

Uranium decay series radionuclides in the Western Equatorial Pacific Ocean and their use in estimating POC fluxes

Gillian Peck

J. David Smith

Introduction

The naturally occurring radionuclides ^{226}Ra , ^{210}Pb and ^{210}Po are members of the ^{238}U decay series and have been used to study the kinetic aspects of material cycling in the ocean (Bacon *et al.*, 1976; Ritchie and Shimmield, 1991). These studies utilise the observed radioactive disequilibria in the ^{226}Ra , ^{210}Pb and ^{210}Po system. Particle fluxes may also be studied using disequilibria among naturally occurring radionuclides. $^{226}\text{Ra}/^{210}\text{Pb}$ and $^{210}\text{Pb}/^{210}\text{Po}$ ratios cover time scales of months to years and are suitable tracers for studying particle fluxes in the upper layer of the ocean.

^{210}Pb is added to the upper ocean by fallout from the atmosphere and by decay of ^{226}Ra in the water column. ^{210}Po is produced in seawater by decay of the ^{210}Pb . Both ^{210}Pb and ^{210}Po are removed from the upper ocean by radioactive decay and by adsorption onto particles followed by sinking. The input of ^{210}Pb from the atmosphere and removal by sinking particles combine to give a vertical concentration profile that can be used to calculate the ratios of the contributing processes. Measurements of the fractions of the radionuclides in the dissolved and particulate phases have been used in steady-state

box-models of adsorption/settling and radioactive decay to calculate radionuclide residence times (Bacon *et al.*, 1976; Ritchie and Shimmiel, 1991; Towler and Smith, 1997). A likely mechanism for the removal of these radionuclides is adsorption onto other non-living biogenic material followed by sinking. Carbon dioxide in the atmosphere dissolves in the surface layer of the ocean. Transfer of carbon to the deep ocean is facilitated by fixation into particulate organic matter in the euphotic zone. Sinking of these biogenic particles from the upper layers of the ocean to the deeper layers is an important pathway in the global carbon cycle. Particle fluxes must be quantified if accurate carbon cycle models are to be developed.

Analyses were carried out on water samples of 30–40 l for particulate matter and 10 l for dissolved species using specially developed methods. These methods were developed with the specific aim of using small volumes of seawater to reduce the sampling time required when at sea. ^{226}Ra , ^{210}Pb and ^{210}Po profiles for the Bismarck Sea and western equatorial Pacific Ocean are presented. Using the ^{226}Ra , ^{210}Pb and ^{210}Po data, and a box-model based on that proposed by Bacon *et al.*, 1976, the average residence times of dissolved ^{210}Po and ^{210}Pb and particulate ^{210}Po in two layers of the upper 300 m of the ocean were estimated. The residence time of particulate ^{210}Po was used with the concentration of particulate organic carbon (POC) to estimate the flux of POC from the upper layer of the water column to the deeper layer. This work was a contribution to the international Tropical River-Ocean Processes in Coastal Settings (TROPICS) project.

■ Sampling

Water samples were collected at 5 locations in the Bismarck Sea and western equatorial Pacific Ocean during a strong El Niño phase on the August 1997 cruise of the *R.V. Franklin* (FR07/97) (Table 1). 10 l poly-vinyl chloride Niskin bottles on a rosette sampler were used to collect water from five depths at each station. This permitted collection of 3 bottles at 5m, 50m and 100m depth, and 4 bottles at 200m and 300m depth in two casts.

Station No. (Lat:Long)	Depth (m)	Specific Activity (Bq.m ⁻³)						
		²²⁶ Ra ^a	²¹⁰ Pb			²¹⁰ Po		
			Dissolved	Particulate	Total	Dissolved	Particulate	Total
1. 2°48'S; 145°06'E	5	-	2.78±0.09	0.033±0.004	2.81	0.71±0.03	0.34±0.01	1.05
	50	-	2.86±0.09	0.042±0.004	2.90	0.84±0.04	0.28±0.01	1.12
	100	-	2.45±0.08	0.066±0.005	2.52	0.82±0.04	0.19±0.01	1.01
	200	-	2.82±0.09	0.162±0.007	2.98	1.69±0.11	0.20±0.01	1.89
	300	-	2.81±0.08	0.159±0.007	2.97	1.60±0.08	0.22±0.01	1.82
2. 2°09'S; 144°00'E	5	1.73	3.82±0.09	0.031±0.004	3.85	0.82±0.04	0.34±0.01	1.16
	50	1.73	2.65±0.08	0.035±0.003	2.69	0.92±0.05	0.35±0.02	1.27
	100	1.82	1.82±0.07	0.047±0.004	1.87	1.52±0.06	0.17±0.01	1.69
	200	1.82	2.37±0.07	0.055±0.003	2.43	2.47±0.12	0.12±0.01	2.59
3. 0°00' N; 142°59'E	300	2.06	2.24±0.07	0.057±0.004	2.30	1.37±0.06	0.15±0.01	1.52
	5	1.41	3.14±0.10	0.044±0.003	3.18	0.74±0.03	0.33±0.01	1.07
	50	1.64	2.96±0.09	0.028±0.004	2.98	1.06±0.04	0.45±0.02	1.51
	100	1.61	2.81±0.09	0.035±0.004	2.85	1.16±0.05	0.24±0.01	1.40
4. 0°00'N; 146°60'E	200	1.97	2.10±0.07	0.060±0.003	2.16	1.90±0.10	0.18±0.01	2.08
	300	2.71	2.15±0.07	0.060±0.004	2.21	1.26±0.06	0.10±0.01	1.36
	5	0.96	3.01±0.09	0.031±0.004	3.04	0.71±0.04	0.41±0.01	1.12
	50	1.18	3.58±0.09	0.061±0.004	3.64	1.18±0.06	0.34±0.01	1.52
5. 0°00'S 152°00'E	100	1.52 ^b	2.76±0.10	0.032±0.003	2.79	1.53±0.06	0.19±0.01	1.72
	200	2.21	2.56±0.09	0.085±0.005	2.65	1.48±0.07	0.18±0.01	1.66
	300	2.35	2.83±0.09	0.072±0.004	2.90	1.42±0.07	0.17±0.01	1.59
5. 0°00'S 152°00'E	5	1.02	3.21±0.09	0.026±0.004	3.24	0.70±0.04	0.35±0.01	1.05
	50	1.11	3.73±0.10	0.019±0.003	3.75	1.12±0.04 ^c	0.32±0.01	1.32
	100	1.44	3.39±0.10	0.058±0.004	3.45	1.13±0.04	0.22±0.01	1.35
	200	1.22	3.28±0.08	0.057±0.004	3.34	1.40±0.06	0.13±0.01	1.53
	300	1.21	2.53±0.07	0.050±0.003	2.58	1.57±0.07	0.12±0.01	1.69

^a ²²⁶Ra data lost at station 1.

^b Value taken as average of stations 3 and 5.

^c Value taken as average of stations 4 and 5.

Table 1

Activity of radionuclides in depth profiles collected on FR07/97.
Particulate matter retained on 0.45 mm Millipore filter.

Experimental

Upon recovery sub-samples (~5 l) were removed for nutrient and particulate organic carbon analyses. The remaining volume was pressure filtered through Millipore HA membrane filters (47 mm diameter, pore diameter 0.45 µm). 10 l of filtered seawater from each depth was transferred to a glass vessel for the pre-concentration of

radionuclides. The filters containing the samples of particulate matter were placed in filter holders and stored at 4°C for later processing ashore.

Dissolved ^{226}Ra , ^{210}Po and ^{210}Pb were pre-concentrated from the filtered seawater samples using a modification of the method of Towler *et al.* (1996). Only a brief summary is given here. Filtered seawater (10 l) was acidified with HCl and standard additions of the yield tracers ^{208}Po (0.2 Bq), ^{133}Ba (8.0 Bq) and stable Pb (3 mg). After 1-2 h, the samples were neutralised by addition of sodium hydroxide solution. MnO_2 -coated magnetite was added to each sample and stirred vigorously for 1 h. The magnetite was then simply collected using a magnet. The loaded magnetite adsorbent was stored under pure water in 50 ml plastic bottles and returned to the shore laboratory for further processing.

In the laboratory, the MnO_2 was dissolved in $\text{H}_2\text{O}_2/\text{HCl}$ and Po was spontaneously plated onto a spinning silver disc (Hamilton and Smith, 1986) that was presented for alpha-spectrometry. ^{210}Po was counted immediately and the activity of ^{210}Pb in the seawater sample was inferred from a second plating and measurement of ^{210}Po after allowing a suitable time for ingrowth. Recovery of the stable Pb yield tracer was measured using atomic absorption spectrometry and the appropriate correction made to the ^{210}Pb activity. ^{226}Ra in the residual solution was measured by liquid scintillation counting (Cooper and Wilks, 1981) after successive precipitations with PbSO_4 and BaSO_4 followed by re-solution in EDTA. A toluene-naphthalene scintillant was used. ^{226}Ra concentrations were corrected using the measured recovery of the ^{133}Ba yield tracer (Tinker & Smith, 1996).

Filters containing particulate ^{210}Pb and ^{210}Po were spiked with standard additions of stable Pb (3 mg) and ^{208}Po (0.2 Bq) and digested in gently boiling 2M HCl for 2 hours. The samples were filtered and the Po measured after plating on a silver disc as described previously. ^{210}Pb was inferred from a second count of ^{210}Po after ingrowth. All sample activity calculations involved correction from the mid-point of the count time to the time of sample plating/separation and also a correction for the period between plating and sampling. POC was determined after warming the defrosted

filters in super clean HCl in alumina ceramic micro boats, to remove PIC. This was followed by analysis of samples in the solid sample chamber of a Shimadzu 500 high temperature (900°C) catalytic analyser.

Results

Radionuclide data for the two Bismarck Sea and three equatorial Pacific Ocean profiles are summarised in Table 1. All errors are based on 1σ counting errors. These results are discussed in more detail elsewhere (Peck and Smith, 2000).

Modeling

Material balance equations based on the steady-state model of Bacon *et al.* (1976) were used to estimate the residence times and fluxes of ^{210}Pb and ^{210}Po from the upper layer of the ocean via the sinking of particles. A number of assumptions were required and are discussed in greater detail elsewhere (Peck and Smith, 2000). Density profiles plotted as σ_t vs. depth indicated that the base of the thermocline was at approximately 100 m depth, this corresponding to the base of the main pycnocline. Calculations, therefore, assumed a surface layer that was 100 m thick. This surface layer is referred to as Layer 1 in the model. The remaining samples were collected from 100-300 m depth. This range was chosen as the second layer and is referred to as Layer 2. The inventories in each layer were calculated for dissolved ^{226}Ra , dissolved and particulate ^{210}Pb and dissolved and particulate ^{210}Po . These inventories were then entered in the material balance equations that follow to calculate the flux and residence times of dissolved and particulate ^{210}Pb and ^{210}Po . Using the flux of ^{210}Pb , ^{210}Po and the concentrations of particulate organic

carbon, estimations of particulate organic carbon flux were made. The particulate organic carbon (POC) flux, R ($\text{mg C cm}^{-2}\cdot\text{year}^{-1}$), was estimated using the equation shown below (15).

$$R = P_{\text{Po}} \left(\frac{C}{A_p} \right)$$

Where P_{Po} is the removal rate of particulate ^{210}Po ($\text{mBq}\cdot\text{cm}^{-2}\cdot\text{year}^{-1}$), from each layer, calculated in the box model, C is the inventory of the POC (mg C cm^{-2}) calculated for each layer and A_p is the inventory of the radionuclide ($\text{mBq}\cdot\text{cm}^{-2}$) for each layer. These results are multiplied by 27.4 to convert from $\text{mg C cm}^{-2}\cdot\text{year}^{-1}$ to $\text{mg C m}^{-2}\cdot\text{day}^{-1}$. The results are summarised in Table 1.

Discussion

The equatorial Pacific Ocean is the largest oceanic source of CO_2 to the atmosphere and has also been proposed to be a major site of organic carbon export to the deep sea (Murray *et al.*, 1994). Much of what is known about the equatorial Pacific has come from the US Joint Global Ocean Flux Study (JGOFS-EqPac). The JGOFS studies set out to better characterise carbon fluxes in the high nutrient low chlorophyll (HNLC) regions of the central and eastern equatorial Pacific Ocean. These studies have suggested that the variability of remote winds in the western Pacific Ocean and tropical instability waves are major factors controlling physical and biological variability of these waters (Murray *et al.*, 1994). Carbon fluxes strongly depend on climate variability and in the equatorial Pacific Ocean the El Niño Southern Oscillation (ENSO) plays a major role in seasonal and annual variability in the productivity of these waters.

In contrast to the eastern/central equatorial Pacific Ocean, much less work has been done in the western equatorial Pacific Ocean. Barber and Kogelschutz, 1990, suggested that the ENSO, through modulation of the east-west tilt of the equatorial nitracline, was a

primary source of new production variability, reducing new production in the eastern Pacific and increasing it in the western Pacific during El Niño. Primary production in the western equatorial Pacific has been reported from the Australian JGOFS program during non El Niño and El Niño phases (Mackey *et al.*, 1997). In 1990 (FR08/90) from 5°S to 5°N along 155°E primary productivities of 96–241 mg C m⁻².day⁻¹ were recorded, productivities for the 1992 (FR05/92) and 1993 (FR08/93) cruises were in the range 220–620 mg C m⁻².day⁻¹ (Mackey *et al.*, 1997). The 1990 cruise was after the 1988/89 La-Niña but before the 1991/92 El-Niño. The 1992 and 1993 cruises were at the middle to end of a prolonged El-Niño event. This increase in productivity during an El-Niño phase supports the link proposed by Barber and Kogelschutz (1990).

Until recently POC fluxes in the western equatorial Pacific had not been recorded (Dunne *et al.*, 2000). In this study POC fluxes were calculated using the POC inventory with the removal rate and inventory of particulate ²¹⁰Po. The average POC flux sinking out of Layer 1 was 104 mg C m⁻².day⁻¹ and from Layer 2 was 180 mg C m⁻².day⁻¹, an increase of POC flux with depth. In the western equatorial Pacific Ocean POC fluxes of 49.2 mg C m⁻².day⁻¹ at 0°N,167°E (Rodier and Leborgne, 1997), 118.8 mg C m⁻².day⁻¹ for 0°N,165°E and 97.2 mg C m⁻².day⁻¹ at 0°N,175°E (Dunne *et al.*, 2000) have been reported for depths of 100 m, 120 m and 120 m respectively. These POC fluxes are in a similar range to the fluxes reported in this study for Layer 1. However, increase in carbon flux down the water column is not expected in the western equatorial Pacific Ocean and the results from this work are not strongly supported by the productivity results for this region. Increased fluxes of particulate matter of 130 mg C m⁻².day⁻¹ at 50 m and 210 mg C m⁻².day⁻¹ at 250 m in the Mediterranean Sea, off Monaco have been reported by Fowler *et al.*, 1986. POC fluxes for the central and eastern equatorial Pacific Ocean have been more widely studied and those cited in this paper range from 23–146 mg C m⁻².day⁻¹. POC fluxes calculated from data collected on FR07/97 and comparative results from the literature are summarised in Table 2.

Carbon flux depends strongly on the physical processes; horizontal advection, diffusion, upwelling rates and wind speeds. In the equatorial Pacific these processes have been shown to cause variation in

Location	Depth (m)	POC Flux (mg C m ⁻² day ⁻¹)	Year of Sampling	Method
This Study*				
2°48'S, 145°06'E	100	70-125	August 1997	Box Model:
2°09'S, 144°00'E		104 ± 21	(El-Niño)	Polonium-210
0°00'N, 142°59'E				
0°00'N, 146°60'E	300	150-210		
0°00'S, 152°00'E		180 ± 22		
<hr/>				
Rodier & Leborgne 1997				
0°N, 167°E	100	49.2	October 1994	Drifting
0°N, 150°W	100	204	(El-Niño)	sediment trap
Dunne <i>et al.</i> 2000				
0°N, 165°E	120	70.8	October 1994	Combined
0°N, 150°W	120	146.4	El-Niño	drifting
				sediment
				trap/Th-234
0°N, 165°E	120	118.8	April 1996	
0°N, 175°E	120	97.2	Mild La-Niña	
Murray <i>et al.</i> 1996				
0°N, 140°W	120	72	February 1992	Combined
0°N, 140°W	120	120	August 1992	drifting
			(El-Niño)	sediment
				trap/Th-234
Bacon <i>et al.</i> 1996				
0°N, 140°W	120	23	March-April 1992	
	120	29	October 1992	Th-234
			(El-Niño)	
Raimbault <i>et al.</i> 1999				
0°N, 150°W	200	80-90	November 1994	Drifting
			(El-Niño)	sediment trap
Fowler <i>et al.</i> 1986				
Off Monaco	50	130	N/A	Sediment trap
	150	136		
	250	210		
Buesseler <i>et al.</i> 1995				
0°N, 140°W	100	36-60	1992	Th-234
Karl <i>et al.</i> 1996				
Station ALOHA	150	29	Average over	Drifting
22°45'N, 158°W			1990-1992	sediment trap
Central North Pacific				

*POC fluxes reported are the range and average values for the five sampling sites.

Table 2
Particulate organic carbon fluxes for oceanic seawater samples.

primary productivity with strong interannual and seasonal variability (Mackey *et al.*, 1997). Variability in the physical processes of horizontal advection, diffusion and wind speed would play a greater

role in the variability of POC flux from the upper layer of the ocean at the equator in the Pacific Ocean. These processes would not effect the lower layer to the same extent. Possible explanations for the observed increase in POC flux from the lower layer are; upwelling of nutrient rich water or diel migration of zooplankton. Estimates of POC export flux using ^{234}Th found an increase in upwelling by a factor of two causing the POC export flux to increase by 50% at the equator (Buesseler *et al.*, 1995).

Steinberg *et al.* (2000) found that approximately 15-50% of zooplankton biomass above 500 m vertically migrates into surface waters at night. Zooplankton biomass in the upper 160 m can nearly double at night due to vertically migrating zooplankton. This migration can cause increased POC fluxes in the mid-layers of the ocean.

Conclusion

There is a wide range of reported POC fluxes in the upper layers of the ocean. It is a common feature of the use of radionuclides as tracers of marine processes, that radionuclides of different half-lives yield particle fluxes of different magnitudes. Particle fluxes estimated using the same radionuclide system by different workers are generally similar. Care must be taken if particle fluxes obtained using one radionuclide system are to be compared with those obtained using different radionuclides or from the use of sediment traps.

Comparisons of POC fluxes obtained from the same study site using different radionuclide systems and using sediment trap measurements would help quantify the aspects of particle sinking that each method actually determines. This work has added to the literature for estimates of POC fluxes in the western equatorial Pacific Ocean, but highlights that future studies aimed at further understanding the relationship between the chemical, physical and biological processes in the ocean are warranted.

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