Study of Carbon Cycle in the Surface Ocean by Using Radionuclides
（Abstract of the Final Report）

Contact person　　　KUSAKABE, Masashi
　　　　　　　　Director, Nakaminato Laboratory for Marine Radioecology
　　　　　　　　National Institute of Radiological Sciences
　　　　　　　　Isozakicho 3609, Nakaminato,Ibaraki,311-1202 Japan
　　　　　　　　Tel:+81-29-265-7141, Fax:+81-29-265-7141
　　　　　　　　　E-mail: masashi@nirs.go.jp

Total Budget for FY2003-FY2005　　　110,742,000Yen　　　(**FY2005**; 32,340,000Yen)

1. Introduction

　　The ocean plays an important role in carbon cycle in the earth's surface, because about 2/7 of carbon dioxide (CO_2) emitted into the atmosphere by human activity is eventually to be absorbed into the ocean.　The CO_2 absorbed is converted to an organic matter through photosynthesis of phytoplankton.　While a part of the organic matter sinks to the depths as particles, its majority decomposes to become inorganic carbon again.　These processes are influenced by not only biological processes but also chemical and physical processes.　They include; (1) gas exchange between the atmosphere and ocean, (2) fixation of the carbon by photosynthesis, (3) settling of organic particles, (4) decomposition of settling particles, (5) aggregation/disaggregation of settling particles, (6) supply of the nutrients from the depths, (7) horizontal migration of the nutrients.　Most of the processes are mutually related, so that any single process does not determine the material balance of carbon in the ocean.　In the conventional studies of carbon in the ocean, efforts have been made to concentrate on a few processes.　Although many interesting results have been obtained, this kind of approach would sometimes fail to give a whole image of complex system of carbon behavior in the surface water.　The carbon cycle in a surface ocean is the starting point of the carbon circulation in the whole ocean.　Therefore, it is indispensable to describe quantitatively and synthetically the phenomena in the surface ocean and to analyze them when predicting change and variation of earth environment.

2. Research Objective

　　This research aims at evaluating the parameters in the above-mentioned processes (except for gas exchange) and clarifying a mutual relationship among them quantitatively and synthetically.　Natural radionuclides are utilized in this study as follows: (i) Phosphor isotopes (^{32}P, ^{33}P); phosphor (P) is an essential nutrient to growth of phytoplankton.　It can serve as a tracer to estimate parameters related to biological activity such as plankton growth, nutrients uptake, etc.　(ii) Thorium isotopes (^{228}Th、^{230}Th、^{234}Th); Thorium (Th) is known to have a strong affinity to particles in sea water.　This characteristic can be used to elucidate the particle behavior.　Three kinds of Th isotopes with different half-lives will be used to estimate transportation and transformation rates of particles.　(iii) Radium isotopes (^{226}Ra、^{228}Ra); Radium (Ra) is soluble in sea water.　Its distribution is totally controlled by physical processes such as advection and mixing of seawater.　The physical parameters will be estimated based on their distributions.　(iv) Radioactive beryllium (^{7}Be); ^{7}Be is supplied

from the atmosphere. Its half-life is appropriate to estimate a mixing rate of surface water. Each parameter obtained by the data analysis of these radionuclides is applied to dissolved/particle nutrients, carbonate species, particulate organic carbon, and dissolved oxygen etc. Eventually the carbon cycle in surface water will be clarified synthetically.

3. Methods
(1) Development of the in situ pump large-volume filtration and concentration system

All the commercially available in situ filtration systems utilize batteries, so that their pumping power is not enough to filter several m^3 of seawater in a reasonable amount of time. Only the system developed

Fig. 1   In situ large Volume filtration

by Bishop et al. (1985) has specifications matched to our requirement. Power is supplied to their system directly from a ship. Based on their concept, we have developed an in situ filtration system.

The system we developed consists of dual filtration lines: one for relatively small volume filtration (~hundreds liters) and the other for large volume filtration (several m^3). Each line has two kinds of filters and an adsorbent (Fig. 1). The main line has a prefilter with pore size of 70 μm and a filter with pore size of 1 μm; beneath the filters there are a pair of adsorbents and a flow meter. Another line has a prefilter (a filter cartridge with 1-μm pore size), a pair of adsorbent, and a flow meter.

The whole system was tested at sea off Tokai Village. About 7 m^3 of seawater could be filtered for 4 hrs of operation and more than 60% of the water went through the main line. The test results were satisfactory for this study.

(2) Adsorbent

Active alumina (granular) and ferric hydroxide were tested for the adsorbent of P and Be in seawater in a laboratory. While active alumina adsorbed P in fresh water with an efficiency of ~63%, only 19% of seawater P was adsorbed onto it, that is inappropriate for our study. Fe-impregnated filter cartridges showed various performances depending on their pore sizes; the cartridge with smaller pore size (0.5 μm) had better adsorption efficiency of about 92% than that with a larger pore size. However, a filter with smaller pore size has a slower flow rate. Considering the flow rate, filtration volume of seawater and adsorption efficiency, we chose an Fe-impregnated filter cartridge of 5-μm pore size to be appropriate for our study. This cartridge was also efficient for adsorption of Be in seawater. In the field test, about 35-52% of P in seawater was adsorbed onto the cartridges; they are significantly lower efficiency than the laboratory test due to the faster flow rate, but still sufficient enough for our study.

Mn-inpregnated filter cartridges were used to concentrate seawater Th and Ra. This method has been in use for many years, so that only minor modification was made for our system.

(3) Analytical methods

Main efforts was made for improvement of analytical methods for P isotopes because their activity in sea water are extremely low and half-lives are very short. A liquid scintillation counter was purchased based on its counting background; it has the lowest background in the market. Optimization of the counter was made to achieve the detection
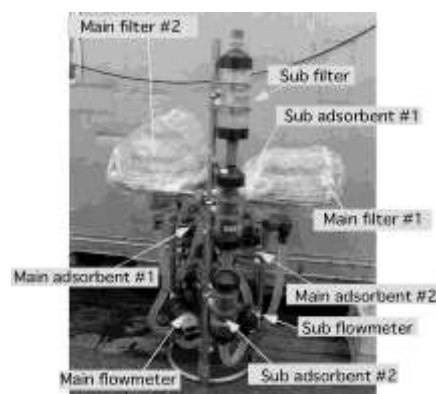
limit of ^{32}P and ^{33}P to be ~0.2 dpm for 10 hrs counting. Repeated counting made the limit even lower to be less than 0.1 dpm. Thus, the analytical method for P in seawater was established

4. Observations

Samples were taken during the three cruises in the Pacific Ocean by using the in situ large volume seawater filtration system.

The arctic waters in the northern North Pacific are rich in nutrients and yet poor in chlorophyll contents. Based on the previous observations, its low biological productivity is attributed to limited supply of iron to the waters. In order to understand biogeochemical response to the artificial addition of Fe to the surface ocean (Fig. 2A), Fe solution was sprayed in a square of 8 km by 8 km at around 48°N, 166°E on July 20 (day 0). On days 2 (D02), 4 (D04), 9 (D09), 23 (D23), and

Fig. 2. Sampling locations.
A: R/V Hakuho-maru cruise in 2004
B: R/V Mirai cruise in 2004
C: R/V Hakuho-maru cruise in 2005

31 (D31), the samplings from surface to 300 m depth were made inside the Fe patch by using the filtration system. Volume of the water filtered through the system ranged from 3 to 10 m³. During the cruise of R/V Mirai in Nov.-Dec., 2004, stations along the 155°E were occupied for the sampling by using the filtration system (Fig. 2B). In addition, during the cruise of R/V Hakuho-maru in Aug.-Sep., 2005, stations along the 160°W were occupied for the sampling (Fig. 2C). The aim of these cruises was to survey the geographical variation of biogeochemistry in the North Pacific Ocean.

5. Results and Discussion
(1) the northwestern North Pacific
(a) POC and PON

Vertical profiles of large particle concentration showed decrease with depth in general, similar to those of particle organic carbon (POC) and particle organic nitrogen (PON). Their C/N ratio in surface water was about 6 and increased with depth to 8. Generally concentration of small particles decreased with depth from the surface to 50 m depth and then increased slightly downward. Concentrations of POC and PON in the small particles were high in the surface and decreased to the 100 m depth. Their C/N ratio was 6 at the surface and increased by two-fold at the 150 m depth.

(b) Th isotopes

[234]Th concentration in large particles was less than 0.2 dpm/L and showed a slight increase at 50 m depth in general. [234]Th concentration in small particles taken on D02 had the highest concentration of 0.8 dpm/L at the surface and decrease with depth. That taken on D09 was less than 0.2 dpm/L. Dissolved [234]Th on D02 had the lowest concentration of 0.2 dpm/L and increased to 1.1-1.2 dpm/L at 50-100 m depth. That on D09 showed more than
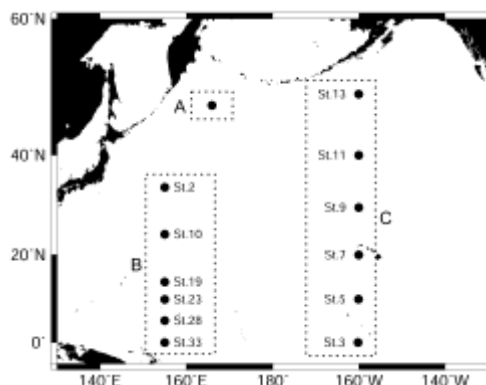
Table 1. Residence times of P in the northern North Pacific

Stn.	D m	Residence time (days)	
		In small particle	In solution
D02	0	< 1	1 ± 0
	10	2 ± 1	9 ± 1
	20		23 ± 3
	60		39 ± 17
D04	0	< 1	< 1
	10	< 1	6 ± 1
	20		6 ± 1
	60		31 ± 13
D09	0	6 ± 1	6 ± 1
	10	6 ± 1	6 ± 1
	30	6 ± 1	20 ± 4
	50		25 ± 11
	75		25 ± 9
D23	0	6 ± 3	13 ± 2
	10		17 ± 4
	30		17 ± 4
	50		25 ± 11
	75		25 ± 11
D31	0	< 1	13 ± 2
	10		20 ± 4
	30		22 ± 5
	50		22 ± 5
	75		30 ± 13

1.5 dpm/L at 30 m depth and 2 dpm/L at 50-100 m depth. More than 70% of total ^{234}Th was found to be dissolved ^{234}Th at all the stations except D02.

Based on the above observations, POC export fluxes were calculated for D02 and D09. While a residence time of Th in small particles was relatively constant to be 0.3-0.4 months, that in dissolved form changed significantly from 0.7 months on D02 to 3.0 months on D09, reflecting the doubling of dissolved Th inventory in a week. POC/Th ratios also showed significant difference, leading to a factor of two differencec of POC flux between D02 (7.9 mmol/m^2/day) and D09 (4.1 mmol/m^2/day).

(c) P isotopes

Activity of radioactive P varied with time and depth, ranging from 0.01 to 0.96 dpm/m^3. Its isotopic ratio in dissolved form increased with depth; it was in the range of 0.75 and 1.71. The isotopic ratio (^{33}P/^{32}P) in the small particles was only detected in the surface water to be 0.64-0.86. Based on the non-steady state model, the residence times of P in small particles and solution were calculated. Results are shown in Table 1. The residence time of P in solution increased with depth、 and was longer than that of small particles. While P in solution in the surface water is mixed with old P in the depth, P in particles may contain relatively new P derived from plankton. Budget calculations of P during the induced blooming were made. The results are shown schematically in Fig. 3. A thicker arrow indicates a larger flux. Based on the available data on radioactive P, the carbon cycle in the study area can be described qualitatively as follows; organic particles which was increased by the addition of Fe was transported to the depths within one day and surface suspended particles (<1 μm) became dissolved organic material within 1-2 weeks. It took another 2 weeks or more for the material to be decomposed to inorganic material.

(2) the western North Pacific

In the course of the iron enrichment experiment, activity of dissolved radioactive P in the surface water of the western North Pacific ranged from 0.11 to 1.61 dpm/m^3. The particle radioactive P was only found in the small particles and its concentration was in the range of 0.04 - 0.19 dpm/m^3. While the isotopic ratio (^{33}P/^{32}P)
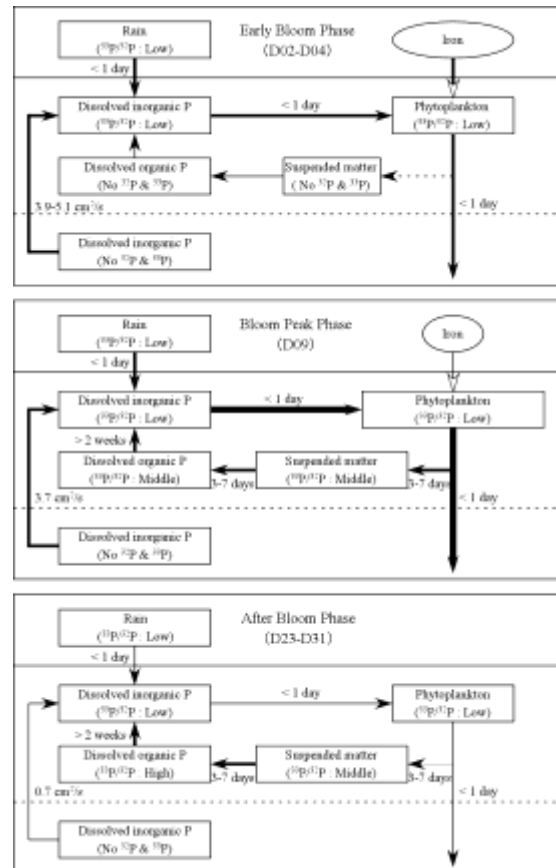

Fig. 3. Schematic diagrams of the P cycle during the induced bloom in the northern North Pacific.

Table 2. Residence times of P in small particles and solution in the western North Pacific

Stn.	D m	Residence time (days)	
		In small particle	In solution
Stn.02	0	22 ±9	32 ±5
Stn.10	0	8 ±3	22 ± 5
	30		32 ±7
	50		39 ±8
Stn.19	0	22 ±5	26 ±4
	10	22 ±5	29 ± 6
	30		34 ± 7
	50		39 ± 8
Stn.23	0	8 ± 3	16 ± 2
	10	8 ± 3	17 ±3
	30		22 ±5
	50		41 ± 14
Stn.28	0	8 ± 2	7 ±1
	10	11 ±4	7 ±1
	30		16 ±3
Stn.33	0	13 ± 4	12 ± 2
	10	13 ±6	14 ± 3
	30		19 ± 4
	50		22 ± 5

in dissolved P generally increased with depth from 0.63 to 1.29, that in small particles was from 0.64 to 0.86. Table 2 shows the residence time of P in small particles and in solution calculated. Shorter residence times were found at the stations with a high precipitation rate (Stn.28) reflecting high input of 'young' P. Compared to the northern North Pacific, long residence times existed in the area of low biological activity, implying that nutrient cycle takes a longer time in the low latitudes.

Fig. 4. Schematic diagram of the P cycle in the low latitudes.

Nutrients cycles in the low latitudes are summarized schematically in Fig.4.

(3) the central North Pacific

Based on the deficiency of ^{234}Th from its parent nuclide ^{234}U, and POC/Th ratio, export fluxes of POC at 100 m depth were calculated at the equator and 10° N: they are $0.3 - 1.0$ mmol/m^2/day. These are significantly lower than those in the western North Pacific, implying lower biological activity. Distributions of radioactive P along 160° W is related with its production rate in the atmosphere. While the nutrient cycle in the oligotrophic waters in the survey area has the same pattern as that in the middle latitude of the western North Pacific, that in the heterotrophic waters has the same pattern as the western subarctic waters after Fe addition (D31). These results suggest that there are two major patterns in the nutrients cycles in the North Pacific.