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^{234}Th measured particle export from surface waters in north-western Mediterranean: comparison of spring and autumn periods

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Abstract

^{234}Th was used to quantify the short-term variability of particle dynamics and of POC export during transition periods in surface waters over the north-western Mediterranean. As a part of DYNAPROC I and II cruises, two intensive time-series of ^{234}Th were carried out near the DYFAMED station (43° 25′N–7°51′E) during late spring (May, 1995), when the system changes towards oligotrophy, and during autumn (October, 2004), when the stratification is disturbed by wind. Particulate fluxes derived from ^{234}Th measured in the upper water column and in drifting sediment trap showed large differences between the two situations: the flux decreased from high to low values during late spring, at the difference of the autumnal situation where the fluxes were always low. ^{234}Th-derived POC fluxes, calculated from the ^{234}Th/^{238}U disequilibrium in the water column and POC/^{234}Th ratio on trapped material, and export ratios (ThE: ratio of ^{234}Th-derived POC export to primary production) showed a large range, from 8 to 110 mgC m^{-2} d^{-1} and 3–55%; the lowest values were observed at the end of the productive period (end May) and in automn. The ^{234}Th-derived information is in agreement with the annual variations in Mediterranean Sea productivity. From these experiments during transition periods, it is not obvious that renewal of nutrients by wind events is strong enough to sustain significant export after the end of the productive period or to initiate significant export in autumn.

1 Introduction

To estimate the seasonal variability of particle dynamics in surface waters over the north-western Mediterranean Sea, we employ the natural radionuclide ^{234}Th. The preferential scavenging of the particle-reactive daughter ^{234}Th ($t_{1/2}$=24.1 days) while its soluble parent, ^{238}U, remains nearly constant, provides an appropriate tool for assessing temporal variations of the removal of particles from surface waters, at a time scale of weeks (Coale and Bruland, 1985; Buesseler et al., 1998, 2006; Moran and Buesseler, 1992; Charette et al., 1999; Benitez-Nelson et al., 2001; Cochran and Masqué, 2003; Giuliani et al, 2007). The main application is to examine more in detail the downward flux of particulate material out of the upper mixed layer of the ocean particle sources, in order to better understand the magnitude and the efficiency of the oceanic biological pump. The first experiments on particle export, like the US JGOFS North Atlantic Bloom Experiment, were mainly focused on surface waters in spring (Buesseler et al., 1992; Schmidt et al., 1992). Over the last decade, had emerged a more general question: what controls the efficiency of particle transport between the surface and deep ocean (Buesseler et al., 2008), which implies to consider different situations: photic versus twilight zones or open ocean versus margin by example.

The present work was focused more particularly on transition periods: the spring transition, from the productive system in spring to oligotrophy, and the autumnal disturbance of the stratification of surface waters by wind events. We present two time-series of ^{234}Th (profiles and drifting traps) for the DYFAMED station. Our objectives was to compare particle dynamics and the magnitude of particulate carbon export using ^{234}Th and POC data during two contrasted transition periods at the DYFAMED station in the north-western Mediterranean Sea. The first times-series in May 1995 was previously published (Schmidt et al., 2002) and served as a comparison.

2 Material and methods

2.1 Study area

As part of the JGOFS-France DYFAMED programme, a time-series station was situated in the open central zone of the Ligurian Sea (north-western Mediterranean) and has been regularly occupied since 1991. This area is characterised by the circulation of the Liguro-Provencal current, which creates a frontal structure (Béthoux et al., 1988) and acts as a physical barrier to lateral advection of nutrient-rich, near-surface waters (Schmidt and Reyss, 1996). Therefore, changes in biological activity at the station in the central zone are driven mainly by vertical processes.

2.2 Measurements

Repeated profiles of ^{234}Th were sampled between the surface and the trap depth during both cruises. Immediately after sampling, the 20 l of seawater was passed through a 0.45 μm pore size filter to separate dissolved from particulate phases. Within one month after the collection, particulate ^{234}Th (^{234}Th^P) was directly measured on the filter as trapped particles. Isolation and purification of dissolved ^{234}Th (^{234}Th^D) was carried out on board ship within 24 h after seawater collection, using an anion-exchange procedure at sea, activities and chemical efficiencies, based on ^{229}Th, were determined at the lab using a single γ-counting (Schmidt and Reyss, 2000). ^{229}Th was determined from γ rays at 40 and 100 keV, and ^{234}Th from 63 and 92 keV, using two low-background, high-efficiency well-type detector (Canberra) (Schmidt and Reyss, 1996). Standards used for the calibration of the γ detector were IAEA standards (RGU-1). Due to technical problem, part of sampling was not measured. Uncertainties of ^{234}Th activities were calculated for each sample by propagation of the statistical errors from γ-counting. Precision estimates were variable, reflecting the counting rate of each sample, which depends on the chemical efficiency (between 20 to 60%), the decay of the initial ^{234}Th activity (between 20 to 80%). As a result, propagated 1σ errors range between 5 to 20% for the particulate phase, and between 5 to 15% for the dissolved phase. Total ^{234}Th (^{234}Th^T) represents the sum of dissolved and particulate ^{234}Th activities; error on ^{234}Th^T is calculated by propagation of errors on ^{234}Th^P and ^{234}Th^D.

To sample the settling flux directly, free-floating sediment traps (automated time-series sediment trap, PPS5, Technicap, 1 m^2 opening) were deployed 4 time (17–22 September; 24–29 September; 3–8 October; 10–15 October) at the DYFAMED central station for 5 days at each time (trap depth: 200 m). The 24-collecting cups were filled with filtered seawater previously collected at depth, filtered on 0.45 μm pore size filter and poisoned with formalin. Upon recovery, swimmers (living zooplankton) were removed from the samples prior splitting and an aliquot (10%) was subsampled for ^{234}Th analysis. These aliquots were grouped together to form a single sample per mooring was filtered on GF/F; ^{234}Th activities were also measured by γ spectrometry. Protocols for particulate carbon and nitrogen are described in Marty et al. (2008).

Usually, the U–Salinity relationship (Chen et al., 1986) is appropriate for estimating dissolved ^{238}U in the open ocean; but for marginal seas like the Mediterranean Sea, the U concentration must be controlled (Rutgers van der Loeff et al., 2006). Seawater samples were collected for ^{238}U determination. Uranium was concentrated from 2 l seawater, as previously described for ^{234}Th, in the presence of a known amount of ^{232}U spike and 20 mg Fe. Then uranium activities were determined by α-counting (Schmidt and Reyss, 1991). ^{238}U activities were 2.81±0.14 and 2.78±0.10 dpm l^{-1} at 100 and 200 m depth respectively; a mean value of 2.8 dpm l^{-1} was used in further calculation of particulates fluxes.

2.3 Irreversible scavenging model of ^{234}Th

^{234}Th as a tracer is widely used and critical for two tasks: to quantify fluxes and residences time of particles, and to calibrate trap efficiency by comparing estimated water-column ^{234}Th fluxes with those measured by traps (Cochran et al, 2000; Cochran and Masqué, 2003; Buesseler et al., 1998, 2006). In surface waters, ^{234}Th activities are the result of a balance between its continuous production from ^{238}U, its decay, its removal onto rapidly sinking particles, and its transport by advection and diffusion. The temporal change in total ^{234}Th is expressed by the classical transport equation:

$$\delta A^{\mathrm{Th}}/\delta t = \lambda A^{\mathrm{U}} - \lambda A^{\mathrm{Th}} - P + V \qquad (1)$$

where A^{U} is the ^{238}U activity, A^{Th} is the total ^{234}Th activity, λ is the decay constant of ^{234}Th (=0.0288 day^{-1}), P is the net removal flux of $^{234}\mathrm{Th}^{P}$, and V is the sum of the advective/diffusive fluxes (Savoye et al., 2006 and references therein). Measurements of both dissolved and particulate ^{234}Th allow us to calculate rates of exchange between dissolved and particulate phases, removal fluxes and particle residence times (as $^{234}\mathrm{Th}^{P}/P$). The DYFAMED station is located in the central part of the north-western

Mediterranean Sea, outside the influence of the Liguro-Provencal current. During the DYNAPROC I and II cruises, horizontal advection remained weak (Andersen and Prieur, 2000; Andersen et al., 2008). Therefore we assume that both the advective and diffusive terms are negligible.

Time-series as collected during DYNAPROC I and II cruises allow the use of the non-steady-state (nss) model. In this case, the solution of Eq. (1) is (Buesseler et al., 1994)

$$^{234}\mathrm{Th}_2 = ^{238}\mathrm{U}(1 - e^{-\lambda t}) + ^{234}\mathrm{Th}_1 e^{-\lambda t} - (P_{\mathrm{nss}}/\lambda)(1 - e^{-\lambda t}) \quad (2)$$

where $^{234}\mathrm{Th}_2$ and $^{234}\mathrm{Th}_1$ are the activities of $^{234}\mathrm{Th}$ at time t_1 and t_2 (t=t_2-t_1) and P_{nss} is the non-steady state particulate $^{234}\mathrm{Th}$ flux.

$$P_{\mathrm{nss}} = (\lambda/(1 - e^{-\lambda t}))(^{238}\mathrm{U}(1 - \mathrm{e}^{-\lambda \mathrm{t}}) + ^{234}\mathrm{Th}_1 \mathrm{e}^{-\lambda \mathrm{t}} - ^{234}\mathrm{Th}_2) \quad (3)$$

Then, POC fluxes via settling particles can be derived from $^{234}\mathrm{Th}$ data (Buesseler et al., 1992 Buesseler et al., 2006; Cochran et al., 2000):

$$P^{\mathrm{POC}} = (\mathrm{POC}/^{234}\mathrm{Th})P \quad (4)$$

with $\mathrm{P}^{\mathrm{POC}}$ the flux of particulate carbon, POC/^{234}Th the ratio of POC to ^{234}Th in settling particles, and P the particulate ^{234}Th flux. Thereatfer these calculated POC fluxes are referred as ^{234}Th-POC fluxes. ThE, as defined by Buesseler et al. (1998), is the ratio of POC export derived from ^{234}Th to primary production.

3 Results and discussions

3.1 Hydrography, and chlorophyl distributions

The first time-series during the DYNAPROC I cruise corresponds to the transition period from the productive system in spring to oligotrophy, when the stratification of surface waters could be disturbed by wind events. This period was influenced by variations in wind intensity. Before mid-May and after 25 May winds were weak ($<8\,m\,s^{-1}$). Between those times wind events occurred: first a brief event on the 13th, peaking at $16\,m\,s^{-1}$, and then a period of successive wind events after the 19th (Andersen and Prieur, 2000). Despite some wind-induced mixing, chlorophyll a concentrations showed a clear decrease throughout May 1995 associated with a rapid community succession in the favor of small cells (e.g. cyanobacteria, green flagellates, Vidussi et al., 2000). The main results of hydrologic and biological observations were summarized in Andersen and Prieur (2000).

The main hydro-biological characteristics of the Dyfamed site during the DYNAPROC II cruise (13 September–17 October 2004) (JD257–292) are presented in Andersen et al. (this issue). Briefly, this seasonal transition period was marked by low nutrient stocks, and strong water column stratification partially disrupted at the end of the cruise. An apparent stability of the hydro-biological structure of the water column prevailed during the five weeks sampling period that was disturbed by various episodic meteorological events. Two strong wind events (speed>20 nds) took place on 25 September (JD269) during the Leg 1, and further on 10 and 12 October (JD284 and JD286) during the second Leg. These two last wind events induced a strong decrease of air temperature, a beginning of de-stratification and the thermocline deepening. The most outstanding event was the intrusion of low salinity water masses (<38.3) that occurred twice below the thermocline (circa between 15 and 75 m) (Andersen et al., this issue). The first intrusion lasted from 21 September (JD266) to 30 September and was larger in size and intensity than the second one that lasted from 9 October (JD283) to 12 October. At the beginning of the cruise, two deep-chlorophyll maxima (DCM, 50–60 m and 90 m depth) were detected, resulting in a phytoplankton biomass exceptionally high for the time period (Chla concentration of $35–40\,mg\,m^{-2}$). After JD263, only one DCM was observed at 40–50 m depth with Chla concentration of $20–25\,mg\,m^{-2}$ (Marty et al., 2008).

3.2 ^{234}Th distribution and fluxes in the upper waters

Profiles of particulate and dissolved ^{234}Th were taken repeatedly at the main Dyfamed station in late spring between 0 and 80 m and in autumn between 0 and 300 m (Fig. 2). ^{238}U activities, about 2.8 dpm L^{-1}, are slightly above the predicted values from the U-S relationship, as already reported for this area (Schmit and Reyss, 1991).

During the transition period in May 1995, profiles are quite similar with moderate deficits (<33%) in the upper 50 m. Only on May 29 was ^{234}Th^{T} close to equilibrium with ^{238}U. A time evolution of ^{234}Th activities is noticeable. The first profile of the month shows a deficit in sub-surface waters, around 30–40 m. A week later, ^{234}Th^{T} presents a more extended deficit from the surface to about 30–40 m. Thereafter ^{234}Th^{T} profiles indicate a gradual evolution toward equilibrium. Mean 0–40 m ^{234}Th^{P} decreases from about 0.4 dpm l^{-1} at the beginning of the month to minimum values in mid-May, after which it increases by about a factor of 2 at the end of the observations (Table 1). The mean 0–40 m ^{234}Th^{T} deficit follows a similar trend, from 12±7% in early May to 6±3% (or nearly equilibrium) at the end of May, with a maximum of about 20±4% in mid-May.

Particulate ^{234}Th fluxes, measured in short trap deployments at 200 m depth, reflect rather well the vertical distribution of ^{234}Th, with values decreasing from about 547–595 dpm m^{-2} d^{-1} in mid-May to 108 dpm m^{-2} d^{-1} at the end of the month (Fig. 3; Table 1). POC/^{234}Th ratios range from 26.8 to 43.6 μmol dpm^{-1} in suspended particles of the upper 40 m, and from 4.9 to 7.8 μmol pm^{-1} in sinking particles collected by traps at 200 m.

During the autumnal transition period, particulate ^{234}Th was extremely variable from negligible to 0.57 dpm l^{-1} and represented up to 19% of the total ^{234}Th. Surprisingly ^{234}Th^{P} presented high values even in depth, at about 200–300 m (Fig. 2). Total ^{234}Th activities were less variable, with depth or with time, ranging from 2.4 dpm l^{-1} to about 3 dpm l^{-1}. A limited deficits (17%) was observed in the upper 30 m the 3 October. In fact most of profiles presented nearly equilibrium state (^{234}Th/^{238}U=1). As the ^{234}Th deficit is due to exported particles, this persistent equilibrium state along the observed period may indicate that particle export was not efficient to suppressed during the sampling period or few weeks before.

As already observed during the first experiment, this vertical distribution of ^{234}Th is in agreement with particulate ^{234}Th fluxes, measured by short-term drifting trap at 200 m depth. Over about 5 weeks, ^{234}Th^{P} fluxes were almost constant (91–138 dpm m^{-2} d^{-1}) in the lower range of those recorded in late spring. POC/^{234}Th ratios ranged from 11.9 to 24.1 μmol dpm^{-1} in suspended particles of the upper 60 m, and from 2.6 to 4.2 μmol dpm^{-1} in sinking particles collected by traps at 200 m (Table 1).

3.3 Particle export during transition periods

The nss model was applied to the two intensive time-series (Table 1). During the DYNAPROC I experiment, P_{nss}, the non-steady state particulate ^{234}Th flux, decreased significantly from mid to end May (Table 1), as observed in drifting trap. As a result, ^{234}Th-POC showed a similar decrease, from 110 to 17 mgC m^{-2} d^{-1}, associated with a drastic reduction in the efficiency of carbon export to deeper layers, as indicating by the low ThE values (3–4 %) observed end May. The evolution throughout May was explained by the spring transition period from a mesotrophic regime, where active grazing occurred, towards an oligotrophic production regime with reduced export (Vidussi et al., 2000; Schmidt et al., 2002).

The same method was applied to the DYNAPROC II dataset (Table 1): the calculation of particulate ^{234}Th flux was done for the upper 60 m, as deficits and mixed layer were never observed deeper. Due to incomplete profiles especially mid October, P_{nss} was calculated only between the 17 September and the 3 October. The low value of P_{nss}, resulting from the nearly absence of deficit, along with low POC/^{234}Th ratios in trapped particles leads to weak ^{234}Th-POC fluxes (around 10 mgC m^{-2} d^{-1}). ThE ratio ranged between 4 and 6%, far below those observed early May by example. Buesseler (1998) showed that open ocean is usually characterized by low export ratio (ThE < 5–10%), except during blooms like those observed at NABE (20–79%, Buesseler et al., 1992) or during more episodic export pulses. Surface waters of the Dyfamed site during the autumn transition follow this general rule (Table 1).

A general trend observed for both DYNAPROC experiment is the discrepancy between ^{234}Th derived and trapped POC fluxes, the latter being always lower. One explanation could be related to trap efficiencies during these experiments considering an earlier assessment that sediment traps can both under and over trap (Michaels et al., 1994). ^{234}Th-POC fluxes, however, were calculated from the upper 0–60, and one could not exclude degradation processes between 60 m and 200 m, the depth of the drifting trap.

A second explanation could be related to advective influences. As part of the MedFlux program, sampling was conducted at the DYFAMED site based on water column profiles (March, May and June 2003; March and April 2005) and on a mooring that included an time series sediment trap with a target depth of 200 m. The distinctly different temporal patterns of the fluxes obtained by the two methods led to the conclusion, that the two are influenced by fundamentally different processes (local settling flux of particles and Th in the traps vs advective influences) prior scavenging history in the water column Th profiles (Cochran et al, in press). Such a process must be considered to explain the discrepancy between ^{234}Th-POC fluxes, derived from discrete depth profiles of ^{234}Th in the upper 0–80 m, and POC fluxes at 200 m, as determined from short-term drifting trap mooring. First, the two DYNAPROC (I and II) cruises were performed on shorter time scales, based on high frequency sampling during periods, where little vertical advection were reported (Andersen et al., 2000, 2008). Therefore one could consider that the above process was not dominant during the DYNAPROC experiments.

Main factor explaining the large reduction in POC export from upper surface to depth is more likely in relation with recycling of organic matter. There are several evidences, as recorded in the drifting traps during the DYNAPROC II experiment, which are discussed more in details in Marty et al. (2008): – the high atomic C/N ratios of trapped materials, highlighting the partial degradation of organic matter, – the very low chlorophyll fluxes along with the high phaeopigment and fee lipid contributions to the settling material. The high particulate ^{234}Th activities, even at depths deeper to 60 m (Fig. 2), are in agreement with the general picture of a high recycling of organic matter during the autumn transition period.

3.4 Implication for carbon export

Interesting periods are the transitions when the stratification of surface waters could be disturbed by wind events. During the DYNAPROC-I and -II , the time-series of ^{234}Th in May 1995 and in October 2004 allowed us to estimate more accurately particulate and POC fluxes using a non-steady-state assumption. ^{234}Th-POC fluxes from the upper 40 to 60 m showed a large decrease throughout the spring transition period, from 110 mgC m^{-2} d^{-1} in early May to less than 20 mgC m^{-2} d^{-1} after mid-May, and rather low values (8–13 mgC m^{-2} d^{-1}) in October during the autumn transition period. Rough estimates of ThE (export ratio) are consistent - in spring with a system evolving toward oligotrophy and - in autumn with a system dominated by high recycling of organic matter. Therefore, from these experiments, it is not obvious that renewal of nutrients by wind events is strong enough to sustain significant export after the end of the productive period or to re-activate export during the period where the stratification is destabilized. This is consistent with results from Marty et al. (2008) that showed that export fluxes were mostly sustained by N_2-fixation.

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Particle export during transition periods in N-W Mediterranean

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Table 1. Mean 0–60 m particulate ^{234}Th, total ^{234}Th and C/N ratios of suspended particles at the DYFAMED station; $^{234}Th^P$ fluxes based on non-steady state (P_{nss}). $^{234}Th^P$ fluxes and POC/$^{234}Th^P$ of trapped particles. Primary production and average POC export flux from the upper 60 m, calculated as explained in the text, based on the mean 0–80 m non steady state $^{234}Th^P$ fluxes and POC/$^{234}Th^P$ of settling particles of the corresponding periods. ThE ratio is the ratio of POC export derived from ^{234}Th to primary production, as defined by Buesseler (1998).

Surface waters 0–60 m	C/N	P_{nss} (dpm m^{-2} d^{-1})	Trap period (dpm m^{-2} d^{-1})	$^{234}Th^P$ flux (μmol dpm^{-1})	POC/$^{234}Th^P$ (mean)	Primary C / N (mgC m^{-2} d^{-1})	^{234}Th-POC production (mgC m^{-2} d^{-1})	ThE export flux (%)	range
1995									
see Schmidt et al.			10–15 May	547–596	5.2		204–384	110	29–55
(2002) for details			25–31 May	108	4.9		468–588	17	3–4
2004									
17 Sept.–3 Oct.	7.3–8.7	257	17–22 Sept.	104	4.2	8.5	212	13	6%
			24–29 Sept.	91	3.4	7.6	197	10	5%
			3–8 Oct.	138	2.6	8.7	219	8	4%
			10–15 Oct.	<100	<1.8	11			

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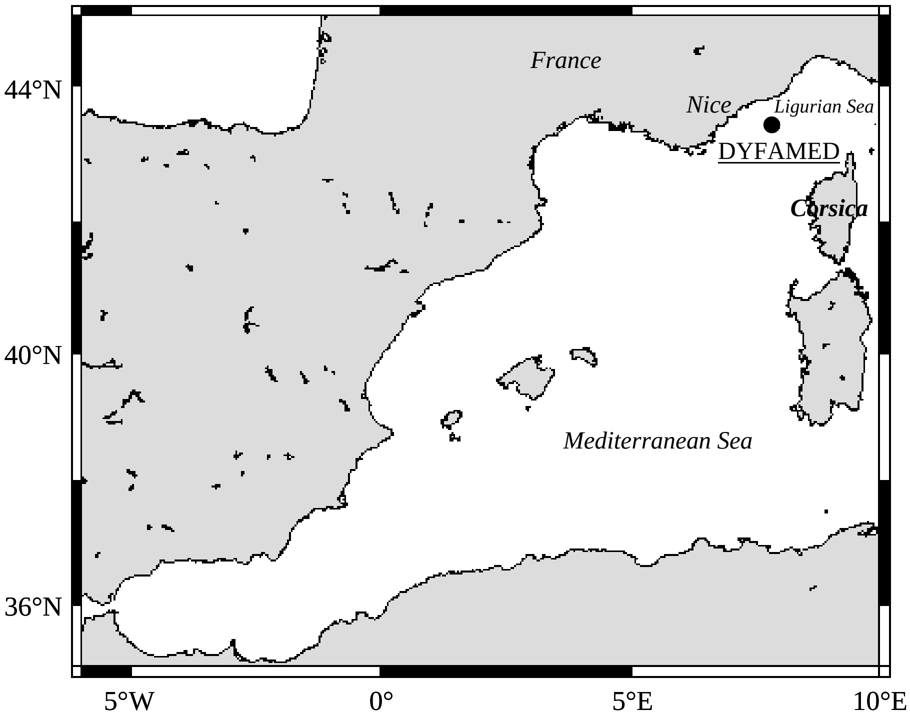

Fig. 1. Location of the main DYFAMED station in the north-western Mediterranean sea

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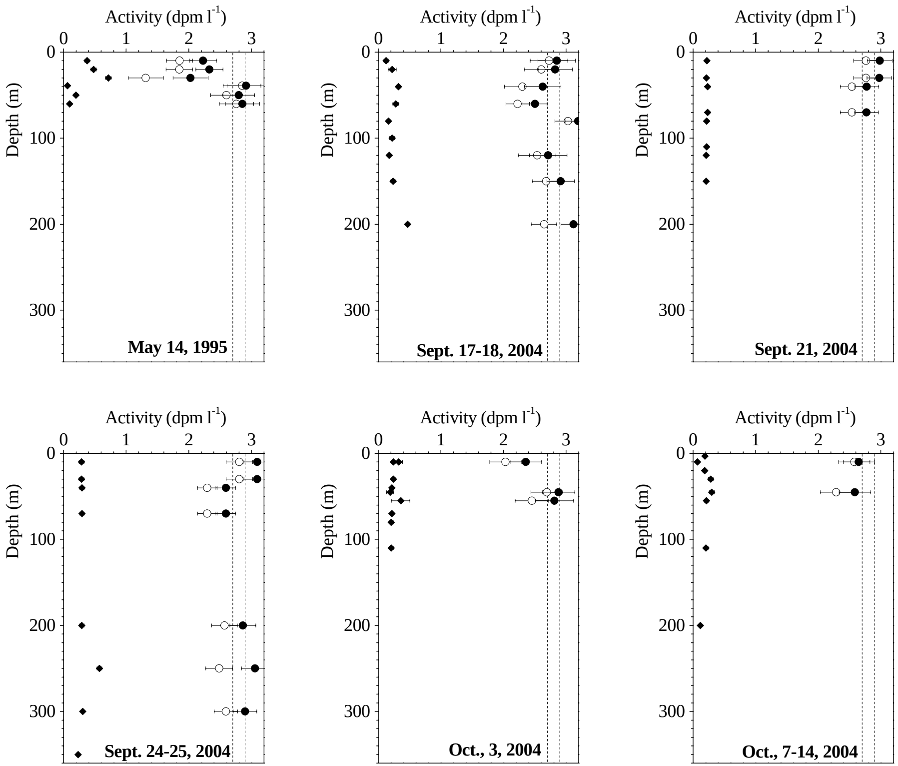

Fig. 2. Intensive survey of ^{234}Th in the 0–300 m water column in September/October 2004. A profile of the DYNAPROC I experiment is plotted for comparison; the complete dataset is already presented in Schmidt et al. (2002). Dates of sampling are indicated on each graph. $^{234}Th^P$ (filled circle), $^{234}Th^D$ (open circle) and $^{234}Th^T$ (filled diamond). The dashed lines correspond to the mean activity of 238U. Error bars represent 1σ error for dissolved and particulate ^{234}Th and propagated for Th^T.

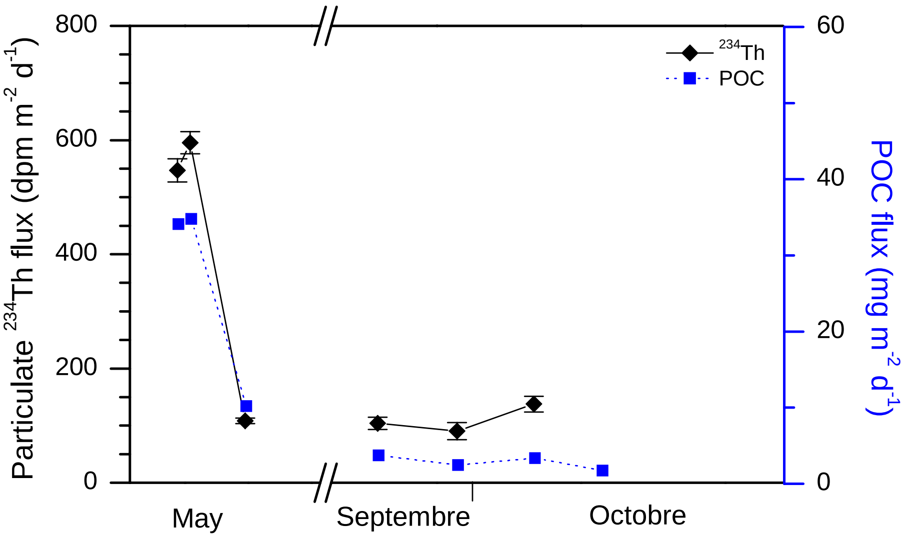

Fig. 3. Particulate ^{234}Th (dpm m^{-2} d^{-1}) and organic carbon (mg m^{-2} d^{-1}) fluxes in drifting traps.