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# Phosphorus cycling in the North Pacific Subtropical Gyre using cosmogenic $^{32}P$ and $^{33}P$

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*Abstract*

The North Pacific Subtropical Gyre (NPSG) has been hypothesized to be in transition from a nitrogen (N)-limited system to one predominantly limited by phosphorus (P) as a result of a two-decade-long selection for $N_2$-fixing organisms. In this study, the naturally occurring cosmogenic radioisotopes, $^{32}P$ (half-life = 14.3 d) and $^{33}P$ (half-life = 25.3 d), were measured and $^{33}P/^{32}P$ activity ratios were used to estimate radioactive P residence times at Sta. ALOHA (22°45′N, 158°00′W) in the NPSG from February 1999 to July 2000. The $^{33}P/^{32}P$ activity ratio in the total dissolved P pool varied considerably but systematically; high ratios correlated with periods of enhanced primary production ($^{14}C$ incorporation). Marine particulate $^{33}P/^{32}P$ activity ratios were similar to those found in the source (i.e., rain). Smaller size classes had longer apparent residence times. The observation that the activity ratio of $^{33}P/^{32}P$ closely follows primary production suggests that atmospherically derived $^{32}P$ and $^{33}P$ atoms track the most ''bioavailable'' pool of P within the NPSG ecosystem. These preferred substrates were removed from the dissolved phase via plankton uptake during periods of high productivity. Our results suggest that the soluble nonreactive P pool, which is substantially larger than the soluble reactive P pool, is a potentially important source of P to organisms and that its utilization can vary significantly on scales of weeks to months.

Phosphorus (P) is an essential nutrient for all living organisms. Compared to studies of carbon (C) or nitrogen (N), two additional bioelements, the distributions and dynamics of inorganic and organic P pools in seawater are less well characterized. Recent evidence suggests that P and trace elements (especially iron) may play a significant role in limiting primary production and nitrogen fixation in selected marine habitats (Martin et al. 1990; Krom et al. 1991; Karl et al. 1997; Behrenfeld and Kolber 1999; Wu et al. 2000; Karl et al. 2001; Sañudo-Wilhelmy et al. 2001). This is particularly true in the western North Atlantic, where enhanced dust deposition has resulted in severe P limitation (Wu et al. 2000). In the North Pacific Subtropical Gyre (NPSG), there is also a hypothesized climate-induced transition from N to P limitation, potentially due to increasing blooms of $N_2$-fixing organisms (Karl et al. 2001). As a result, it is essential that we understand the composition and the residence times of the various P pools within oligotrophic regimes because they may directly affect the magnitude of global primary production and, hence, nutrient cycling and export in the world's oceans.

There have been few studies that directly measure the uptake and remineralization of dissolved P in the water column or the utilization of P within the planktonic pools (e.g., Benitez-Nelson 2000 and references therein). In general, when investigating the marine P cycle, most studies have focused on dissolved inorganic P concentrations and uptake rates to determine P availability, ignoring the potential role of organic P compounds (Perry and Eppley 1981; Sorokin 1985; Harrison and Harris 1986). However, there is reasonable evidence suggesting that dissolved organic P (DOP) might also play a key part in plankton nutrition (e.g., Benitez-Nelson 2000 and references therein). Because DOP concentrations in the open ocean can be more than two orders of magnitude greater than inorganic P concentrations (e.g., Cavender-Bares et al. 2001), this pool is a potentially important source of P to oligotrophic marine ecosystems.

It has been difficult to directly measure the relative size of the bioavailable P (BAP) pool mainly because of the lack of analytical characterization methods. Soluble reactive phosphorus (SRP) is characterized as the P fraction that reacts to form a phosphomolybdate complex under acidic conditions (Strickland and Parsons 1972). Although SRP is typically dominated by orthophosphate, acid-labile organic compounds, such as simple phosphate sugars, are also included (McKelvie et al. 1995 and references therein). The difference between total dissolved P (TDP) and SRP is often referred to as DOP or, more precisely, the soluble nonreactive P (SNP) pool because this pool may also contain inorganic P compounds that do not form phosphomolybdate under acidic conditions. It is most likely a mixture of SRP and SNP that comprises the BAP pool in the NPSG (Björkman et al. 2000).

Concentrations alone, however, provide only limited information on how nutrients affect the magnitude of primary production or export. Understanding the mechanisms of P utilization and their dynamics are of equal importance. These studies have also been hampered by methodology. In this study, we have used the naturally occurring radionuclides,

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$^{32}P$ ($t_{1/2}$ = 14.3 d) and $^{33}P$ ($t_{1/2}$ = 25.3 d), to investigate the dynamics of BAP in the surface waters of the NPSG.

$^{32}P$ and $^{33}P$ are produced in the atmosphere via cosmogenic interactions with argon and enter the oceans via wet and dry deposition, presumably as phosphate (Lal et al. 1960; Lal and Peters 1967; Waser and Bacon 1995; Benitez-Nelson and Buesseler 1999*a*). If the input ratio is either known or assumed to be constant, then the $^{33}P/^{32}P$ activity ratio in any selected P reservoir will increase with increasing age because of the differential decay rates. For example, if the $^{33}P/^{32}P$ input activity ratio was 1.0 at time zero, it would be 1.16 after 1 week and 1.35 after 1 month using a simple steady-state model. Thus, it is possible to estimate the residence times of radioactive P within various size classes integrated over the mean lives of the radionuclides ($\tau_{32}$ = 20.6 d, $\tau_{33}$ = 36.5 d) (Lal and Lee 1988; Waser et al. 1996; Benitez-Nelson and Buesseler 1999*b*).

Because of their low abundance in seawater, $^{32}P$ and $^{33}P$ are difficult to measure. Several thousands of liters of seawater are required for a single determination (Lal and Lee 1988; Lee et al. 1991, 1992; Waser et al. 1996; Benitez-Nelson and Buesseler 1998). Recent developments in analytical techniques have enabled the determination of both $^{32}P$ and $^{33}P$ in dissolved and particulate pools (Benitez-Nelson and Buesseler 1998). In this study, we report data on cosmogenic $^{32}P$ and $^{33}P$ in dissolved and small particle samples from February 1999 to March 2000 at Sta. ALOHA (22°45′N, 158°00′W) in the NPSG. Our results provide relevant information on radioactive P residence times and on the potential role of SNP in primary production.

## Materials and methods

*Sample collections*—Samples were collected on approximately monthly intervals during 4-d Hawaii Ocean Time-series (HOT) Program cruises to Sta. ALOHA between February 1999 (HOT 102) and March 2000 (HOT 113). In July 1999, samples were collected during a 2-week cruise to Sta. ALOHA. TDP and three different size classes of the particulate P (PP) pool (0.2–1.0 $\mu$m, 1.0–10 $\mu$m, >10 $\mu$m) were collected using a procedure similar to that described by Benitez-Nelson and Buesseler (1998). Briefly, approximately 5 $m^3$ of seawater were collected from the uncontaminated seawater line of the R/V *Ka'imikai-O-Kanaloa* (located at a depth of 4 m) during a sampling period of 18 h. In general, seawater was either pumped directly through 142-mm-diameter microfine glass fiber filters (Whatman grade GF/F, nominal pore size ~0.7 $\mu$m) or through a series of 10-, 1.0-, or 0.2-$\mu$m pore size, 6.4-cm-diameter, 25.4-cm-long HYTREX™ polypropylene cartridge filters. The filtrate was then passed into a series of two 6.4-cm-diameter, 7.6-cm-long manganese hydroxide ($Mn(OH)_2$) cartridges and, finally, a 7.6-cm-diameter, 1-m-long polyvinylchloride (PVC) pipe containing iron hydroxide ($Fe(OH)_3$)-impregnated polypropylene filters. This procedure was used to (1) remove or fractionate particles (filters), (2) adsorb potentially interfering radionuclides ($Mn(OH)_2$ cartridges), and (3) scavenge total dissolved $^{32}P$ and $^{33}P$ ($Fe(OH)_3$ pipe). $^{32}P$ and $^{33}P$ activities were measured in PP samples collected from February 1999 (HOT 102) to late March 2000 (HOT 113) and in TDP samples collected from HOT 106 to HOT 113. In HOT 102, HOT 104, and HOT 105, only PP samples collected on 142-mm GF/F filters were measured for $^{32}P$ and $^{33}P$ activities. From HOT 106 to HOT 109, a 1-$\mu$m HYTREX filter was utilized, and from HOT 110 to HOT 113, 0.2-, 1-, and 10-$\mu$m HYTREX filters were used.

Water volumes and flow rates were monitored using a flow meter. Flow rates were kept at 3.8 ± 0.9 L $min^{-1}$. We confirmed the efficiency of P collection by measuring TDP concentrations in the $Fe(OH)_3$ pipe effluent compared to the intake. The $Mn(OH)_2$ cartridges do not adsorb SRP or DOP and were placed directly prior to the $Fe(OH)_3$ pipe to adsorb other radionuclides, such as radium and thorium, that would otherwise interfere with measurement of $^{32}P$ and $^{33}P$ (Benitez-Nelson and Buesseler 1998). Once collected, all samples were placed in clean plastic bags and stored for further processing in the shore-based laboratory.

In order to estimate the regional activity ratio of $^{33}P/^{32}P$ of the source matter, precipitation samples were collected. Most precipitation samples were obtained over week-long intervals using an Aerochemetrics™ wet-only precipitation collector at Volcanoes National Park (elevation = 1,190 m) on the island of Hawaii. At this site, meteorological measurements have been ongoing since 1993 (Heath and Huebert 1999). This location is far removed from anthropogenic sources, and rainfall is sufficient to collect large volumes of precipitation. Rain sample volumes ranged from 0.8 to 3.9 L and were transported to the laboratory for analysis. Additional precipitation samples were collected in a similar manner at Kokee State Park (elevation = 1,220 m) on the island of Kauai and during the May 1999 (HOT 109) cruise using a 1-m-diameter plastic funnel.

*Sample analyses*—All $^{32}P$ and $^{33}P$ samples were purified and measured according to the methods described by Benitez-Nelson and Buesseler (1998). Briefly, filters (PP) and $Fe(OH)_3$ (TDP) samples were combusted in a 500°C oven for approximately 4 h to oxidize the organic filter matrix to $CO_2$ and, thus, reduce the sample mass. Ashed samples were subsequently dissolved in 8 N $HNO_3$, and an aliquot was removed and assayed for phosphate in order to trace the efficiency of the subsequent purification procedure. Seawater and precipitation samples were then purified from all other beta-emitting radionuclides using a series of P-specific precipitations, ammonium phosphomolybdate, and magnesium phosphomolybdate, followed by ion exchange chromatography to remove residual contaminants. Finally, each sample was evaporated to a volume ≤3 ml, transferred to a tared 17-ml liquid scintillation vial, and weighed and an aliquot (50 $\mu$l) was removed to determine the efficiency of the purification. Total concentration factors are on the order of $10^7$. Five milliliters of Ultima Gold A/B liquid scintillation cocktail was added to each sample prior to counting.

All $^{32}P$ and $^{33}P$ samples were counted using a low-level liquid scintillation (LSS) counter, Tri-Carb 2770 TR/SL. The LSS was calibrated over a range of quench values using artificially produced $^{32}P$ and $^{33}P$ solutions that were independently calibrated with a low-level gas flow–proportional beta counter (Benitez-Nelson and Buesseler 1998). Counting re-

Table 1. $^{33}P$ and $^{32}P$ activities (±SE) measured in discrete rain samples collected at Volcanoes National Park on the island of Hawaii unless otherwise noted. All errors are 1 sigma based on a regression of multiple counting periods.

| Sample | Rainfall (mm) | SRP (nM) | $^{33}P$ (dpm $m^{-3}$) | $^{32}P$ (dpm $m^{-3}$) | $^{33}P/^{32}P$ activity ratio |
|---|---|---|---|---|---|
| 3 Dec 1998 | 181.4 | 256 | 710±250 | 1,030±310 | 0.69±0.30 |
| 8 Dec 1998 | 211.6 | <25 | 390±220 | 1,420±330 | 0.27±0.15 |
| 23 Dec 1998 | 31.5 | <25 | 320±90 | 460±200 | 0.69±0.37 |
| 30 Dec 1998 | 24.4 | <25 | 480±260 | 1,570±160 | 0.31±0.12 |
| 12 Jan 1999 | 53.6 | <25 | 560±210 | 670±110 | 0.84±0.26 |
| 20 Jan 1999 | 10.7 | <25 | 1,780±170 | 3,430±400 | 0.52±0.07 |
| 27 Jan 1999 | 240.3 | <25 | 2,600±730 | 3,090±170 | 0.84±0.11 |
| 2 Feb 1999 | 299.0 | 34 | 1,560±350 | 4,760±1,830 | 0.33±0.14 |
| 3 Feb 1999* | 169.0 | <25 | 980±150 | 3,370±1,790 | 0.29±0.16 |
| 11 Feb 1999 | 164.1 | <25 | 340±320 | 930±50 | 0.37±0.34 |
| 16 Feb 1999 | 32.0 | <25 | 660±250 | 1,270±260 | 0.52±0.18 |
| 24 Feb 1999 | 276.1 | 29 | 320±50 | 600±40 | 0.53±0.05 |
| 27 Mar 1999 | 194.6 | 42 | 520±170 | 1,140±150 | 0.45±0.11 |
| 7 Apr 1999 | 247.4 | <25 | 200±40 | 270±40 | 0.74±0.13 |
| 13 Apr 1999 | 171.1 | <25 | 290±50 | 370±100 | 0.77±0.24 |
| 11 May 1999† | — | <25 | 3,370±210 | 1,570±630 | 0.47±0.19 |
| 4 Sep 1999 | 40.6 | <25 | 410±140 | 520±90 | 0.80±0.23 |
| 3 Dec 1999 | 112.3 | <25 | 110±100 | 300±10 | 0.37±0.40 |
| Average | | | 770±160 | 1,590±320 | 0.54±0.05 |

* Collected at Kokee State Park on Kauai.
† Collected during HOT 105 at 22°45′N, 158°W.

gions were chosen so as to minimize the overlap between the two radionuclide peaks and to maintain counting efficiencies at greater than 60%. Typical overlap between the peaks was less than 10%. All samples were counted repeatedly for a period of 13 h over the course of several months in order to follow the decay of each isotope and to ensure purity.

SRP was measured according to the methods described by Strickland and Parsons (1972). A modified SRP measurement, magnesium-induced coprecipitation (MAGIC), was also used on low P–containing samples (Karl and Tien 1992). TDP was determined using the wet persulfate oxidation method described by Menzel and Corwin (1965) with modifications by Thomson-Bulldis and Karl (1998). All ancillary measurements, such as primary production and nutrients, were collected as part of the HOT core biogeochemistry program and measured using the HOT standard protocols (Karl and Lukas 1996).

## Results

*$^{32}P$ and $^{33}P$ activities*—$^{32}P$ and $^{33}P$ activities measured in rain ranged from 110 to 1,500 dpm $m^{-3}$, except for a period of high-activity events that occurred in mid-January and early February of 1999 when activities reached 4,760 dpm $m^{-3}$ (Table 1). The activity ratio of $^{33}P/^{32}P$ in rain ranged from 0.27 to 0.84 and averaged 0.54 ± 0.05 ($n$ = 18; Table 1). In order to check the regional constancy of the $^{33}P/^{32}P$ activity ratio, one pair of rain samples was simultaneously collected on the islands of Kauai and Hawaii in early February. Although activities in the Kauai rain sample were slightly lower (most likely because of 50% less rainfall during the intercomparison) the $^{33}P/^{32}P$ activity ratios were statistically indistinguishable: 0.33 ± 0.14 and 0.29 ± 0.16, respectively. Because of the intermittent rainfall and difficulty with the collection of rain events at sea, only one at-sea sample was collected. The $^{33}P/^{32}P$ activity ratio collected in May 1999 was 0.47 ± 0.19, well within the range of values measured on the Hawaiian Islands. There was no seasonal difference in the $^{33}P/^{32}P$ activity ratio for the land-based collections. In addition, similar ratios were measured on the island of Kauai and at Sta. ALOHA, ~140 km apart, providing further confidence in the regional stability of our $^{33}P/^{32}P$ input measurement.

Marine particle activities ranged from 0.05 to 0.79 dpm $m^{-3}$, with most cruises having activities <0.2 dpm $m^{-3}$ (Table 2). The $^{33}P/^{32}P$ activity ratios measured in small particles (i.e., material retained by 0.2-, 1.0-, or 10-$\mu$m filters) did not vary seasonally and were not significantly different (0.59 ± 0.06; Fig. 1) from those found in rain. During the cruises where more than one particle size class could be measured, the smallest size class had consistently higher $^{33}P/^{32}P$ activity ratios compared to the other size classes (Table 2).

Efficiencies for the collection of TDP-associated $^{32}P$ and $^{33}P$ activities via $Fe(OH)_3$-impregnated filters averaged 60%. Collection efficiencies decreased throughout the course of filtration because of saturation of the $Fe(OH)_3$ filters. TDP samples collected in February (HOT 111) and March 2000 (HOT 112) had collection efficiencies of only 40%, possibly because of either poor impregnation of the iron filters or a change in the chemical composition of DOP that could affect adsorption. Measurement of both MAGIC P and TDP suggests that most of the uncollected material in the filtrate was from the DOP pool. $^{32}P$ and $^{33}P$ activities measured in the TDP samples ranged from 0.54 to 7.30 dpm $m^{-3}$ (Table 2).

In general, the range in $^{32}P$ and $^{33}P$ TDP activities is low and the variation that does exist is most likely related to differences in both rainfall and mixed-layer (ML) depths.

Table 2. $^{33}P$ and $^{32}P$ activities, $^{33}P/^{32}P$ ratios, and radioactive P residence times for dissolved and small particles. All errors are 1 sigma based on a regression of multiple counting periods.

| Sample | Size ($\mu$m) | $^{33}P$ (dpm m$^{-3}$) | $^{32}P$ (dpm m$^{-3}$) | $^{33}P/^{32}P$ activity ratio | SS model (d) | Error (±d) | NSS model (d) | Error (±d) |
|---|---|---|---|---|---|---|---|---|
| Feb 1999 (HOT 102) | >0.7 | 0.09±0.03 | 0.11±0.03 | 0.83±0.27 | 81 | 40 | 20 | 7 |
| Apr 1999 (HOT 104) | >0.7 | 0.15±0.04 | 0.18±0.03 | 0.82±0.22 | 73 | 30 | 20 | 6 |
| May 1999 (HOT 105) | >0.7 | 0.05±0.01 | 0.11±0.01 | 0.46±0.10 | <1 | 1 | <1 | 1 |
| Jul 1999 | TDP | 6.06±0.29 | 7.30±0.82 | 0.83±0.10 | 84 | 18 | 20 | 3 |
| | >1 | 0.04±0.01 | 0.08±0.01 | 0.48±0.10 | <1 | 1 | <1 | 1 |
| Aug 1999 (HOT 107) | TDP | 5.03±0.55 | 3.12±0.48 | 1.61±0.28 | >200 | NA | 52 | 10 |
| | >1 | 0.08±0.02 | 0.19±0.04 | 0.40±0.10 | <1 | 1 | <1 | 1 |
| Oct 1999 (HOT 108) | TDP | 6.14±0.25 | 5.82±1.86 | 1.05±0.16 | >200 | NA | 32 | 6 |
| Nov 1999 (HOT 109) | >1 | 0.07±0.6 | 0.23±0.06 | 0.33±0.30 | <1 | 3 | 7 | 3 |
| Dec 1999 (HOT 110) | TDP | 5.77±1.61 | 6.69±0.35 | 0.86±0.13 | 124 | 21 | 22 | 4 |
| | >0.2 | 0.11±0.05 | 0.35±0.03 | 0.31±0.15 | <1 | 2 | <1 | 2 |
| Feb 2000 (HOT 111) | TDP | 1.15±0.11 | 1.33±0.16 | 0.87±0.12 | 135 | 32 | 22 | 4 |
| | 0.2 to 1 | ND | ND | 0.45±0.13 | <1 | 1 | <1 | 1 |
| | >10 | 0.39±0.05 | 0.52±0.20 | 0.75±0.30 | 37 | 8 | 16 | 6 |
| Early Mar 2000 (HOT 112) | TDP | 0.63±0.21 | 0.54±0.11 | 1.17±0.37 | >200 | NA | 37 | 12 |
| | 0.2–1 | 0.08±0.01 | 0.08±0.00 | 1.06±0.06 | >200 | NA | 32 | 3 |
| | 1–10 | 0.07±0.02 | 0.18±0.06 | 0.42±0.18 | <1 | 4 | <1 | 3 |
| Late Mar 2000 (HOT 113) | TDP | 5.37±0.69 | 5.88±0.69 | 0.91±0.13 | >200 | NA | 25 | 4 |
| | 0.2–1 | 0.64±0.22 | 0.79±0.01 | 0.81±0.14 | 66 | 33 | 19 | 4 |
| | 1–10 | 0.17±0.02 | 0.24±0.01 | 0.68±0.05 | 18 | 4 | 11 | 1 |
| | >10 | ND | ND | 0.55±0.16 | 1 | 1 | 1 | 1 |

* All errors are average; NA, not applicable; ND, no data because no yield recovery.

The lowest activities (0.54–1.13 dpm m$^{-3}$) occurred in samples with low P collection efficiencies and with ML depths >50 m (Table 3; HOT 111 and HOT 112). The $^{33}P/^{32}P$ activity ratio measured in the TDP pool varied from 0.83 (±0.10) to 1.61 (±0.28; Fig. 2). Uncertainties increase with increasing $^{33}P/^{32}P$ activity ratios (i.e., time) because of the larger counting errors at low activities. The activity ratios of $^{33}P/^{32}P$ in TDP were consistently higher than those measured in rain, with the most dramatic difference occurring between the July and August (HOT 107) cruises, when the $^{33}P/^{32}P$ activity ratio in TDP doubled (Fig. 2).

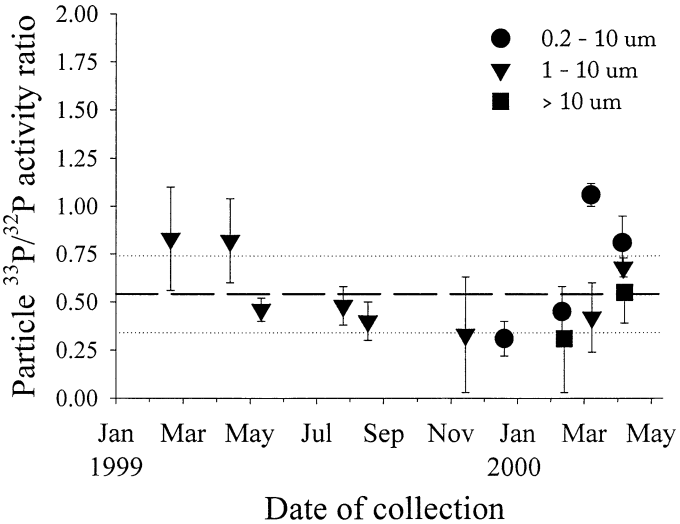



Fig. 1. Particle $^{33}P/^{32}P$ activity ratios. The dashed and dotted lines represent the average $^{33}P/^{32}P$ ratio measured in rain ±1 SD. In February 1999 (HOT 102) and April 1999 (HOT 104), particle samples were collected on GF/F filters.

*P-age models*—There are two simple models of cosmogenic $^{32}P$ and $^{33}P$ that can be used to estimate radioactive P residence times within sampled P pools: a continuous steady-state (SS) model and an age-dependent, or non–steady-state (NSS) model. In the continuous model, the residence time within a particular reservoir is calculated by mass balance, where the input of $^{32}P$ and $^{33}P$ (i.e., via rain) is balanced by various removal mechanisms (i.e., radioactive decay and plankton uptake), such that

$$(^{32}C_{atm})I = (^{32}C_{TDP})\lambda_{32}Z + (^{32}C_{TDP})KZ \quad (1)$$

where $^{32}C_{atm}$ is the concentration of $^{32}P$ (in atoms m$^{-2}$) in the atmosphere, $I$ is the $^{32}P$ (and $^{33}P$) deposition rate (d$^{-1}$), $^{32}C_{TDP}$ is the concentration of $^{32}P$ (in atoms m$^{-3}$) over a specified depth horizon $Z$ (m), $\lambda_{32}$ (= 0.04853 d$^{-1}$) is the radioactive decay rate of $^{32}P$, and K is the uptake rate constant (d$^{-1}$) of $^{32}P$ (and $^{33}P$) by plankton. Multiplying each side of the equation by $\lambda_{32}$ converts concentrations to activities, such that

$$(^{32}P_{atm})I = (^{32}P_{TDP})\lambda_{32}Z + (^{32}P_{TDP})KZ \quad (2)$$

where $^{32}P_{atm}$ is the activity of $^{32}P$ (dpm m$^{-2}$) in the atmosphere and $^{32}P_{TDP}$ is the $^{32}P$ activity (dpm m$^{-3}$) measured in TDP. A similar equation can be written for the PP pool. Using this formulation, the activity ratio of $^{33}P/^{32}P$ in the TDP pool can be written

$$R_{TDP} = R_{atm}\frac{\lambda_{32} + K}{\lambda_{33} + K} \quad (3)$$

Table 3. Mixed-layer depths and P concentration (±SD) and particulate C measured at 5 m. Data presented for July 1999 are from HOT 106. Additional data are available at the HOT website (http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html).

| Sample | Mixed layer* (m) | MAGIC P (nmol kg$^{-1}$) | SRP (nmol kg$^{-1}$) | TDP (nmol kg$^{-1}$) | Particulate C (nmol kg$^{-1}$) |
|---|---|---|---|---|---|
| Feb 1999 (HOT 102) | 102±42† | 53±2 | 100±26† | 250 | 1,860 |
| Apr 1999 (HOT 104) | 128±13 | 70±2 | 135±17 | 350±57† | 1,640 |
| May 1999 (HOT 105) | 36±5 | 44±1 | 90 | 270 | 2,280 |
| Jul 1999 | 62±7 | 74±2 | 117±31 | 320 | 2,460 |
| Aug 1999 (HOT 107) | 50±7 | 40±4 | 70 | 310 | — |
| Oct 1999 (HOT 108) | 79±7 | 62±1 | 90 | 350 | — |
| Nov 1999 (HOT 109) | 72±8 | 34±3 | 48±22 | 290 | 2,060 |
| Dec 1999 (HOT 110) | 89±6 | 65±1 | 113±32 | 390 | 2,100 |
| Feb 2000 (HOT 111) | 88±25 | 48±1 | 110±8.2 | 300±10 | 1,710 |
| Early Mar 2000 (HOT 112) | 56±10 | 86±2 | 112 | 360 | 1,680 |
| Late Mar 2000 (HOT 113) | 71±14 | 44±3 | 100±20 | 260 | 2,470 |

* Defined as Δpotential density ≥0.125 g cm$^{-3}$.
† Standard deviation.

where $R_{TDP}$ and $R_{atm}$ are the $^{33}P/^{32}P$ activity ratios in TDP and in atmospheric deposition, respectively, and $\lambda_{33}$ (= 0.02739 d$^{-1}$) is the radioactive decay constant for $^{33}P$. The radioactive P residence time, $\tau_{res}$, relative to this uptake is shown in Eq. 4.

$$\tau_{res} = \frac{1}{K} \tag{4}$$

Replacing K in Eq. 3 with $1/\tau_{res}$ and solving for $\tau_{res}$ gives Eq. 5.

$$\tau_{res} = \frac{\frac{R_{TDP}}{R_{atm}} - 1}{\lambda_{32} - \lambda_{33}\left(\frac{R_{TDP}}{R_{atm}}\right)} \tag{5}$$

Note that additional removal terms of $^{32}P$ and $^{33}P$ from the TDP pool may be included (such as absorption) in this formulation but will not change the final solution. This model assumes that there is no fractionation of $^{32}P$ and $^{33}P$ between uptake and excretion by marine organisms and that atmospheric input is constant. Theoretical calculations predict that any possible fractionation that occurs is well within the precision (±0.10 dpm dpm$^{-1}$) of our radioisotopic measurement. The greatest uncertainty with the continuous model is that the ratio is constrained between an initial input ratio value and 1.77 ($=\lambda_{32}/\lambda_{33}$) times the initial value (Fig. 3a). Error estimates also increase dramatically as this asymptotic value is approached.

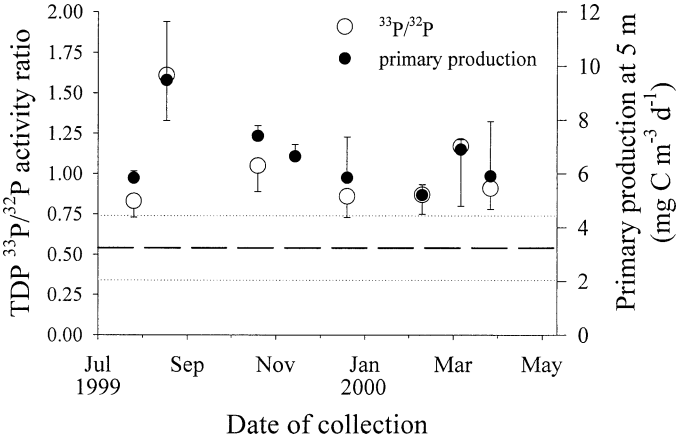



Fig. 2. $^{33}P/^{32}P$ TDP activity ratios. The dashed and dotted lines represent the average $^{33}P/^{32}P$ ratio measured in rain ±1 SD. Primary production rates were determined using in situ $^{14}C$ incubations measured in triplicate at 5 m.

An alternative model assumes NSS P input and an increasing activity ratio of $^{33}P/^{32}P$ through radioactive decay alone.

$$R_{TDP} = R_{atm}\frac{\exp(-\lambda_{33}t)}{\exp(-\lambda_{32}t)} \tag{6}$$

In this scenario, the apparent age of P, $t_{age}$, in the TDP pool is obtained by Eq. 7.

$$t_{age} = \frac{\ln\left(\frac{R_{TDP}}{R_{atm}}\right)}{\lambda_{32} - \lambda_{33}} \tag{7}$$

A unique feature in this model is that there is no constraint on the maximum $^{33}P/^{32}P$ activity ratio. The apparent age model is limited to elucidating radioactive P residence times <100 d because $^{32}P$ and $^{33}P$ activities are below detection at periods greater than 6 half-lives (Fig. 3b).

Using an initial $^{33}P/^{32}P$ activity input ratio of 0.54 ± 0.05 and a continuous uptake model (Eq. 4), the estimated residence time of radioactive P in TDP ranges from 84 ± 18 d to >200 d in most of the cruises ($n$ = 4; Table 2). In many of these cruises, the ratio exceeded the model parameters; that is, ratios exceeded the highest model ratio possible (1.77 × Initial = 0.96). When a NSS model is used (Eq. 6), P ages vary from 20 ± 3 to 52 ± 10 d (Table 2).

The residence times of radioactive P within small particles were typically very short (<1 day) assuming an initial $^{33}P/^{32}P$ activity ratio of 0.54 ± 0.05, regardless of the model used (Table 2). Significantly longer radioactive P residence times (Table 2) were determined for samples collected during March 1999 (>1 μm, HOT 102) and March 2000 (0.2–

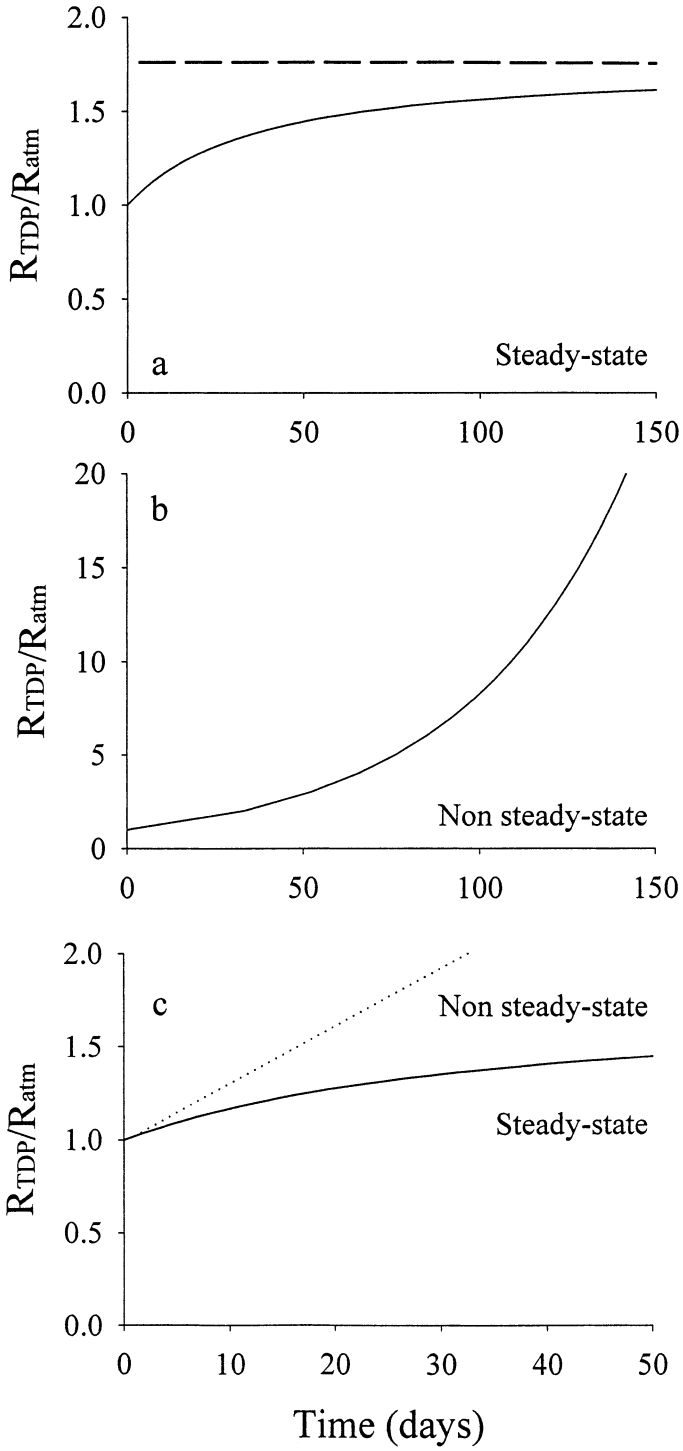



Fig. 3. Expected changes in $^{33}P/^{32}P$ activity ratios based on two different P uptake models versus time. (a) Steady-state P uptake. The dashed line represents 1.77 × $R_{TDP}/R_{atm}$. (b) Non steady-state P uptake. (c) Both models. An initial $R_{TDP}/R_{atm}$ ratio (*see text*) of 1 is arbitrarily chosen for clarity in this presentation.

1 and 1–10 $\mu$m, HOT 113), April 1999 (>1 $\mu$m, HOT 104), and late February 2000 (0.2–1 and 1–10 $\mu$m, HOT 112). Radioactive P residence times also increased with decreasing size class when more than one size fraction was collected (e.g., HOT-111 to HOT-113).

## Discussion

*$^{32}P$ and $^{33}P$ in rain*—One of the primary assumptions necessary for using cosmogenic P radioisotopes in any aquatic system is an estimate of the input $^{33}P/^{32}P$ activity ratio. Lal and Peters (1967) conducted a comprehensive theoretical study on the atmospheric deposition of $^{32}P$ and $^{33}P$ and suggested that the $^{33}P/^{32}P$ activity ratio should be constant. However, observations have found that the input activity ratio in atmospheric deposition varies regionally (Lal et al. 1957; Waser and Bacon 1995; Benitez-Nelson and Buesseler 1999*a*), but not within rain events (Benitez-Nelson and Buesseler, 1999*a*).

The $^{33}P/^{32}P$ activity ratio measured in the NPSG was regionally constant based on precipitation measurements made on the islands of Kauai and Oahu, as well as directly at Sta. ALOHA. Our measured ratios were consistent with those measured in Bombay, India (Lal et al. 1957), and near Vilnius, Lithuania (Luyanus et al. 1970), but lower than those measured in Woods Hole, Massachusetts, Portsmouth, New Hampshire (0.88 ± 0.14), and Bermuda (0.66–1.20) (Waser and Bacon 1995; Benitez-Nelson and Buesseler 1999*a*). Lower $^{33}P/^{32}P$ ratios imply shorter residence times of atmospheric aerosols. When using a continuous input model (Benitez-Nelson and Buesseler 1999*a*) with an assumed $^{33}P/^{32}P$ production ratio of 0.46 (Lal and Peters 1967), an aerosol residence time of <10 d is calculated. The generally lower $^{33}P/^{32}P$ activity ratios measured in atmospheric deposition in this study are consistent with lower tropospheric scavenging associated with intermittent rain events and rapid aerosol transport from Asia (Uematsu et al. 1985).

*$^{32}P$ and $^{33}P$ in particles*—$^{32}P$ and $^{33}P$ particle activities were similar to values measured in the Gulf of Maine and in the Sargasso Sea and had low $^{33}P/^{32}P$ ratios that were indistinguishable from rain measurements (Waser et al. 1996; Benitez-Nelson and Buesseler 1999*b*). Radioactive PP residence times were often <1 d, regardless of the model used, and these rates were similar to results in seawater near Bermuda and in the Gulf of Maine (Fig. 1; Waser et al. 1996; Benitez-Nelson and Buesseler 1999*b*). Short radioactive P residence times within particles imply rapid removal from the water column on the order of 10 m $d^{-1}$ for a 10-m water column depth.

Our low radioactive PP residence time estimates may be related to the method by which the particles were sampled. The majority of particles collected in this study were of just one class defined by a nominal pore size (i.e., ≥1 $\mu$m). We think the P activities and the $^{33}P/^{32}P$ activity ratios measured in these samples reflects the capture of the larger high-activity, but lower ratio particles. Collection of these larger particles would effectively mask the radioactive P signal derived from the higher ratio, low-activity particles.

There are two lines of evidence that support the idea that large particles with high $^{32}P$ and $^{33}P$ activities dominate the estimated radioactive PP residence time. First, in those sampling periods with short radioactive PP residence times (July,

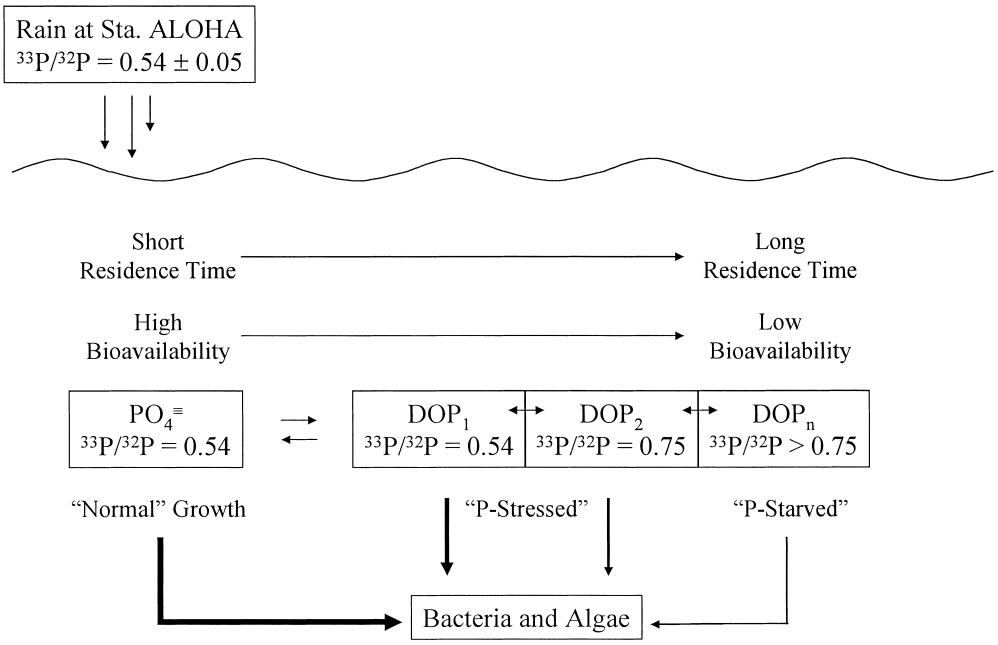



Fig. 4. Conceptual cosmogenic P metabolism model. In this scenario, $DOP_1$ might be considered to be nucleotides, $DOP_2$ monophosphate esters, and $DOP_n$ an assortment of less bioavailable compounds, such as phosphonates or high–molecular weight polymers. $^{33}P/^{32}P$ activity ratios shown for $DOP_2$ and $DOP_n$ were arbitrarily chosen for clarity in this presentation.

August, November, and December), contemporaneous $^{234}Th$ measurements indicated a large export of particles (Benitez-Nelson et al. 2001). Second, the smaller particles ($<1$ $\mu$m) tended to be significantly older than the larger ones. This reflects differences in sinking speeds, as well as mechanisms of formation, and the inclusion of suspended refractory particles.

*$^{32}P$ and $^{33}P$ in TDP*—The $^{32}P$ and $^{33}P$ activities measured in the NPSG are slightly higher than, but comparable to, those measured previously in the Gulf of Maine and off the coast of Southern California (Lal and Lee 1988; Lee et al. 1991, 1992; Benitez-Nelson and Buesseler 1999*b*). Previous research using $^{32}P$ and $^{33}P$ natural abundance detected a steep decreasing gradient in activities in the water column, and this heterogeneity was evident even when the water column was well mixed (i.e., uniform temperature and salinity; Lal and Lee 1988; Lee et al. 1991; Benitez-Nelson and Buesseler 1999*b*). Given the lack of depth information in this study and the surface input of these isotopes, we think our results are only applicable to the upper 10 m of the water column.

The $^{33}P/^{32}P$ activity ratios in TDP varied with the most dramatic change occurring in August 1999. In theory, the observed variation in the TDP $^{33}P/^{32}P$ activity ratio may be due to rainfall cessation or dilution by deep water with a high $^{33}P/^{32}P$ ratio. There is no direct evidence that either process has occurred. Advection of deep waters to the surface would entrain other nutrients and affect the profiles of temperature and salinity. No such trends are apparent. The second scenario of rainfall cessation is also highly unlikely. First and foremost, if rainfall ceased, then the $^{33}P/^{32}P$ activity ratios measured in particles would also increase. However, the particles always had low $^{33}P/^{32}P$ activity ratios, similar to those found in rain. Even if we assume that there was no additional atmospheric input of $^{32}P$ and $^{33}P$ into the NPSG between July and August (HOT 107), the estimated $^{33}P/^{32}P$ activity ratio of TDP does not account for the observed P activities or activity ratio. There was a period of 21 d between the two cruises. If the observed $^{32}P$ and $^{33}P$ activities at the start of this period simply decayed over time, we would have observed an increase in the $^{33}P/^{32}P$ ratio from 0.83 to 1.26, compared to the measured ratio of $1.61 \pm 0.28$. We would further expect total $^{32}P$ and $^{33}P$ activities to decrease because of radioactive decay alone; however, both $^{32}P$ and $^{33}P$ activities measured in August are higher than during the antecedent sampling periods (e.g., August $^{33}P$ activity is 5.0 dpm $L^{-1}$ vs. the expected $^{33}P$ activity of 3.3 dpm $L^{-1}$ for decay alone).

The high variability in radioactive TDP residence times (Table 2) suggests dynamic utilization of P over weekly to monthly timescales. These radioactive P residence time estimates are much shorter than expected in the NPSG based on stable-P mass balance estimates that are on the order of several years (e.g., Karl and Yanagi 1997). The large variation precludes the use of a SS model for radioactive P residence time estimation in the NPSG. Therefore, the remainder of this discussion will focus on NSS behavior and controls on discontinuous P pool dynamics.

TDP apparent ages strongly correlate with $^{14}C$-derived primary productivity rates, with ages increasing with increased primary production (Fig. 2). Thus, when C fixation is high, the low $^{33}P/^{32}P$ BAP pool is preferentially removed, leaving the older (high $^{33}P/^{32}P$), less labile material behind. In fact, the ratio of SRP to the SNP pool is 29%, the lowest fraction

measured when comparable TDP $^{33}P/^{32}P$ activity ratios were made (average ~48%; Table 3). If low $^{33}P/^{32}P$-containing components of the dissolved pool are preferentially removed via biological uptake, then one would predict that the particle $^{33}P/^{32}P$ activity ratios and resulting radioactive P residence times would be consistently lower than those remaining in the dissolved phase (Fig. 1). This is indeed the case.

*Significance*—Although restricted to the near-surface ocean in this study, our results indicate that natural P radioisotopes provide novel tools for studying the in situ variability of P utilization in aquatic ecosystems. Our results suggest that cosmogenic P isotopes track the BAP pool in both PP and dissolved phases. Furthermore, the BAP pool may vary significantly on relatively short time scales (week to month) because of preferential uptake by plankton during periods of high productivity. Finally, our results indicate that the residence time of radioactive P, within specific particle size classes, is a function of both removal by gravitational settling and the ability of selected plankton to utilize less available pools of P.

Our present understanding of the pathways of P utilization within the marine ecosystem is limited. SRP is typically dominated by orthophosphate and as such sets a lower constraint on BAP. It is also believed that orthophosphate is the preferred substrate for microbial metabolism. SNP greatly exceeds SRP by a factor of 3.3 during the course of this study and, under certain conditions, apparently can be efficiently utilized by selected microorganisms. Only a modest fraction of the SNP pool would need to be assimilated to affect the cycling of P in the NPSG significantly. Other estimates of the BAP pool suggest that, at Sta. ALOHA, it may be as much as two times the SRP pool (Karl and Bossard 1985; Björkman et al. 2000). The metabolic and ecological controls on TDP pool bioavailability are not well understood but involve the degree of P stress, trace element coavailability, and other ecosystem processes. The late summer periods at Sta. ALOHA are known to sustain enhanced $N_2$ fixation (Karl et al. 1997). This would tend to select for organisms or unique microbes capable of utilizing otherwise nonavailable DOP substrates via alternative P acquisition pathways (Fig. 4). Consequently, the regulation of nutrient acquisition will have a direct effect on P biodynamics, including the inventories and relative ratios of the cosmogenic P radionuclides as described herein. Such processes would have an even larger effect in marine environments such as the Sargasso Sea, where SRP concentrations are $<1$ nM, but TDP concentrations are several orders of magnitude greater (Wu et al. 2000; Cavender-Bares et al. 2001).

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