3$  days,  $T_d=4-20$  days), Radakovitch et al. (2003) for the Adriatic Sea ( $T_p=1-22$  days,  $T_d=13-42$  days), Muir et al. (2005) for the Thermaikos Gulf, Greece ( $T_p=3-9$  days,  $T_d=2-46$  days), one could note that the values are more or less consistent.

Figure 5a and b shows plots of integrated residence times within BNL for particulate and dissolved  $^{234}\text{Th}$ . Particulate  $^{234}\text{Th}$  residence times calculated for the BNL (Fig. 5a) showed no clear trend with season. In some cases (e.g., S.3 and S.5), the possibility of resuspension of sediments during winter discussed previously is amplified by the increasing residence times of particulate  $^{234}\text{Th}$  (at least in terms of average values) in the BNL caused by resuspended particles at the bottom of these stations. However, the values are considered as low. This is more or less expected in such area, which is characterized by large particle loads; the availability of particulate matter in the BNL of the area in connection with the high affinity of  $^{234}\text{Th}$  to stuck onto particles result in large sinking rates, thus small residence times. These large fluxes are reinforced by the bloom of phytoplankton, which is intense in late winter, resulting in even lower residence times of particulate  $^{234}\text{Th}$  throughout sampling campaigns (summer, autumn, winter, respectively),

according to the average values (summer average:  $1.8\pm 0.4$  days, autumn average:  $0.9\pm 0.3$  days, winter average:  $0.6\pm 0.2$  days). In contrast, the respective residence times of the dissolved fraction of  $^{234}\text{Th}$  in the BNL (Fig. 5b) were higher than of particulate fraction, reversely of what usually happens in the open sea and showed a maximum in winter at the stations of inner Saronikos (S.2–S.7) (Table 2). Given that the bloom of phytoplankton is intense in winter at the surface, it creates biogenic particles that submerge rapidly, resulting in insufficient scavenging times of dissolved  $^{234}\text{Th}$ . On the other hand, the maximum of winter period could be attributed to the localised resuspension activity observed in the BNL of the stations during that season. Resuspended sediments normally scavenge more dissolved  $^{234}\text{Th}$  decreasing  $^{234}\text{Th}$  activity and depleting the BNL. However, there was an insignificant scavenging of dissolved  $^{234}\text{Th}$  in the BNL after resuspension during winter (Table 2) and, as a consequence; dissolved  $^{234}\text{Th}$  remained in the BNL longer. Exceptions were observed at the BNL of stations S.1 and S.2 located in the Elefsis Bay, where maxima were found in autumn.

Regarding TSM inventory variation with seasons (Fig. 5c), it should be stated that maxima were found in winter period and that defines a resuspension signature itself, if one considers what have been already



**Fig. 5** a Residence times of dissolved  $^{234}\text{Th}$  integrated within the Bottom Nepheloid Layer (BNL) for summer 2008, autumn 2008 and winter 2009. b Integrated residence times for particulate  $^{234}\text{Th}$  calculated for the BNL in summer 2008, autumn 2008 and winter 2009. c TSM inventories calculated for the

BNL in summer 2008, autumn 2008 and winter 2009 cruises. d Integrated dissolved and particulate  $^{234}\text{Th}$  residence times plotted against TSM concentrations, both calculated for the BNL, for summer 2008, autumn 2008 and winter 2009. The depth intervals used in all integrations can be seen in Table 2

found according to  $^{234}\text{Th}$  profile and residence time data in the BNL. In order to evaluate the relationship of  $^{234}\text{Th}$  residence times with the concentration of TSM in the BNL of the area of study, their correlations were examined (Fig. 5d). No significant correlation was apparent between dissolved  $^{234}\text{Th}$  and TSM ( $R^2=0.355$ ). Overall, particulate residence times varied very little between seasons, stations and TSM concentrations, showing no correlation ( $R^2=0.112$ ) with the latter, although it has been found that these parameters are usually correlated (e.g., Rutgers van der Loeff et al. 2002b), since the removal rates of particulate  $^{234}\text{Th}$  are primarily controlled by the particle concentration (Baskaran et al. 1996). Residence times of particulate  $^{234}\text{Th}$  were very short during winter period, while the TSM concentrations failed to account the dissolved  $^{234}\text{Th}$  depletion (scavenging rates were low). These factors combined imply that, at some point during winter, a large particle resuspension event occurred, resulting in a marked depletion of dissolved  $^{234}\text{Th}$ . The resuspended particles were removed rapidly from the system, by sinking and/or advection, leaving the signature of resuspension event in the dissolved  $^{234}\text{Th}$  depletion.

This phenomenon indicates, for one more time, that dissolved  $^{234}\text{Th}$  was not efficiently scavenged onto suspended particles near the BNL, because the rapidly sinking particles had inadequate time to adsorb dissolved species from the water column and that caused the lack of correlations. Another important factor for these insignificant correlations, that it was not examined in the present study, is the presence of colloids; it is well known that they play essential role in  $^{234}\text{Th}$  scavenging. For example, Honeyman and Santschi (1989) reported that dissolved  $^{234}\text{Th}$  is primarily associated with colloidal materials, which then aggregate to produce particulate matter. Moreover, Moran and Buessler (1993) reported that significant amounts of dissolved  $^{234}\text{Th}$  were found in the form of colloids. It has been previously observed that in the marine environment of the Saronikos Gulf and the Elefsis Bay colloidal substances are significant (Scoullou et al. 2004b); in addition, colloidal  $^{234}\text{Th}$  was assumed as dissolved  $^{234}\text{Th}$  (only particulate  $^{234}\text{Th}$  was removed using GF/A filters of pore size  $0.6\ \mu\text{m}$ ) in the present and a possible “escape” of colloids might have caused the lack of correlation. Nevertheless, it could be noted that  $^{234}\text{Th}$  cycle in the water column of that coastal region is not controlled by the TSM concentration.

## Conclusions

The present paper shows how the particle-reactive radionuclide  $^{234}\text{Th}$  and its disequilibrium with respect to the mother radionuclide  $^{238}\text{U}$  could be used as a qualitative indication of marine processes occurring in the BNL. The main conclusions can be summarized below.

During summer 2008, excess of ratios was observed in many stations caused by the dissolved fraction of  $^{234}\text{Th}$ . However, according to the specific activity data, remineralization of  $^{234}\text{Th}$  is likely only in the BNL of S.5, due to the continuous sediment mixing caused by the anchors of the mooring vessels.

During autumn 2008  $^{234}\text{Th}$  deficit was found in the water column of most of the stations and that caused intense particle export fluxes to the sediments. The rapid decrease of the dissolved  $^{234}\text{Th}$  activity with the depth in connection to the slight increase of specific activity of  $^{234}\text{Th}$  at the BNL of stations S.3–S.6 could be attributed to dissolved  $^{234}\text{Th}$  scavenging by the particles that dominate the BNL.

Finally, in winter 2009 the situation was different. Resuspension of bottom sediments was clearly observed, since the ratios of total  $^{234}\text{Th}/^{238}\text{U}$  exceeded 1 in the BNL of the stations located in Saronikos (S.3–S.7), although it would be difficult to define what caused the resuspension. The small scavenging rates calculated in the BNL of most of the stations in winter explain the increase of dissolved  $^{234}\text{Th}$  in the BNL, since dissolved  $^{234}\text{Th}$  had insufficient time to get adsorbed onto particulate matter, after that localised resuspension event. An additional reason could be the disaggregation of particulate  $^{234}\text{Th}$ , as a result of mixing processes. Surface excess of the ratios could be attributed to a direct atmospheric event (e.g., Sahara dust events).

The 1 order of magnitude difference between dissolved and particulate  $^{234}\text{Th}$  residence times indicates that scavenging from dissolved to particulate  $^{234}\text{Th}$  could be highly variable, within sampling periods suggesting that the Saronikos Gulf is a highly dynamic environment, in terms of temporal and spatial particle uptake and removal. Comparing these values to reported ones from the relevant literature for similar environment and depths consistent results were obtained.

The possibility of resuspension of sediments during winter obtained directly from  $^{234}\text{Th}/^{238}\text{U}$  ratio profiles

is amplified by the decreasing residence times of particulate  $^{234}\text{Th}$  (at least in terms of average values) in the BNL. This is expected in Saronikos Gulf, where the availability of particulate matter in the BNL in connection with the particle-reactive nature of  $^{234}\text{Th}$  resulted in large sinking rates, thus small residence times. These large fluxes are reinforced by the bloom of phytoplankton, which is intense in late winter, resulting in even lower residence times of particulate  $^{234}\text{Th}$  throughout sampling campaigns (summer average:  $1.8 \pm 0.4$  days, autumn average:  $0.9 \pm 0.3$  days, winter average:  $0.6 \pm 0.2$  days).

In contrast, the respective residence times of the dissolved fraction of  $^{234}\text{Th}$  in the BNL were higher showing a maximum in winter at the stations of inner Saronikos (S.2–S.7). The rapid sinking of particles caused insufficient scavenging times of dissolved  $^{234}\text{Th}$  and, thus, dissolved  $^{234}\text{Th}$  remained in the BNL longer.

Regarding TSM inventories an additional resuspension signature was recorded as accessional evidence to  $^{234}\text{Th}$  profile and residence time data in the BNL.

Finally, it can be concluded that  $^{234}\text{Th}$  cycling in the area is not controlled by TSM, since insignificant correlations were recorded. This might be a result of the presence of colloids, as it is well known that they play essential role in  $^{234}\text{Th}$  scavenging, they are present in the area and, in addition, they were not determined in the study.

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