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Simultaneous measurements of cosmogenic radionuclides ^{32}P, ^{33}P and ^{7}Be in dissolved and particulate forms in the upper ocean

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A technique to determine concentrations of ^{32}P, ^{33}P and ^{7}Be in dissolved and particulate forms, in the upper ocean was developed. By using a large volume in situ filtration and concentration system (LV-FiCS), several tons of seawater at different depths were filtered concurrently through two kinds of filters. The dissolved radionuclides were concentrated onto adsorbents in the LV-FiCS. The radionuclides obtained were further purified by precipitation and ion-exchange chromatography, and quantified by gamma-spectrometry and ultra-low level liquid scintillation counter measurements. The technique was used with good results in a coastal area of Ibaraki, Japan.

Introduction

Phosphorus is one of the essential nutrients for all organisms in the ocean. Compared to studies of carbon and nitrogen, though, the distribution and dynamics of P in seawater have been less well characterized.[1] When investigating the marine P cycle, most studies have focused on dissolved inorganic P concentrations to determine P availability. However, concentrations alone provide only limited information on how P affects the magnitude of primary production or particulate export. It is of equal importance to understand the mechanisms of P utilization and their dynamics, as well as how these processes vary temporally and spatially in the upper ocean. One way to elucidate the upper ocean biogeochemical cycling is using radioisotopes. In essence, radioisotopes behave as a ‘clock’, enabling researchers to trace processes that have occurred over a well-defined time interval. There are two P radioisotopes in the ocean, ^{32}P ($T_{1/2} = 14.3$ days) and ^{33}P ($T_{1/2} = 25.3$ days). Their decay rates are compatible with the time scale of biologically driven processes. ^{32}P and ^{33}P are cosmogenic radionuclides produced in the atmosphere by cosmic ray spallation of atmospheric argon.[2] Upon their production, they are quickly associated with aerosols and are then mainly removed from the atmosphere via wet precipitation.[3] Therefore, using ^{32}P and ^{33}P, the movement of P can be monitored throughout various biological reservoirs and a net ‘age’ of P within each particular pool. Results from previous studies have shown that the radioactive P has enormous potential as a tool to understand the P cycle in marine systems.[1,4–7]

Another cosmogenic radionuclide, ^{7}Be ($T_{1/2} = 53.3$ days) is introduced into the ocean mostly by wet precipitation and it is removed from the water column primarily by radioactive decay. Measurements of ^{7}Be inventories in the water column in the Atlantic showed that most of the ^{7}Be inventory was confined within the top 150 m and that the inventory was close to the secular equilibrium value with its production.[8] These results imply that ^{7}Be concentrations in the upper ocean are not affected significantly by particulate processes on time scales comparable to its mean life. Therefore, simultaneous measurements of ^{32}P, ^{33}P and ^{7}Be would provide information on two valuable parameters: eddy diffusivity in the surface waters, averaged over a period of the order of 2 months and the residence times of radioactive P within various forms over the mean lives of the radionuclides.[9]

Because of their short half-lives and low abundance in seawater, concentrations of ^{32}P and ^{33}P are difficult to measure. Several thousands of liters of seawater are required for a single determination.[4,5,9–11] Since previous researchers have collected the sample onboard ships using a seawater intake pump, they needed a long time (>10 hours) for one sample. Therefore, it is necessary to develop a new method to collect multiple samples in a short time. We have developed a large volume in situ filtration and concentration system (LV-FiCS) so that tons of seawater are filtered through different kinds of filters and then passed through adsorbents to concentrate ultra-trace radionuclides at different depths simultaneously.[12] This technique was used to extract dissolved P and to pick up ^{7}Be from seawater efficiently. In this study, we developed a new technique for the collection and purification of ^{32}P, ^{33}P and ^{7}Be in dissolved and particulate forms using the LV-FiCS. Herein, we report data collected in a coastal area of Ibaraki Prefecture, Japan, while using the new technique.

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Experimental

Overview of the LV-FiCS

The LV-FiCS consists of filtration and concentration modules (FC modules: Fig. 1), an electromechanical cable (EM cable), and a pump control unit. The FC modules are attached with cable clamps below the branching unit in the EM cable. 200-V three-phase AC power for the modules is provided from a power unit of the ship through an EM cable. The FC module consists of the main and auxiliary filtration and concentration units (main-FC and aux-FC units, respectively). Several tons of seawater are filtrated through the main-FC unit, and then the dissolved constituents are concentrated onto adsorbents beneath the main cartridge holders. At the same time, several hundred liters of seawater are filtrated through a cartridge filter on the head of the aux-FC unit, and then the dissolved constituents are concentrated onto other adsorbents in the auxiliary cartridge holders. 90% of the water passed through the module is allocated to the main-FC unit. The filter holder at the top of the main-FC unit has two filtration steps to collect two sizes of particles: a Teflon mesh of 70 μm mesh size (Fluortex COP-70A, Sefar Inc.) and two sheets of GF filters of 1 μm pore size (GF filter; GA-100, Advantec Toyo, Ltd.). These filters are 290 mm in diameter. Two sheets in piles of GF filter are used because only one filter sheet could not withstand the high water flow rates and pressures. Prior to its use in the field, the Teflon mesh was cleaned with 1M HNO_3 in a hot bath and then rinsed with deionized water. The GF filters were precombusted at 450 °C for 2 hours.

Adsorbent

The $Fe(OH)_3$-impregnated filter cartridges (hereinafter designated Fe-cartridges) were used as adsorbent for dissolved P and Be in seawater. Preparation of the Fe-cartridges was based on the method of BENITEZ-NELSON and BUESSELER[11] with modification. Briefly, polypropylene filter cartridges (TCW-PPS series, Advantec Toyo, Ltd.) were cleaned by immersing them in a series of a phosphorus-free detergent, 1M NaOH and 1M HCl for each 12 hours each. Between each immersion, they were rinsed out by flushing them with deionized water for 15 minutes. They were then immersed in a 50% $FeCl_3$ solution at 85–90 °C for 8 hours and in a 3M NH_4OH bath for overnight. The Fe-cartridges were subsequently flushed by passing deionized water through them. Finally they were stored in plastic bags.

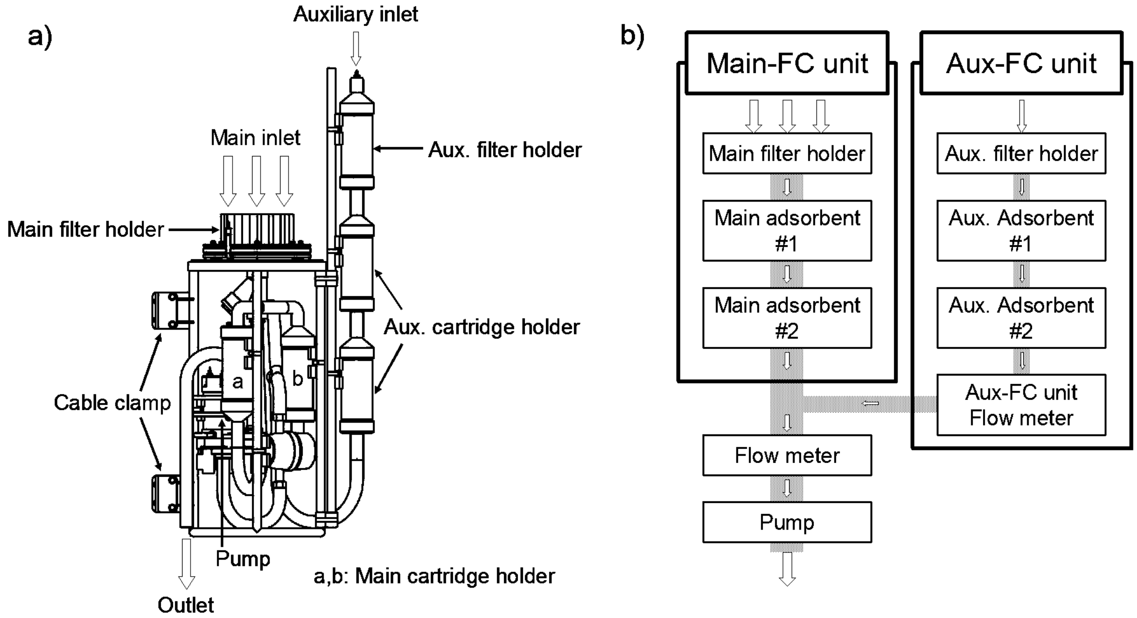

Fig. 1. Schematic drawing of the FC-module of the LV-FiCS (a). Schematic flow diagram of the FC-module (b). Arrows indicate the flow of sea water. The main-FC unit was used for collections of ^{32}P, ^{33}P and ^{7}Be

Field sampling: seawater

On 24 March 2004, seawater samples were collected on the M/V Kaiko Maru No. 5 (Offshore Operation Co., Ltd.) in a coastal area off Tokai-village, Ibaraki Prefecture, Japan, in the western North Pacific (36°23'N, 141°01'E, 522 m depth). The temperature profile suggested that the mixed layer was shallow at 25 m (Fig. 2). Dissolved isotopes of P and Be and particulates with their sizes of >70 μm and 1–70 μm were collected using a LV-FiCS. Six systems at different depths (23–143 m) could filter ca. 4,400–5,500 L of seawater through the main-FC units in 4 hours (ca. 18–23 L/min). Filtrated seawater was then passed through the two Fe-cartridges to extract dissolved P and Be. Surface seawater sample was also collected from the seawater intake line of the M/V Kaiko Maru No. 5. Surface seawater (5,100 L) was pumped directly through a cartridge filter (1 μm pore size) and then passed through the two Fe-cartridges. After sampling, the GF filter sheets and the Fe-cartridges were removed immediately from the system and rinsed with Milli-Q water to remove sea salt. The particulate samples on the filters were stored at –25 °C until analysis. In order to check the collection efficiency of dissolved P, additional seawater samples were taken using a CTD-Rosette multi-sampling system and analyzed for two kinds of stable P, that is, total dissolved P (TDP) and soluble reactive P (SRP) according to the methods described by GRASSHOFF et al.[13]

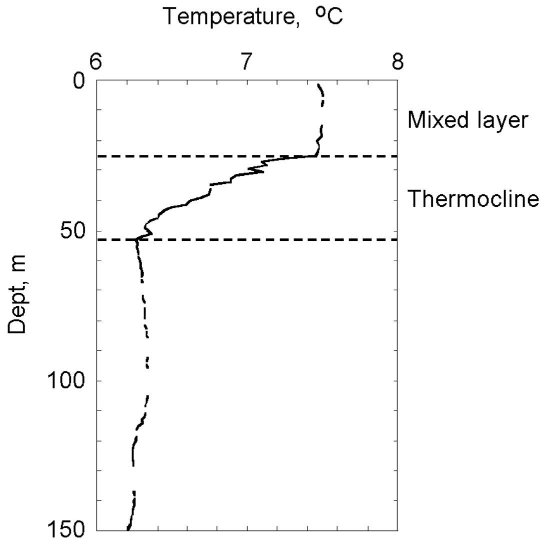

Fig. 2. Vertical profiles of temperature in a coastal area of Ibaraki Prefecture, Japan

Field sampling: rain

In order to estimate regional activity ratios of the cosmogenic radionuclides, rainwater was collected on the site of the Nakaminato Laboratory, National Institute of Radiological Sciences (36°22'N, 140°38'E). From February to May 2004, seven rain samples (18–85 L) were collected using three 76-cm-diameter plastic buckets. Rain samples were acidified with HCl to pH<2, and spiked with 100 μmol of KH_2PO_4 and 10 μmol Be solution as carriers and yield monitors. $FeCl_3$ solution (1 g Fe) was added into the samples, and then, NH_4OH was added slowly to precipitate $Fe(OH)_3$ with P and Be. After standing for 24–48 hours, the $Fe(OH)_3$ precipitate was separated from the supernatant by filtration through a glass fiber filter (47 mm ϕ, 0.45 μm; GF/F, Whatman International, Ltd.), and washed with deionized water to remove from potassium, sodium and other major cations and anions.

Sample analyses

Purification and detection of P isotopes were done based on the method described by BENITEZ-NELSON and BUESSELER[11] with modification. All reagents used were of analytical grade. Briefly, two kinds of filters with particulate matters and Fe-cartridges were combusted at 500 °C for approximately 4 hours to reduce the sample mass and convert all of P and Be into inorganic forms. P and Be were then extracted with 8M HNO_3 + 30% H_2O_2 for particulate forms and 8M HCl + 30% H_2O_2 for $Fe(OH)_3$ samples, for 12 hours while heating to 80–90 °C. Then the samples were filtered using a GF/F glass fiber filter to remove the residue. An aliquot of the solution was saved for the measurement of stable P which is used as a yield tracer for radioactive P. Marine samples were then spiked with 10 μmol Be solution as yield monitors. Large amounts of iron in the solution derived from the Fe-cartridge were repeatedly extracted with diisopropyl ether until the aqueous phase turned from brown to pale yellow.

Ammonium molybdate solution was added to the sample solutions at 45 °C until a yellow precipitate of ammonium phosphomolybdate appeared. The precipitate was allowed to settle for at least 1 hour. After settling, the precipitate was filtered using a GF/F glass fiber filter. This acid-insoluble precipitate separates P from Be and almost all other anions and cations with the exception of Pb, Bi, Sn and Zr.[14] The supernatant obtained from the phosphomolybdate precipitate reaction was used for beryllium analysis. The precipitate was dissolved in concentrated NH_4OH. The pH of the NH_4OH solution was lowered to 3–4 with 8M HCl and then the $MgCl_2/NH_4Cl$ reagent[15] was added. Next, drops of NH_4OH were added while stirring, leading to the formation of a white crystalline precipitate (magnesium ammonium orthophosphate hexahydrate). Excess NH_4OH was added, and the precipitate was allowed to settle for at least 1 hour. The precipitate P sample was filtered using a GF/F glass fiber filter and dissolved in 8M HCl for the next step, separation by ion-exchange chromatography.

The P sample was then passed through an anion-exchange column (AG 1×8 100–200 mesh, Bio-Rad Laboratories, Inc.) in order to remove any residual Fe(III) in the sample and other elements such as Cu, Cd and Zn.[11] The sample eluent was then passed through a cation-exchange column (Amberlite IRC-718, Rohm and Haas Co.) to remove residual β-emitting contaminants such as ^{210}Pb and ^{210}Bi.[11] Finally, the sample was evaporated to a volume of ≤3 mL, and then transferred to a tared 7-mL non-static liquid scintillation vial, and weighed. An aliquot (50 μL) was saved for determination of stable P to estimate the efficiency of the purification. Four milliliters of Ultima Gold AB (Packard Instrument, Co.) scintillation cocktail were added to each sample prior to counting.

All ^{32}P and ^{33}P samples were counted using an ultra-low level liquid scintillation (LSS) counter, Tri-Carb 3170TR/SL (Packard Instrument, Co.), which can resolve the two energy peaks of the isotopes (90–1700 keV and 10–90 keV, respectively) from each other. The LSS was calibrated over a range of quench values using the certified standard solution of ^{32}P and ^{33}P. Regions of interest for ^{32}P and ^{33}P were chosen so as to minimize the overlap between the two peaks. Typical overlap between the peaks was less than 10%. Eventually counting efficiencies of ^{32}P and ^{33}P became greater than 58%. Background counting rates in the ^{32}P and ^{33}P regions were 0.79±0.05 cpm and 0.82±0.08 cpm on average, respectively. The detection limits of ^{32}P and ^{33}P by the ultra-low level liquid scintillation counting, which were twice the standard deviations of the background cpms, were 0.10 cpm (0.15 dpm) and 0.16 cpm (0.23 dpm), respectively. All samples were counted repeatedly for 600 minutes over the course of several months in order to follow the decay of each isotope and to identify other β-emitting contaminants. The counting times were optimized for better counting statistics taking into account the decay of P isotopes before and after their counts.

All ^{7}Be sample solutions saved from the supernatant of the phosphomolybdate precipitation action were reduced to 20 mL via evaporation on a hot plate and were placed in plastic cups. The activities of ^{7}Be sample solutions were determined by γ-spectrometry using a high-purity REGe detector (GX2519, Canberra Industries, Inc.). An aliquot was removed to determine the chemical yield of the purification. The stable Be concentrations were measured by a quadrupole-type ICP-MS (HP-4500, Yokogawa Analytical Systems). The activities of ^{7}Be in dissolved samples could be quantified by determining the $Fe(OH)_3$ collection efficiency from:

$$\text{Collection efficiency} = 1 - B/A \qquad (1)$$

where A and B are the ^{7}Be activities of the first and second Fe-cartridges in the series, respectively.

Results and discussion

Adsorbent and chemical purification

The Fe-cartridge was tested in the laboratory for its ability to adsorb P and Be in seawater. $Fe(OH)_3$ was impregnated onto filter cartridges of various pore sizes (1 μm, 5 μm and 25 μm). Large-scale extraction tests were conducted by passing 1,800 L of 0.5 μm filtered seawater spiked with 10 μmol/L Be, 10 μmol/L dissolved inorganic phosphorus (DIP) and 2 μmol/L dissolved organic P (DOP) (0.5 μmol/L ATP and 1.5 μmol/L glucose-1-phosphate) through two Fe-cartridges.

Results of the absorbent test in the laboratory are listed in Table 1 and shown in Fig. 3. Adsorption efficiencies for DIP, DOP and dissolved Be were almost constant during the time that it took to pass 1,800 L of seawater through (Fig. 3). Since the concentrations of P and Be in the adsorbent test significantly exceeded those of ordinary surface seawater, the Fe-cartridge had enough capacity for their adsorption. However, the Fe-cartridges showed various adsorption efficiencies (83–98%) and flow rates (4–14 L/min) depending on their pore sizes and chemical species (Table 1). LEE et al.[10] also reported that the adsorption efficiency for beryllium onto $Fe(OH)_3$ was higher than those for phosphorus. It have been speculated that Fe(III) hydroxide ligand facilitates instantaneous complexation with Be compared with a wide range of chemical P compounds.[16] The Fe-cartridges with smaller pore size (1 μm) had better adsorption efficiencies than cartridges with a larger pore size. However, cartridge with smaller pore size has a slower flow rate. Considering the flow rate, filtration volume of seawater and adsorption efficiency, we chose the cartridge filter of 5-μm pore size to be appropriate for our study.

Table 1. Comparison of the adsorption efficiencies with various pore sizes of the Fe-cartridge for DIP, DOP and Be when treating 1800 L

Pore size, μm	Average flow rate, L/min	Adsorption efficiency, %		
		DIP	DOP	Be
1	3.8	94.3 ± 0.3	95.0 ± 0.7	97.5 ± 0.8
5	14.1	90.0 ± 0.5	88.4 ± 0.8	94.2 ± 0.9
25	14.3	85.5 ± 0.4	83.0 ± 0.8	89.4 ± 0.8

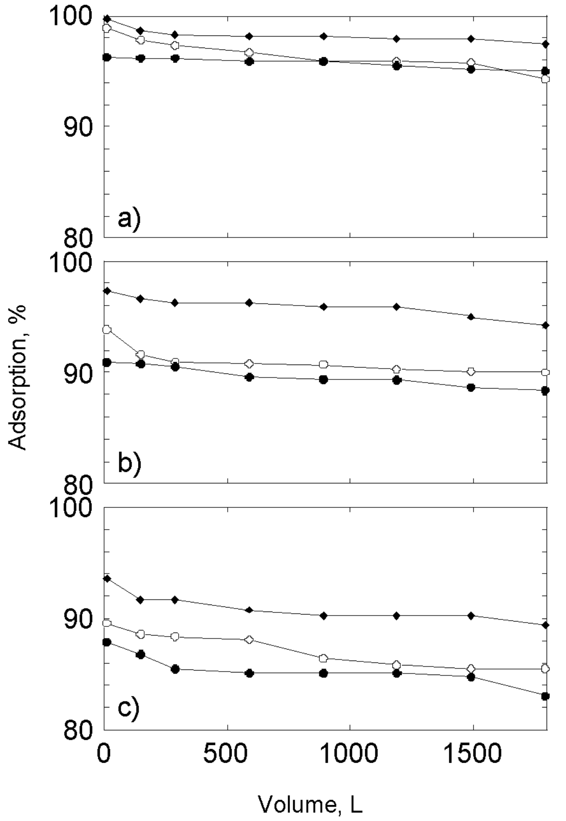

Fig. 3. Adsorption efficiencies of DIP (○), DOP (●) and Be (◆) onto the Fe-cartridges with various pore sizes versus passed volume of seawater; (a) 1-μm pore size; (b) 5-μm pore size; (c) 25-μm pore size

The concentrations of SRP and TDP, and the filtration volume of LV-FiCS are listed in Table 2. Recoveries of P and Be from seawater onto the Fe-cartridge were calculated and are shown in Table 2: recovery for P was based on the TDP concentration measured separately by bottle sampling and the amount of P on the Fe-cartridge and that for Be was estimated using Eq. (1). The recoveries of TDP and ^{7}Be via the Fe-cartridge of the LV-FiCS were lower (72±6% and 87±3%, respectively) than those of the laboratory test (Table 1). The lower recovery was ascribed to the higher flow rate of the LV-FiCS. However, the amounts of TDP and ^{7}Be collected using the LV-FiCS with the Fe-cartridges were enough for their measurements.

Yields of chemical purification ranged from 77 to 95% for P and 82 to 100% for Be. The stable P blanks had values of 50.5±6.8 μmol-P in the Fe-cartridge and less than 1 μmol-P in the reagents used in chemical purification. The blank P value was equivalent to <7% of the total measured natural stable P concentrations in seawater samples (>780 μmol-P), and was, thus, sufficiently low.

Marine samples

Results of measurements of ^{32}Pe, ^{33}P and ^{7}Be activities in dissolved and suspended particulate forms in seawater are listed in Table 3. The data were corrected for radioactive decay to the time of the sample collection. The profiles of the concentrations of SRP and TDP and activities of ^{32}P, ^{33}P and ^{7}Be are shown in Fig. 4. The activities of ^{32}P and ^{33}P in all marine samples were 0.03–3.68 dpm/m^{3} for TDP and 0.10–0.13 dpm/m^{3} for suspended particles (Table 3). Below the mixed layer, the SRP and TDP concentrations increased gradually, while ^{32}P and ^{33}P activities in TDP decreased rapidly (Figs 4a and 4b). The activities of dissolved ^{7}Be remained constant from the surface to the 95 m depth (77–88 dpm/m^{3}) and decreased slightly with depth below that (Fig. 4c). On the other hand, the activities of suspended particulate ^{7}Be were all below the detection limit (<2 dpm/m^{3}).

Table 2. Concentrations of SRP and TDP, the flow rates of LV-FiCS, and the recoveries of TDP and dissolved ^{7}Be

Depth,	SRP,	TDP,	LV-FiCS		Recovery of LV-FiCS	
m	μM	μM	Volume, m^{3}	Average flow rate, L/min	TDP, %	^{7}Be, %
0	0.45	0.59	5.1	29.4	65.9 ± 1.2	85.0 ± 4.6
23	0.48	0.56	5.5	22.8	66.5 ± 0.5	86.4 ± 3.9
47	0.54	0.78	4.4	18.3	77.9 ± 1.0	91.0 ± 3.8
71	0.62	0.93	5.0	20.9	76.5 ± 0.8	90.6 ± 3.2
95	0.79	1.03	5.1	21.2	72.8 ± 0.9	87.2 ± 5.5
119	0.83	1.09	5.5	22.8	66.7 ± 0.6	84.2 ± 3.5
143	0.83	1.09	4.7	19.5	78.9 ± 0.8	87.3 ± 3.9

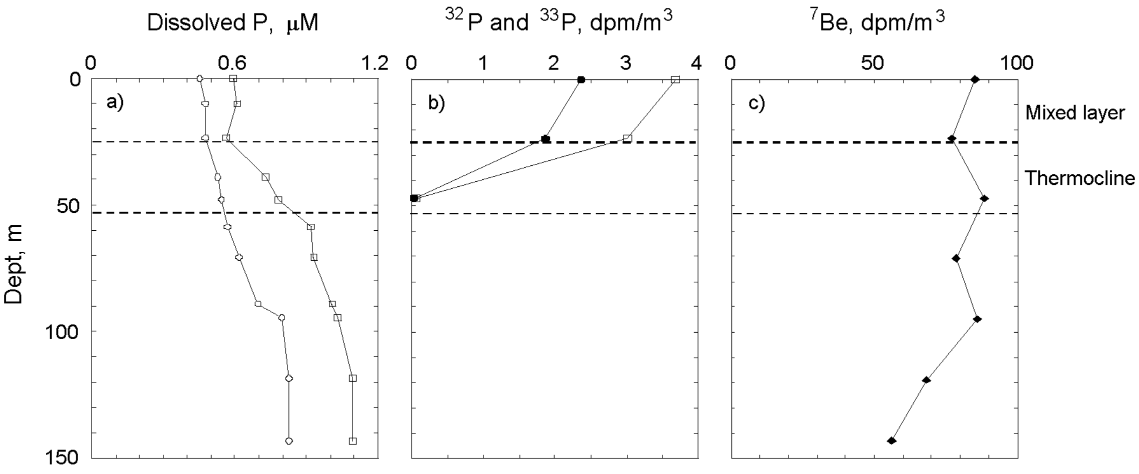

Fig. 4. Vertical profiles of (a) SRP (○) and TDP (■), (b) ^{32}P (●) and ^{33}P (□) activities of TDP, and (c) dissolved ^{7}Be activities in a coastal area of Ibaraki Prefecture, Japan. Error bars are based on the 1σ counting statistics

Table 3. Activities of ^{32}P, ^{33}P and ^{7}Be in a coastal area of Ibaraki Prefecture, Japan

Depth, m	^{32}P-TDP, dpm/m^3	^{33}P-TDP, dpm/m^3	^{33}P/^{32}P-TDP activity ratio	^{32}P-part., dpm/m^3	^{33}P-part., dpm/m^3	$^{33/32}$PP -part. activity ratio	^{7}Be-diss., dpm/m^3	^{7}Be-part., dpm/m^3
0	2.36 ± 0.19	3.68 ± 0.16	1.56 ± 0.15	0.10 ± 0.02	0.13 ± 0.02	1.37 ± 0.31	85.3 ± 8.0	B.D.
23	1.86 ± 0.03	3.02 ± 0.10	1.62 ± 0.06	B.D.	B.D.	B.D.	77.2 ± 5.4	B.D.
47	0.03 ± 0.01	0.05 ± 0.01	1.75 ± 0.81	B.D.	B.D.	B.D.	88.3 ± 5.2	B.D.
71	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	78.6 ± 4.9	B.D.
95	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	85.9 ± 7.6	B.D.
119	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	68.3 ± 4.6	B.D.
143	B.D.	B.D.	B.D.	B.D.	B.D.	B.D.	56.0 ± 5.2	B.D.

All errors are 1σ based on a regression of multiple counting periods.
B.D. = Below detection.

Our measurements indicated that most ^{7}Be in seawater was present in dissolved form. This result suggested that particulate scavenging may play a minor role in the behavior of ^{7}Be in the surface ocean. LAL and LEE[4] and LEE et al.[9] observed a similar decrease of ^{32}P and ^{33}P with depth. They considered that these concentration gradients were mainly caused by radioactive decay of P during vertical mixing of the surface ^{32,33}P-rich water with deep ^{32,33}P-poor water through the thermocline, and there was only a little effect by the particulate export of P in their calculation. The marked difference between radioactive P and ^{7}Be depth profiles in dissolved from showed that the time scales of vertical mixing below the mixed layer were longer than a few weeks but shorter than a few months.

The measured ratio of ^{33}P/^{32}P found in particle, 1.37±0.31, was similar to that found in rain, 1.27±0.02 (average ratio of the rain in March, 2004; see below), indicating rapid turnover of P on the order of a few days. However, the ratios of ^{33}P/^{32}P found in TDP were significantly higher than that found in rain. In other words, P in dissolved form was much older than particulate P. This result would be caused by the composition of dissolved P. There are two kinds of dissolved P in the ocean; SRP and soluble non-reactive P (SNP). SRP is relatively fresh and readily available to biological activity, while SNP is not easily utilized by organisms. Therefore, SNP should be much older (high ^{33}P/^{32}P) than SRP. If the ratio of SNP to TDP is high, the apparent ^{33}P/^{32}P ratio of TDP would also rise. The SNP generally ranges from 0–50% of the TDP pool in coastal marine environments,[17] to as great as 75% in the open ocean.[18] In fact, the SNP ranged from 14–34% of TDP in this study. For this reason, the ^{33}P/^{32}P ratio in TDP would be higher than that in suspended particle. If SRP instead of TDP could be used for the application of P residence time estimation, then it would be predicted that SRP residence time would be much shorter than TDP.[7]

Table 4. ^{32}P, ^{33}P and ^{7}Be activities measured in discrete rain samples collected at the Nakaminato Laboratory, National Institute of Radiological Sciences

Date	Rainfall, mm	^{32}P, dpm/L	^{33}P, dpm/L	^{7}Be, dpm/L	^{33}P/^{32}P activity ratio	^{7}Be/^{32}P activity ratio	^{7}Be/^{33}P activity ratio
3 Feb 2004	8	0.89 ± 0.02	1.12 ± 0.03	89.4 ± 1.7	1.25 ± 0.05	100.0 ± 3.0	80.2 ± 2.7
18 Mar 2004	13	0.52 ± 0.01	0.66 ± 0.02	21.1 ± 0.6	1.26 ± 0.04	40.3 ± 1.3	31.9 ± 1.2
20 Mar 2004	17	0.60 ± 0.01	0.77 ± 0.02	24.5 ± 0.7	1.28 ± 0.04	40.7 ± 1.4	31.8 ± 1.2
13 May 2004	27	0.40 ± 0.01	0.35 ± 0.00	37.0 ± 0.8	0.87 ± 0.02	91.8 ± 2.7	106.0 ± 2.7
19 May 2004	19	0.44 ± 0.00	0.41 ± 0.00	47.2 ± 0.6	0.94 ± 0.01	107.3 ± 1.5	114.6 ± 2.0
20 May 2004	68	0.27 ± 0.00	0.26 ± 0.01	25.8 ± 0.6	0.96 ± 0.02	95.2 ± 2.5	98.8 ± 3.0
31 May 2004	26	1.49 ± 0.01	0.99 ± 0.01	109.6 ± 2.4	0.66 ± 0.01	73.5 ± 1.7	110.6 ± 2.7

All errors are 1σ based on a regression of multiple counting periods.

Rain samples

Results of measurements of ^{32}P, ^{33}P and ^{7}Be activities in rain samples are listed in Table 4. The data were corrected for radioactive decay to the start of the sampling time. The activities of ^{32}P and ^{33}P measured in rain ranged from 0.26 to 1.49 dpm/L, while the activities of ^{7}Be ranged from 21.1 to 109.6 dpm/L. The activity ratio of ^{33}P/^{32}P in rain ranged from 0.66 to 1.28 (1.03±0.24 on average), while the ratios of ^{7}Be/^{32}P and ^{7}Be/^{33}P ranged from 31.8 to 114.6 and their averages were 78.4±27.9 and 82.0±36.0, respectively. Several researchers have conducted comprehensive measurements of ^{32}P and ^{33}P in rain and have suggested that the ^{33}P/^{32}P ratios should be constant for all seasons.[2,3] However, from observations it was found that the activity ratio in rain varied regionally.[2,3,19] The average ratio here was close to that observed for the East China Sea (0.99)[7] but higher than that of the island of Hawaii (0.54).[1] Previous measurements of ^{33}P/^{32}P ratios suggested that the higher ratio was predominately of stratospheric origin. WASER and BACON[3] observed an increase in the ratio of ^{33}P/^{32}P in integrated rain samples collected in Bermuda to values as high as 1.20 during March, April and July 1991, and January and February 1992. In general, stratosphere/troposphere exchange (STE) appears to be most vigorous in the spring (February – April) and at midlatitudes in the Northern Hemisphere.[20–22] Actually, the high ratios of ^{33}P/^{32}P here were seen in the spring (February and March). On the other hand, the ratios of ^{7}Be/^{32}P and ^{7}Be/^{33}P in rain showed little correlation with the STE process. Further studies are required clarifying the difference in scavenging between phosphorus and beryllium.

Conclusions

A technique for the simultaneous collection and purification of radioactive P and ^{7}Be was described. A large volume in situ filtration and concentration system (LV-FiCS) enabled us to filter ca. 4,400–5,500 L of seawater from different depths in the upper ocean. We demonstrated this technique in a coastal area of Ibaraki Prefecture, Japan. Efficiencies for the collection of TDP and dissolved ^{7}Be via the Fe-cartridges averaged 72% and 87%, respectively. The new sampling technique gave results of radioactive P with good analytical precision. The profiles of dissolved ^{32}P, ^{33}P and ^{7}Be suggested that the time scales of vertical mixing below the mixed layer were 1–2 months.

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