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The biogeochemical cycling of phosphorus in marine systems

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Abstract

The cycling of phosphorus (P) in the ocean has long been viewed from a geological perspective that tends to focus on balancing P sources (riverine and atmospheric) and sinks (sedimentary burial) over long (> 1000 years) time scales. There have been substantially fewer treatises, however, that have sought to review current understanding of the processes which effect the distribution of P between these two endpoints. In this paper, a comprehensive review of the biogeochemical cycling of P within the oceans is given, with particular attention focused on the composition and recycling rates of P within the water column.

Keywords: phosphorus; nutrient cycling; marine ecosystems; turnover rates; biogeochemical cycling

1. Introduction

Phosphorus (P) is an essential nutrient utilized by all organisms for energy transport and growth. Yet, little is known about the role P plays in the production and distribution of plankton in the world's ocean. One of the major reasons for this relative lack of understanding is the dominant, but slowly changing view that P only limits production over geologically long time scales in marine systems (> 1000 years, Hecky and Kilham, 1988; Codispoti, 1989). The theory behind this P limitation is relatively simple. Over prolonged time scales, phytoplankton N requirements can be met through the process of N_2-fixation (McCarthy and Carpenter, 1983; Tyrell, 1999). This hypothesis assumes that the standing stock of N_2-fixing organisms will increase as the N:P ratio in the ocean decreases. Since the reservoir of N_2 in the atmosphere is so large, N_2-fixing organisms would eventually be limited by other nutrients. Given the long residence time of P in the ocean compared to other potentially bio-limiting nutrients and trace elements, such as silica and iron, P is often regarded as the 'ultimate' limiting nutrient over long time scales (Redfield, 1958; Van Cappellen and Ingall, 1994, 1996; Tyrell, 1999).

Unfortunately, this common perception has resulted in the study of P to be focused on the identification and balance of oceanic P sources and sinks (Froelich et al., 1982; Ruttenburg, 1993; Howarth et al., 1995; Follmi, 1996; Delaney, 1998). The intermediate steps, i.e. the transformation processes of P

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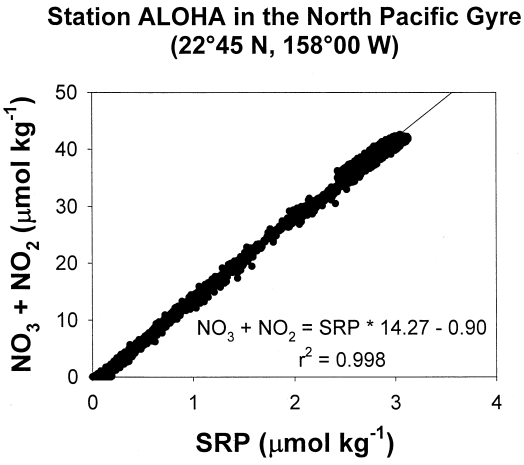

Fig. 1. Inorganic N versus SRP at Station ALOHA (22°45N, 158°00W) in the North Pacific Gyre. Note that inorganic N reaches zero prior to SRP. Data compiled from the JGOFS Hawaiian Ocean Time-series (HOT) Program (Karl et al., 1999).

within the water column, have been relatively ignored. The idea that P is unimportant in limiting marine phytoplankton growth over short time scales stems from the work of Redfield et al. (1963). In their study, Redfield et al. (1963) noted that the ratio of C:N:P within particulate organic matter is ubiquitous at 106:16:1. Hence, they hypothesized that phytoplankton required these elements in the above ratios for balanced growth. Since then, the Redfield ratio has been used to evaluate nutrient limitation in various oceanic regimes (Ryther and Dunstan, 1971; Boynton et al., 1982; Downing, 1997). Global oceanic surveys of dissolved inorganic nutrients (GEOSECS, TTO) discovered that when plotting inorganic N versus inorganic P, N concentrations tended to decrease to zero first, leaving a small, but detectable residual P concentration (e.g. Fig. 1). These results led others to suggest that over short time scales, N was the most important nutrient in limiting phytoplankton growth in the open ocean (Thomas, 1966; Ryther and Dunstan, 1971; Goldman et al., 1979; Codispoti, 1989).

Unfortunately, this presumption of a single limiting nutrient, i.e. N, has many inherent weaknesses. Perhaps the most obvious is related to the plots of inorganic N and P concentrations, which completely ignores the potential role of organic nutrients and trace metals in plankton production. Although inorganic N and P are the most readily available forms of nutrients to plankton, several studies have shown that organic nutrients can be utilized by phytoplankton as well (Chu, 1946; Kuentzler, 1965; Cembella et al., 1984a; Berman et al., 1991; Van Boekel, 1991; Bronk et al., 1994). Jackson and Williams (1985) plotted total dissolved P (TDP) versus total dissolved N (TDN) in the North Pacific and found that TDP is exhausted just prior to TDN (e.g. Fig. 2). They suggested, using the above assumptions, that P may limit phytoplankton production. However, this could only be inferred as neither nutrient actually decreases to zero concentrations. Nonetheless, that the nutrient depleted surface waters have a TDN to TDP ratio similar to that of Redfield, implies that both DOP and DON are important sources of N and P in the upper water column. Since then, evidence that P, rather than N, may limit community production has been found in regimes ranging from restricted (Smith and Atkinson, 1984; Granéli et al., 1990; Krom et al., 1991) and shallow-marine areas (Fourqurean et al., 1992; MacRae et al., 1994) to the open ocean, oligotrophic sites of the North Atlantic and North Pacific (Cotner et al., 1997; Karl et al., 1997).

Another discrepancy that is often overlooked when discussing nutrient limitation is the difference between standing stocks of specific nutrients and the

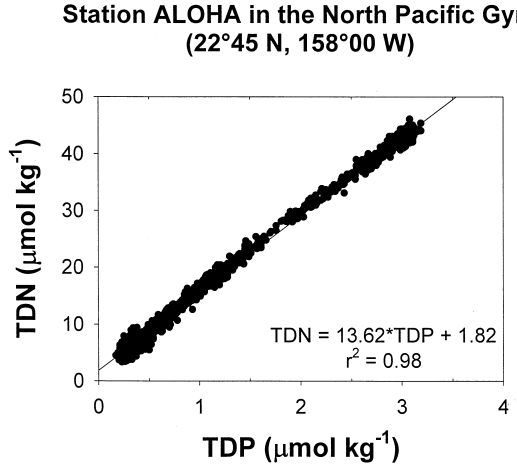

Fig. 2. Total dissolved N (TDN) versus TDP at Station ALOHA. Note that TDP reaches zero prior to TDP. Data compiled from the JGOFS HOT Program (Karl et al.,1993, 1999).

flux of nutrients between various dissolved and particulate pools. Depending on the pool size, nutrients which have long turnover times suggest either a lack of bioavailability or need. Short turnover times, on the other hand, suggest that a particular nutrient is both bioavailable and necessary for growth and production. This information, coupled with new molecular methods for evaluating the in situ nutrient status of plankton can provide important insight into the controls of nutrient limitation (Scanlan and Wilson, 1999). Regardless, measuring the concentration of a nutrient alone, does not provide any insight into these processes.

In recent years, the debate of N versus P limitation has also come to include the role of trace elements, such as iron, and other nutrients, such as silica (Howarth et al., 1988a,b; Martin et al., 1994; Hutchins and Bruland, 1998; Dugdale and Wilkerson, 1998; Cavender-Bares et al., 1998). Many studies have shown the potential growth limiting effects of these other elements in various environments. In fact, Fe may limit the rate of N_2-fixation and the growth of N_2-fixing organisms (Falkowski, 1997; Karl et al., 1997). If true, this would have long standing implications for the 'ultimate' control of phytoplankton growth over long time scales.

Nonetheless, understanding the water column biogeochemical cycling of all nutrients and trace metals is essential for elucidating the current and future effects of both natural and anthropogenically induced changes in nutrient composition on the plankton productivity and speciation of the world's oceans. Areas which would most likely suffer the greatest impact of man's activities are along the cost, simply due to its proximity to the Earth's major population centers. A recent controversial study by Tyrell (1999) suggests that because P limits production over long time scales, it is not necessary to restrict the inputs of other nutrients, such as N, into coastal ecosystems. This view is too simplistic and does not take into account the wide variety of organisms with different strengths and weaknesses that exist in the marine realm. In fact, increased and/or changing nutrient input ratios have been clearly shown to reduce food web diversity, alter phytoplankton composition and even increase in the intensity and frequency of toxic dinoflagellate blooms, or red tides (e.g., Nixon, 1993).

The open ocean is also not immune from man's activities due to large-scale atmospheric transport and deposition of anthropogenic emissions. For example, inorganic N and P surface ocean concentrations were examined in detail by Fanning (1989). He found that inorganic N concentrations were below detection (< 0.2 to 0.37 μM) and inorganic P at or above detection (> 0.015 μM) in most areas of the world's oceans. However, he also found that the reverse circumstance occurred in surface waters of the North Pacific and North Atlantic, areas downwind of the most populated and urbanized regions of eastern Asia and North America. Paerl (1993) has further confirmed the potentially large source of N to marine environments via acid rain. More recently, Migon and Sandroni (1999) determined that atmospheric anthropogenic P inputs slightly increased the annual new production within the western Mediterranean basin. Given that N has a much larger natural and anthropogenic atmospheric source than P, an increase in inputs could lead to phosphorus limitation of surface waters over time (Fanning, 1989; Paerl, 1993; Carpenter and Romans, 1991; Karl et al., 1997). In this study, a much needed review of the oceanic P cycle is given. Special consideration is given to the processes that effect the distribution and cycling of P *within* the upper ocean. Only brief synopses of P sources and sinks are discussed.

2. The history of phosphorus

P is the eleventh most abundant element in the Earth's crust. It was first discovered in 1669 by the German alchemist, Hennig Brand, who noted that a white solid could be obtained that not only glowed in the dark, but also spontaneously ignited in air. Hence, its name P, literally means 'light bearing' and is derived from the Greek words 'Phos' (light) and 'Phorus' (bearing). The importance of P as a nutrient was not realized until the mid-1800s. Shortly thereafter, a technique was developed for the production and introduction of P as a soluble fertilizer to soils; via phosphorite dissolution by H_2SO_4, a method still utilized today (Follmi, 1996). As a result, the search for phosphorites intensifed dramatically and deposits have been found all over the world, from Algeria to

the United States (Cook et al., 1990; Follmi, 1996). In the marine realm, the first recovery of a phosphorite deposit occurred during the famous *H. M. S. Challenger* expedition (1873–1876). Since then, marine phosphorites have been found throughout the seafloor and their past and present mechanisms of formation have been intensely studied (e.g. Follmi, 1996)

Interestingly, it was not until the early 1900s that the role of P in the transfer of energy was realized. The discovery of adenosine triphosphate (ATP) in the 1930s and 1940s revolutionized the understanding of cellular energy metabolism (e.g. Corbridge, 1990). By 1940, it had been well established that phosphate esters are key components of cells. The identification of the molecular structure of DNA by Watson and Crick in 1953 firmly established the importance of P in the growth and development of all organisms. Over the last few decades, enormous research in the field of biochemistry has continued to demonstrate the importance of P in a wide variety of metabolic processes (e.g. Bridger and Henderson, 1983; Lehninger et al., 1993).

3. Oceanic P sources and sinks

3.1. Sources

3.1.1. Riverine

Phosphorus enters the oceans predominantly through rivers (Fig. 3). Continental weathering of crustal materials, which contain on average 0.1% P_2O_4, is the major source of riverine P. It is difficult to determine the natural riverine flux of P due to the temporal variability in riverine water mass fluxes and anthropogenic effects due to deforestation and the use of fertilizers. Attempts to estimate these inputs have been mostly based on water flux and concentration measurements from areas which have been *relatively* unaffected by man's activities, and include such rivers as the Ob, Congo, and Amazon

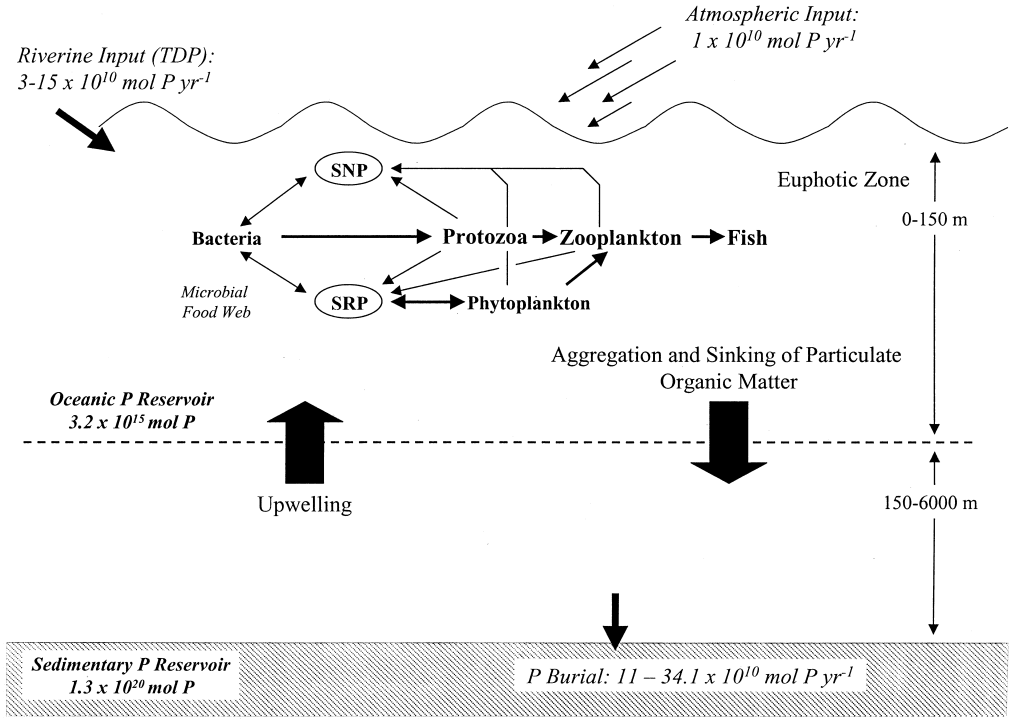

Fig. 3. The pre-anthropogenic marine P cycle. See text for details on fluxes.

(e.g. Judson, 1968; Gregor, 1970; Meybeck, 1982). Froelich et al. (1982) used annual denudation rates determined from sodium mass balances and undisturbed river systems to estimate a maximum input of total P to the oceans of close to 3.3×10^{11} mol P yr^{-1}. Howarth et al. (1995) found a marginally lower input of total phosphorus of 2.6×10^{11} mol P yr^{-1}, based on riverine flux estimates from over 2500 years ago. If one were to include man's activities, such as deforestation and the use of fertilizers, the total P flux increases by over a factor of three, to $7.4–15.6 \times 10^{11}$ mol P yr^{-1} (Froelich et al., 1982; Howarth et al., 1995).

The above estimate is the maximum amount of total P that could enter the marine realm. The majority of the total P riverine input is in the particulate phase. Most of these particles are removed rapidly in the nearshore via sedimentation. Hence, most of the riverine derived P which enters the oceanic cycle is in the dissolved phase. The pre-anthropogenic flux of total dissolved P (TDP) that enters the ocean is hypothesized to range from 3 to 15×10^{10} mol P yr^{-1} (Froelich et al., 1982; Ruttenberg, 1993; Howarth et al., 1995; Delaney, 1998). However, estimating the dissolved component has been difficult. The concentration of dissolved P can be substantially modified as: (1) a result of adsorption/desorption on to and off of particle surfaces, (2) biological uptake and remineralization, and (3) dissolution of particulate P via redox reactions (Froelich et al., 1982; Howarth et al., 1995). In fact, biological and chemical processes on particulate matter could increase the flux of dissolved P by as much as a factor of five higher than the estimate given above (Fox et al., 1986; Berner and Rao, 1994). Most published values of TDP inputs, however, are not based on direct measurement. Rather, inorganic P is measured, and a poorly defined ratio of inorganic P to TDP (range 0.2 to 0.7, avg. $\sim$ 0.4; Froelich et al., 1982; Meybeck, 1982) is applied to estimate a global TDP input. Furthermore, it should be mentioned that the samples used to determine this ratio may or may not have been filtered. Unfiltered samples may overestimate TDP, and hence the TDP derived riverine input (Meybeck, 1982).

Unfortunately, estimates of the river flux of P will continue to be poor because of the addition of anthropogenic sources. There is currently no other way to determine pre-agricultural riverine water mass fluxes and P concentrations other than by direct measurement. As stated previously, several estimates have found that man's activities have increased the riverine flux of P by a factor of three. Some of the more heavily impacted rivers have 10–100 times the P concentration of pre-agricultural levels (Meybeck, 1982; Howarth et al., 1995).

3.1.2. Atmospheric

The atmospheric delivery of P to the ocean has been studied to an even lesser extent than that of the riverine flux. By far the most cited studies for the global marine deposition of P stems from the research conducted by Graham and Duce in the late 1970s and early 1980s (Graham and Duce 1979, 1981, 1982). Although limited, their findings suggest a number of important features regarding the magnitude (estimated to be 4.5×10^{10} mol P yr^{-1}) and composition of global aeolian P deposition. Compositional analysis of aerosols was conducted on marine air hypothesized to not have been impacted to a large degree by anthropogenic sources (samples taken from Hawaiian and Samoan islands). Reactive phosphorus (that fraction soluble in distilled water and comprised predominantly of orthophosphate) was 25–30% of the total P measured. This fraction was also highly correlated with aluminum, indicating a crustal (Asian dust) origin. An additional 25–30% of the total P was acid-soluble in 1 N HCl and highly correlated with sodium, indicating a marine source. It was suggested that this fraction was most likely comprised of P compounds commonly found in marine bacteria and they hypothesized that a large portion was polyphosphates. The remaining P fraction was soluble only after high temperature oxidation ($\sim$ 500°C), indicating highly condensed polyphosphates and/or organic material. Interestingly, this fraction showed no correlation with either sodium or aluminum. In general, it is expected that the solubility of P found in aerosols will depend on the source, size of particle, sea surface meteorological conditions and biology. For example, Lepple (1971) determined that only 8% of P in Saharan dust particles was soluble in seawater, significantly less than the average $36 \pm 15\%$ found by Graham and Duce (1982) in bulk aerosol samples collected at Narragansett, RI.

The studies conducted by Graham and Duce provided the necessary groundwork for increasing the understanding of P atmospheric deposition. However, more research still needs to be done. For example, although the data of Graham and Duce was compiled from a series of samples taken over a several year period from the Pacific and Atlantic oceans, most sampling occurred over discrete time intervals often lasting less than 3–4 months. Sampling in the North Pacific also did not include the peak in Asian dust, which typically occurs during the spring. It has been found that most (> 80%) of the mineral dust input from Asia to the North Pacific occurs in several bursts lasting just 3–5 days and varies interannually (Parrington et al., 1983; Uematsu et al., 1983; 1985). Thus, the Graham and Duce estimates could greatly underestimate total P deposition (Duce, 1986).

Assuming 22% of the P found in aerosols is soluble in seawater, approximately 1×10^{10} mol P yr^{-1} is atmospherically derived. This is equivalent to 6–33% of the pre-anthropogenic TDP input from rivers. Other estimates of atmospheric P deposition have been made using geochemical tracers of continental crust (Chadwick et al., 1999) and deep sea records of eolian deposition (Rea, 1994). In general, these estimates tend to be lower, ranging from 0.2 to 1.4×10^{10} mol P yr^{-1}, when applied globally. Differences are most likely the result of the time scales over which the measurements are integrated (i.e. several months for the direct measurements of Graham and Duce (1979, 1981, 1982) versus several thousand years from the Rea (1994) and Chadwick et al. (1999) estimates).

Regardless of the absolute magnitude, the relative importance of atmospheric P deposition is expected to be substantially higher with increasing distance from shore, such that in the oligiotrophic regions of the world's oceans, it may be a significant source of P to the upper ocean. The atmospheric flux of P, when averaged annually, accounts for less than 1% of the new production in either the North Atlantic or North Pacific Oceans (e.g. Duce, 1986). However, short bursts in atmospheric P fluxes (four to eight times higher than average), particularly in the spring, could substantially elevate biological productivity over brief periods (Duce, 1986). For example, discrete pulses of P to oligotrophic, P-limited systems such as the Mediterranean, have been found to increase plankton biomass and carbon export over short time-scales (Migon and Sandroni, 1999). It should also be noted that the above estimates of atmospheric P deposition are based only on that fraction of P that is soluble in distilled water within a 12-h period. A larger fraction may be soluble in seawater. Furthermore, marine bacteria have the ability to hydrolyze specific organic compounds that are not necessarily otherwise soluble (e.g. Cho and Azam, 1988). Thus, atmospheric P deposition could be underestimated by as much as 50%, by neglecting the acid soluble and high temperature soluble P fractions.

3.1.3. Volcanic

There have been very few studies that specifically examine volcanic activity as a potential source of P to marine ecosystems (Yamagata et al., 1991; Resing, 1997). It is likely that these emissions would be more local in nature and thus, only have an impact over limited temporal and spatial scales, depending on the magnitude and length of eruption. Yamagata et al. (1991) used laboratory experiments to simulate condensation from high-temperature (> 1000°C) volcanic gasses. Their studies showed that the gas, P_4O_{10}, produced via volatization of basalt, condensed to form water-soluble polyphosphates (predominantly as PO_4) upon rapid cooling. Phosphate concentrations within these volcanic gas condensates (collected from Mount Usu, Hokkaido, Japan) were high, and ranged from 6–9 μM.

More recently, Resing (1997) studied the marine geochemistry at the ocean entry point of lava from the Pu'u O'o vent of Kilauea Volcano on the Big Island of Hawai'i. Included in this study was the measurement of reactive P (PO_4) in the steam plume created by the lava entering seawater. Four steam plume samples (~ 1 l in volume over 1 m^2 of area) were taken over several minutes in March and January 1995, and had phosphate concentrations which ranged from 21 to 36 μM. A simple calculation demonstrates the potential importance of the steam plume to local P deposition. Assuming that 30 μmol m^{-2} of P is produced every 10 min and that this remains constant over time, this would be equivalent to an annual production of 0.6 mol of P m^{-2}, over 5000 times greater than the total P deposition per m^2

of area measured by Graham and Duce (1979) on the Hawaiian and Somoan Islands in 1975 and 1976. It should also be noted that at the time of the Graham and Duce measurements, Kilauea volcano was *inactive*, thus no lava flows or gas production were occurring. The latest eruption of Kilauea volcano has been ongoing since 1983.

Care must be taken with the above calculation, however, as it is still a very local point source of P to the marine environment. With increasing distance from the volcano, it is highly likely that the concentration of P within the plume will decrease dramatically, such that its impact on a global scale is minor. Nonetheless, the regional importance to upper ocean P deposition from the Kilauea Volcano plume could be quite dramatic over spatial scales as large as 1000 km away (based on unpublished satellite imagery, J. Porter).

3.2. Sinks

The removal mechanisms of P from marine systems have been recently reviewed in detail by Delaney (1998) and Follmi (1996). Thus, only a brief description of these processes will be given here. As P has no stable gaseous form, its only removal from the world's oceans is through sedimentary burial. However, this process is inefficient, and less than 1% of the P which reaches the seafloor is ultimately trapped in sediments and removed from the marine P cycle. The development of sequential extraction techniques has enabled closer examination of the dominant pathways of P removal from the oceans (Ruttenberg, 1992; Berner et al., 1993). There are essentially four processes which have been identified as important removal mechanisms of P from the water column: (1) organic matter burial, (2) P sorption and precipitation with clays, and iron oxyhydroxide particles, (3) phosphorite burial, and (4) hydrothermal processes (Froelich et al., 1982; Mach et al., 1987; Howarth et al., 1995; Follmi, 1996; Delaney, 1998).

3.2.1. Organic matter burial

By far the largest transport of P from the upper water column to sediments is through biological uptake and incorporation into sinking particulate organic matter. Jahnke (1996) estimated that the total flux of organic carbon to the seafloor (>1000 m) is 3.3×10^{13} mol C yr^{-1} and is distributed almost equally between coastal margins and gyres. Using the Redfield et al. (1963) molar ratio of P:C of 1:106, or the recently upwardly revised ratio of Anderson and Sarmiento (1994) of $1{:}117\pm14$, gives a sedimentary flux of P of approximately $2.8–3.1\times10^{11}$ mol P yr^{-1}. In order to estimate the burial of P, one must know the ratio of P to C of buried sedimentary matter. This information is difficult to obtain. Depending on the study, the ratio of P:C in marine sediments has been found to remain constant, become elevated over that found in Redfield et al. (1963) (Froelich et al., 1982; Mach et al., 1987), or vary with organic carbon content, depth and sedimentation rate (Reimers, 1982; Ingall and Van Cappellen, 1990; Burdige, 1991; Reimers et al., 1996). Even with all of these potential difficulties in elucidating the P:C ratio and in determining organic C burial, most estimates range from 1.1 to 2.0×10^{10} mol P yr^{-1}, less than 10% of that which reaches the seafloor (Froelich et al., 1982; Mach et al., 1987; Delaney, 1998). Differences between calculations depend on either the amount chosen for organic C export or the ratio of P:C utilized. One value does stand higher than the rest, that of Ruttenberg (1993), who determined an organic P burial flux of 4.1×10^{10} mol P yr^{-1}. This higher estimate is the result of using suspended matter fluxes to continental and pelagic realms and P:C ratios found from three distinct sites (Long Island Sound, Mississippi Delta, Equatorial Atlantic), rather than global organic C export rate estimates.

3.2.2. P sorption and iron coprecipitation

Until recently, a major sedimentary sink of P was thought to be via incorporation into the matrix of $CaCO_3$ shells. Froelich et al. (1982) measured the P concentration in sediments containing greater than 90% $CaCO^3$. Using an average P concentration of 300 ± 80 ppm and an estimated $CaCO^3$ burial flux of 1.4 a 10^{13} mol $CaCO_3$ yr^{-1}, Froelich et al. (1982) determined that $CaCO_3$–P burial was 1.45×10^{10} mol P yr^{-1}, almost 50% of that buried with organic matter. However, the advent of better cleaning techniques of foraminiferal calcite shells, has since re-

duced the concentration of P associated with $CaCO_3$ to levels less than 10% of that found previously (Palmer, 1985; Sherwood et al., 1993). Rather than being incorporated into the $CaCO_3$ matrix, it appears that P is adsorbed onto the surface of shells via iron oxyhydroxide coatings. Recent estimates have revised the importance of the oxyhydroxide P sink upwards to $4.0–5.3 \times 10^{10}$ mol P yr^{-1} by including coastal (deltaic) environments, a region not considered in previous P mass balance estimates (Ruttenburg, 1993; Howarth et al., 1995).

It appears that much of the oxyhydroxide P adsorption occurs within sediments and is related to particle type, size, and organic matter concentration (Howarth et al., 1995; Delaney, 1998). Sedimentary redox reactions, however, may make P associated with oxyhydroxide removal only temporary. Based on Ocean Drilling Project cores taken in the equatorial Pacific and equatorial Atlantic, Delaney (1998) estimated that up to 40% of the total P burial was associated with oxyhydroxide or loosely sorbed P in sediments younger than 5 Ma. However, in older sediments, only 5–15% of the total P burial was associated with this sink. A large percentage of the remaining P fraction may have undergone a "sink switch" and been buried only after conversion into authigenic apatite mineral phases (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1994, 1996; Slomp et al., 1996; Delaney, 1998).

3.2.3. Phosphorite burial

The burial of phosphorites has long been recognized as an important removal pathway of P from the oceans (e.g. Tribble et al., 1995). However, its magnitude remains one of the most uncertain of all of the potential removal mechanisms for P. As stated earlier, $>90\%$ of the particulate P which reaches the seafloor is remineralized and released into sedimentary pore waters. A percentage of the released P is subsequently precipitated to form authigenic apatite, most often in the form of carbonate fluoroapatite (CFA). The controls of CFA formation are unclear but have been hypothesized to include microbial activity, redox conditions, and pH (e.g. Follmi, 1996). In the past, authigenic P formation had been considered important only in specific environments, such as in coastal upwelling regions, and during certain periods of the geologic past (Jahnke et al., 1983; Schuffert et al., 1998). However, recent evidence has found authigenic P formation in coastal, non-upwelling regimes, as well as deep within open ocean sediments cores (Ruttenberg and Berner, 1993; Reimers et al., 1996; Filippelli and Delaney, 1994, 1996; Slomp et al., 1996). The expanding number of identified apatite deposits has greatly increased the relative importance of this sink. Phosphorite burial estimates have risen from a low of $<0.4 \times 10^{10}$ mol P yr^{-1} by Froelich et al. (1982) in the early 1980s to over 20 times higher, $>8 \times 10^{10}$ mol P yr^{-1}, in the mid-1990s (Ruttenberg, 1993; Filippelli and Delaney, 1996). If these estimates are correct, then phosphorite burial is the major removal pathway of P from the oceans.

3.2.4. Hydrothermal processes

Froelich et al. (1982) hypothesized that hydrothermal activity was a net sink rather than a net source for P to the ocean. Hydrothermal vent fluid contains a large fraction of reduced iron that can quickly oxidize to form ferric oxyhydroxides in seawater. As stated previously, these oxyhydroxides are efficient in scavenging dissolved P and thus, sedimentation of this material may comprise a P sink of close to 0.4×10^{10} mol P yr^{-1} (Froelich et al., 1982). More recently, Wheat et al. (1996) examined the removal of P via both low and high temperature hydrothermal processes, and determined that the majority of removal was associated with low temperature mechanisms. Wheat et al.'s (1996) estimates of 0.65×10^{10} mol P yr^{-1} includes secondary formation of iron hydroxides and apatites, and is only slightly higher than the previous estimates of Froelich et al. (1982).

3.3. Residence times

Estimates of the oceanic residence time of P in the ocean are steadily decreasing as more information regarding P burial rates comes to light. The global marine inventory of dissolved P is close to 3.2×10^{15} mol P. The residence time of P relative to the known P sources discussed above ranges from 20,000 to 80,000 years (Table 1). The residence time of P based on known P sinks has decreased from a high of 80,000 years to less than 10,000 years as the

Table 1
Pre-anthropogenic marine P sources and sinks

SOURCES		
Riverine	TDP: $3–15 \times 10^{10}$ mol P yr^{-1}	Froelich et al., 1982; Howarth et al., 1995; Delaney, 1998
Atmospheric	Soluble reactive P: 1×10^{10} mol P yr^{-1}	Graham and Duce, 1979, 1981, 1982
Volcanic	Unknown, but most likely of only regional impact.	Yamagata et al., 1991; Resing, 1997
Total	$4–16 \times 10^{10}$ mol P yr^{-1}	
SINKS		
Organic matter burial	$1.1–4.1 \times 10^{10}$ mol P yr^{-1}	Froelich et al., 1982; Mach et al., 1987; Ruttenberg, 1993; Delaney, 1998
Precipitation with oxyhydroxides and clay adsorption	$1.45–5.3 \times 10^{10}$ mol P yr^{-1}	Froelich et al., 1982; Ruttenberg, 1993; Howarth et al., 1995
Phosphorite Burial	$> 8 \times 10^{10}$ mol P yr^{-1}	Ruttenberg, 1993; Filippelli and Delaney, 1996
Hydrothermal	$0.4–0.65 \times 10^{10}$ mol P yr^{-1}	Froelich et al., 1982; Wheat et al., 1996
Total	$11–34.1 \times 10^{10}$ mol P yr^{-1}	
RESIDENCE TIME	Assuming a global P inventory of 3.2×10^{15} mol P	
Maximum estimate:	20,000–80,000 years (Based on Sources)	
Minimum estimate:	9300–29,100 years (Based on Sinks)	

importance of coastal regimes in P removal and phosphorite deposits have been included (Ruttenberg, 1993; this paper). Given the lack of information regarding the magnitude of phosphorite deposits as a P sink, the residence time of P could be substantially shorter. For example, doubling the phosphorite burial rate decreases P residence times to less than 8000 years. Increasing the removal rate of P from the oceans suggests that a similar increase in P inputs must be considered in order to maintain mass balance. Given the lack of information regarding riverine and atmospheric inputs, it is not hard to imagine that one or the other may have been substantially underestimated.

The reduction in the residence time of P will have a large impact on current views of P cycling over geologic time scales. For example, other nutrients, such as silica, may play a more significant role in plankton production, and hence particulate export (Dugdale and Wilkerson, 1998; Hutchins and Bruland, 1998; Canvender-Bares et al., 1999). Furthermore, it is not entirely clear that processes, such as denitrification and N_2-fixation would be able to respond to changes in P cycling over shorter intervals. A recent model by Tyrell (1999) suggests that the oceanic inputs of P ultimately control the rate of N_2-fixation. But this may not be the case if P inputs are substantially higher than previously thought. The role of other nutrients in N_2-fixation, such as Fe, may ultimately decrease the global role of P.

4. P cycling within the ocean

4.1. Methods of measurement

Before one can discuss the cycling of P within the oceans, it is first necessary to understand the methodologies by which P concentrations are measured. Currently, the distribution of P in aquatic systems is most often defined analytically. This is one of the biggest hurdles in elucidating P composition and cycling in marine systems.

4.1.1. Dissolved inorganic P

The dissolved P pool is generally delineated as that material which passes through a 0.2–0.7 μm pore size filter. In most studies, the dissolved inorganic P pool is characterized using the formation of 12-molybdophosphoric acid or phosphomolybdate under acidic conditions. This procedure was first

developed by Osmond (1887), but not widely utilized until several decades later (Deniges, 1920; Murphy and Riley, 1962). Upon reduction, phosphomolybdate produces a blue colored complex, the intensity of which is measured spectrophotometrically. Unfortunately, there are several major difficulties in using this technique.

The first is that during P complexation, molybdate will also react with other ions, such as silica, arsenate and germanium. In order to avoid and/or reduce these interfering actions, various steps have been included into the above procedure, ranging from changing sample acidity to adding new reagents (Baginski et al., 1967; Alghren, 1970; Campbell and Thomas, 1970). Throughout the years, numerous modifications to the phosphomolybdate method have resulted in a number of variations to the original method used to measure P in the oceans (Murphy and Riley, 1962; Strickland and Parsons, 1972; Broberg and Petterson, 1988).

The second and more problematic difficulty with the above technique is that during sample acidification, which is necessary to form the phosphomolybdate complex, an unknown proportion of acid-labile organic compounds, such as simple sugars and monophosphate esters, will be hydrolyzed (McKelvie et al., 1995 and references therein; Thomson-Bulldis, 1997). As a result, the concentration of dissolved inorganic P in seawater will be inflated. Several attempts have been made to reduce this overestimation, including the reduction of acid and reagents added, a reduction in the acid contact period, and the addition of new reagents (Chamberlain and Shapiro, 1969; Dick and Tabatabai, 1977; Lee et al., 1992). However, the success of these techniques is still under question. Tarapchak (1983) found that the hydrolysis of dissolved organic phosphorus (DOP) compounds occurred rapidly in both acidic and non-acidic molybdate solutions. As a result, Dick and Tabatabai (1977) used a citrate–arsenate reagent to complex the surplus molybdate in the sample solution, thereby reducing the potential for DOP hydrolysis. Unfortunately, general use of this technique has been poor. Thus, a more appropriate term for the fraction measured using the phosphomolybdate technique is soluble reactive phosphorus or SRP.

The last major issue is the detection limit of SRP in the open ocean. Although the phosphomolybdate technique is by far the most utilized, its detection limit is 30 nM when using a typical spectrometric cell path length of 10 cm. The most common method for lowering the detection limit (and minimizing interferences) is through solvent extraction techniques either just before or immediately following the reduction of the phosphomolybdate complex. These solvents include a wide variety, ranging from isobutanol to benzene (Martin and Doty, 1949; Watanabe and Olsen, 1962; Broberg and Petterson, 1988; McKelvie et al., 1995). Although detection limits can often be lowered by up to a factor of 10, organic extractions are slow, laborious, and decrease the analytical accuracy. Furthermore, many of the organic solvents involved are hazardous.

A more recent technique is the MAGIC method developed by Karl and Tien (1992) and subsequently modified by Thomson-Bulldis and Karl (1998). This method concentrates SRP by the in situ precipitation of brucite [$Mg(OH)_2$] under alkaline conditions followed by acidic dissolution measurement via phosphomolybdate. Using this method, P concentrations can be determined to less than 5 nM with a precision of ± 1 nM. Modifications by Thomson-Bulldis and Karl (1998) include a reduction in alkaline conditions, such that possible adsorption and hydrolysis of specific organic compounds is reduced. This new method appears to be successful, but has yet to be used widely in the field.

It should be mentioned that a number of researchers have used other methods to better try and elucidate the dissolved inorganic phosphorus fraction, as opposed to SRP, more accurately. These techniques include electrochemical, chromatographic and enzymatic assays (Stevens, 1979; Glazier and Arnold, 1988; Haddad and Jackson, 1990). However, many of these methods suffer from a lack of sensitivity and their inability to be applied to environmental samples (McKelvie et al., 1995). None are widely used by oceanographers today. Future technological developments may make these methods much more available for standardized use in the future.

4.1.2. Total dissolved and dissolved organic P

The concentration of TDP is generally quantified by using high temperature and/or pressure in the presence of a strong oxidizing reagent (McKelvie et al. 1995). In this manner, all of the P within the

sample is converted to inorganic P, which is then measured using the phosphomolybdate method. The difference between TDP and SRP is often referred to as the DOP component. This DOP fraction, however, can also contain non-reactive inorganic compounds, such as polyphosphates (Strickland and Parsons, 1972; Thomson-Bulldis, 1997). Thus, this fraction should really be termed soluble non-reactive P, or SNP.

The original method for the measurement of TDP involved perchloric acid digestion (Hansen and Robinson, 1953; Strickland and Parsons, 1972). However, this technique has been abandoned by many researchers due to the difficult and hazardous nature of working with perchloric acid. As a result, more common methods now measure TDP using persulfate oxidation, UV oxidation or a mixture of both. The persulfate method described by Menzel and Corwin (1965) (later modified by Koroleff, 1983) and the UV method of Armstrong et al. (1966) (later modified by Ridal and Moore, 1990) have been the most widely used techniques to measure TDP in recent years.

These methods, however, have been tested using known, specific P containing compounds, and results indicate that neither may fully convert TDP to phosphate (Ridal and Moore, 1990; Keroul and Aminot, 1996; Thomson-Bulldis, 1997; Monaghan and Ruttenberg, 1999). Monaghan and Ruttenberg (1999) found that the persulfate method tended to under-recover certain compound classes, such as phosphonates and phospholipids, by as much as 45%. However, it appears that this may depend on the specific organic complex tested, as Thomson-Bulldis (1997) conducted a similar experiment and found no such occurrence when using different organic P complexes within these same compound classes. Thomson-Bulldis (1997), however, did find substantial under-recoveries of nucleotide di- and tri-phosphates, as well as inorganic polyphosphates (under-recoveries $\lambda \geqslant 70$–80%) when using UV oxidation. It should be noted that although Armstrong et al. (1960) also found no oxidation of polyphosphates using the UV oxidation method, they did find complete oxidation of compounds, such as RNA and phosphoic acid. Ridal and Moore (1990) compared the two individual techniques with a combined UV, persulfate oxidation method and found that the combination gave TDP values which were 1.25 to 1.5 times higher in Gulf Stream surface waters than by either method alone. It is unclear as to what the chemical speciation of the hereto undetected P was in these waters. Unfortunately, the combination of both persulfate and UV oxidation techniques is still not commonly used.

Another method for measuring TDP uses high temperature combustion with magnesium sulfate and/or nitrate (Solorzano and Sharp, 1980). While these methods generally tend to have better recoveries (again based on specific P compounds, Monaghan and Ruttenberg, 1999), they are not as often utilized due to the extensive sample manipulation involved.

4.2. P distributions

The average global concentration of SRP in the oceans is 2.3 μM and this pool is by far the largest reservoir of dissolved P (Fig. 4). In general, SRP concentrations decrease with increasing distance from the continent, such that lowest concentrations are typically found in the surface waters of the North Pacific and North Atlantic Oceans (Karl et al., 1997; Ormaza-Gonzalez and Statham, 1991). In the coastal ocean, the seasonal cycle of phytoplankton blooms and summer time stratification reduces surface water SRP concentrations to levels typically less than 0.2 μM. During the rest of the year, riverine inputs and strong vertical mixing (which mixes nutrient enriched deep water into the surface, and induces light limitation of phytoplankton), generally maintains SRP concentrations to levels higher than 0.5 μM. In open ocean upper waters, biological uptake depletes SRP to levels typically less than 0.2 μM throughout the year, with concentrations increasing with increasing depth in the water column (GEOSECS, TTO). Maximum SRP concentrations tend to coincide with the deep water dissolved oxygen minimum. Below 1000 m, concentrations typically remain constant at levels that range from 2 to 3 μM.

While the concentration of SRP has been examined in a number of environments, the concentration of SNP has not. SNP is dominated by organic P compounds, but can contain inorganic polyphosphates as well. In general, the SNP pool contributes 0.5–3.4% of the total dissolved organic carbon (DOC) measured in marine systems (Williams, 1975).

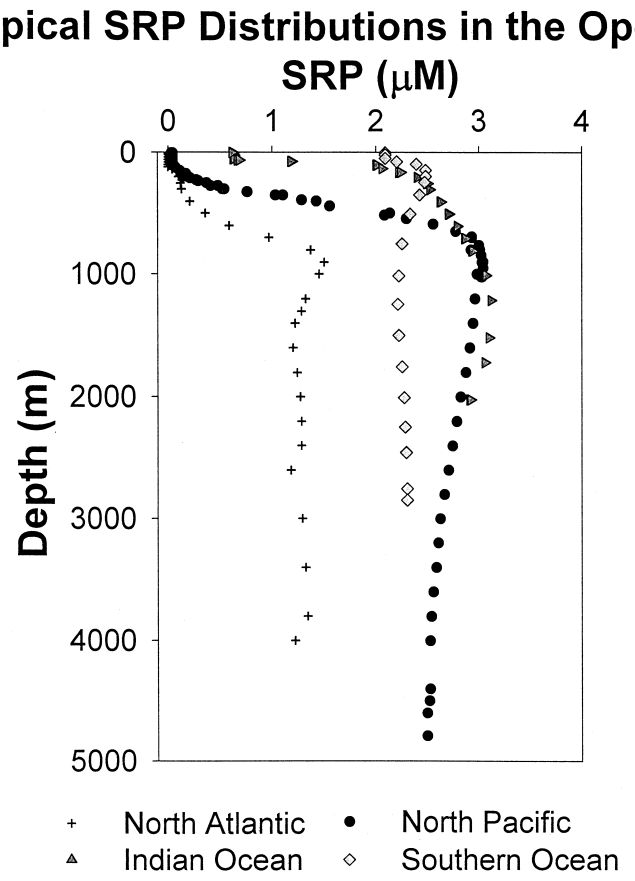

Fig. 4. Typical distribution of SRP in the world's major oceans: North Atlantic (plusses), North Pacific (black circles), Indian Ocean (gray triangles) and Southern Ocean (gray diamonds). North Pacific data compiled from the JGOFS HOT Program (Karl et al., 1999). North Atlantic data compiled from the JGOFS Bermuda Atlantic Time Series (BATS) Program. Indian Ocean and Southern Ocean data compiled from GEOSECS (http://ingrid.ldgo.columbia.edu).

Only recently have comprehensive measurements of SNP in a variety of marine systems been made (Karl and Yanagi, 1997). In surface waters, SNP concentrations range from less than 200 nM (North Atlantic and North Pacific) to as high as 1.7 μM (Azov Sea) (e.g. Romakevich, 1984; Karl et al., 1997). Concentrations tend to be higher in surface waters along the coast, decreasing with increasing depth and distance from shore. In deeper waters, SNP concentrations are generally less than 0.3 μM, although concentrations close to 2 μM have been measured at depths of 500–1000 m (Romakevich, 1984).

In coastal marine environments, the SNP pool generally ranges from 0–50% of the TDP pool (Romakevich, 1984). In contrast, in the open ocean, SNP can be as great as 75% (Karl and Yanagi, 1997). The SNP pool has even been found to exceed SRP by an order of magnitude in some environments (Strickland and Austin, 1960; Smith et al., 1985). Thus, the importance of identifying the composition of the SNP pool increases with greater distance from shore.

Particulate P concentrations have been studied to an even lesser extent than SNP. Concentrations can vary from less than 10 nM to as high as 0.3 μM (Romakevich, 1984). The ratio of C:P found in sinking particulate material is often characteristic of fresh organic material and has a Redfield ratio of 106–117:1, suggesting that most of the P in this form is associated with marine organic matter (Re-

dfield et al., 1963; Anderson and Sarmiento, 1994). As a result, higher particulate P concentrations tend to be associated with areas of high primary production, along the coast and in the upper water column (Jahnke, 1996).

For many years, there has been the widely held view that particulate P is preferentially remineralized relative to C and N (Menzel and Ryther, 1964; Knauer et al., 1979; Minster and Boulahdid, 1987; Martin et al., 1994). These findings are mostly based on sediment trap and hydrographic studies, which depict a shallower maximum in dissolved SRP concentrations relative to C and N. However, recent evidence suggests that this is not the case (Anderson and Sarmiento, 1994). Rather, the shallower maxima in SRP concentrations with depth, when compared to N, is due to the removal of nitrate via denitrification in low-oxygen waters and subsequent horizontal advection (Anderson and Sarmiento, 1994; Tyrell and Law, 1997). Analysis of P:C ratios at depths greater than 400 m are similar to those found in fresh organic matter and are both constant with depth and oceanic regime (Anderson and Sarmiento, 1994).

4.3. P composition

The composition of P within marine systems has been difficult to constrain, given the aforementioned difficulties in measuring inorganic and organic P species. The principal form of dissolved inorganic P in seawater is as HPO_4^{2-} ($\sim$87%). Less than 30% exists in the free form, with the remainder mostly associated as ion pairs with sodium, magnesium, and calcium. Relative abundances are dependent not only on pH and temperature, but also on the availability of cations and competing anions (Cembella et al., 1984a,b).

The number of studies which have sought to elucidate the marine organic P composition have been few and most rely on the identification of size and particular compound classes (i.e. nucleotides) rather than identifying specific P containing compounds (i.e. 1-glucose phosphate) (Table 2). Molecular weight size fractionation of the SNP pool has been conducted using cross flow ultrafiltration and gel chromatography techniques (Hicks, 1981; Matsuda et al., 1985; Ridal and Moore, 1990; Clark et al., 1998; Suzumura et al., 1998). In general, low molecular weight compounds (LMW $<$ 10 kDa), comprise 50–80% of the SNP pool. High molecular weight compounds (HMW $>$ 50 kDa) are the second largest fraction, close to $\sim$15%. Compounds which lie between 10 and 50 kDa are less than 5% of the SNP pool. LMW SNP decreases rapidly with increasing depth, such that it is typically undetectable by 1000 m, suggesting that this fraction is biologically labile (Ridal and Moore, 1990; Suzumura et al., 1998). Matsuda et al. (1985) fed specific SNP size fractions ($<$ 0.5, 0.5–10, 10–100 kDa) to the red-tide dinoflagellate, *Gymnodinium*, and determined that each fraction was bioavailable, with the 0.5–10 kDa fraction stimulating the most growth.

Some of the first research into identifying the actual composition of organic P was conducted by Phillips (1964). In this study, thin layer chromatography was used to separate dissolved organic P into various fractions. Based on adsorption characteristics, three fractions were hypothesized to contain nucleotides and/or polynucleotides (53–65%), compounds necessary for energy transfer within the cell and cellular coordination. The remaining three fractions were not adsorbed and were thus, believed to represent other phosphorylated hydrocarbons, such as lipids.

Direct measurements of specific nucleotides and nucleic acids have since verified the presence of nucleotides in natural systems. ATP concentrations were determined in waters from Southern California and Antarctica using bioluminescence techniques (Azam and Hodson, 1977; Azam et al., 1979; Hodson et al., 1981; Nawrocki and Karl, 1989). Concentrations were low, and ranged from $<$ 100 to 1200 ng l^{-1}, less than 1% of the SNP pool. Nawrocki and Karl (1989) further found that in Antarctica, the concentration of ATP varied seasonally, peaking with the advent of the spring bloom. This led to the suggestion that much of the ATP measured was released during the active growth and metabolism of phytoplankton. Larger molecules, such as DNA and RNA, rarely exceed concentrations of 20 nM in coastal environments, and are typically less than 5 nM offshore (DeFlaun et al., 1986; Paul et al., 1986; Karl and Bailiff, 1989).

Polyphosphates have been hypothesized to be as much as 50% of the SNP pool in near-shore waters (Armstrong and Tibbets 1968; Solorzano and Strickland, 1968; Solorzano, 1978). However, this figure is

Table 2
Composition of SNP in the marine environment

SNP compound class	%Composition (method)[a]	Reference
Bulk SNP		
Monophosphate Esters	10–100% (Enzymatic Assays)	Strickland and Solorzano, 1966; Kobori and Taga, 1978; Taft et al., 1977; Chrost et al., 1986
	55–77% (0–100 m; Modified UV oxidation)	Karl and Yanagi, 1997
	50% (> 100 m; Modified UV oxidation)	
Nucleotides and nucleic acids	23–45% (0–100 m; ≈ Persulfate — modified UV)	Karl and Yanagi, 1997
	50% (> 100 m; ≈ Persulfate — modifiedUV)	
	10–100% (Enzymatic Assays)	Strickland and Solorzano, 1966; Kobori and Taga, 1978; Taft et al., 1977; Chrost et al., 1986
	ATP: < 1% (Firefly bioluminescence)	Azam and Hodson, 1977; Azam et al., 1979; Hodson et al., 1981; Nawrocki and Karl, 1989
	DNA/RNA: < 5% (Multiple methods)	DeFlaun et al., 1986; Paul et al., 1986; Karl and Bailiff, 1989
Phospholipids	3–11% (Cross Flow Filtration (CFF) and Polymyxin B treatment)	Suzumura et al., 1998
Phosphonates	5–10% (^{31}P NMR)	Clark et al., 1998
Polyphosphates	0–50% (≈ Acid Reflux — UV oxidation)	Armstrong and Tibbets, 1968; Solorzano and Strickland, 1968; Solorzano, 1978
Size fractionated SNP		
LMW (< 10 kDa)	50–80% (CFF)	Matsuda 1985; Ridal and Moore, 1990; Suzumura et al., 1998
HMW (> 10 kDa)	20–50% (CFF)	Matsuda et al., 1985; Ridal and Moore, 1990;
HMW (> 50 kDa)	15% (CFF)	Suzumura et al., 1998
Monophosphate esters	10% (Alkaline phosphatase treatment)	Suzumura et al., 1998
	75% (^{31}P NMR)	Clark et al., 1998
Nucleic acids	25% (Phosphodisterase treatment)	Suzumura et al., 1998
Phospholipids	38–46% (Polymyxin B treatment)	Suzumura et al., 1998
Phosphonates	25% (^{31}P NMR)	Clark et al., 1998

[a]All values are based on surface waters (upper 100 m) unless otherwise noted.

most likely an overestimate as polyphosphate concentrations were not identified directly. Rather, samples were subjected to two different hydrolysis techniques, UV radiation and acid reflux. The difference in P concentration was theorized to be predominantly due to polyphosphates. However, recent evidence (see TDP analysis) indicates that nucleic acids, such as RNA and DNA, are not fully hydrolyzed by these methods (Thomson-Bulldis, 1997). Regardless, the concentration of polyphosphates was found to vary seasonally and with plankton speciation, with the highest concentrations measured in the late spring and during red-tide blooms. Polyphosphates are compounds used by organisms for energy storage (Watanabe et al., 1989). Thus, increases in these compounds have been attributed to excretion by zooplankton and phytoplankton (Lorenzen, 1967) and cell death and rupture (Solorzano, 1978).

Further elucidation of the structural components of marine SNP has been found using ^{31}P Nuclear Magnetic Resonance (NMR). Clark et al. (1998) found that the HMW (1–100 nm size range) fraction of SNP, or 19–38% of the total dissolved organic matter, was dominated by phosphorus esters and phosphonates. In plankton, phosphonates are associated with phosphonolipids, compounds used in cell structure. Their relative abundance within marine phytoplankton (< 3%), however, is significantly lower than that found in the dissolved organic phosphorus pool (5–10%). This result led Clark et al.

(1998) to suggest that other P containing components must be preferentially removed in order to increase the relative concentration of phosphonates in the water column.

Confirmation that phosphorus monoesters are a large fraction of SNP was obtained by Karl and Yanagi (1997). Continuous flow UV decomposition was used to characterize part of the SNP pool within the oligotrophic North Pacific. In the upper water column (<100 m), they found that on average, 66% of the SNP pool (50% of TDP) was most likely dominated by monophosphate esters, compounds used by microorganisms for metabolic functions. In contrast, in the deeper waters this fraction decreased to less than 50% of the SNP Pool, indicating preferential remineralization of one component over the other. The remaining fraction was hypothesized to contain primarily nucleotide di- and triphosphates, nucleic acids and other compounds resistant to UV hydrolysis, such as polyphosphates.

Enzymatic techniques have further corroborated the importance of DOP compounds as a potential source of P in natural systems. In these studies, specific enzymes, such as alkaline phosphatase and nucleotidase, are added to samples and their destruction of dissolved organic P monitored. Using the specificity of these particular enzymes for certain P containing compounds has enabled the identification of several classes of dissolved organic compounds in seawater. Alkaline phosphatase has been the most commonly used in enzymatic studies. Although it has a high specificity for the monophosphate ester bond, the strength of hydrolysis may vary between different types of monophosphate ester compounds. It should be noted that these bonds are also found in polyphosphates and nucleotides, such as ATP, but not in DNA (Heppel et al., 1962; Koshland, 1965; Suzumura et al., 1998).

Strickland and Solorzano (1966), Kobori and Taga (1978) and Solorzano (1978) used alkaline phosphatase to elucidate the hydrolyzable fraction of SNP in both coastal and open ocean regimes. While there was no detectable hydrolysis in open ocean samples, coastal waters contained hydrolyzable SNP concentrations that ranged from 0.03 to 0.45 μM, or up to 50% of the SNP measured (Kobori and Taga, 1978). Chrost et al. (1986) conducted a similar experiment in the North and Baltic Seas, and found that 80–200 nM, 100% of the SNP measured, was hydrolyzed. Chrost et al. (1986) also found that alkaline phosphatase derived from *Escherichia coli*, which was used in the previous studies, was inhibited at SRP concentrations that exceeded 1.6 μM. Thus, the fraction of SNP subject to enzyme hydrolysis in the study by Kobori and Taga (1978) could be considerably higher. Although Taft et al. (1977) found that the fraction of P hydrolyzable by alkaline phosphatase was less than 10% of the SNP pool in coastal waters, they noted that peaks in concentration occurred during the summer. This further suggests that this fraction is not only biologically produced, but also labile on seasonal time scales.

Suzumura et al. (1998) has conducted one of the most complete analyses of the composition of SNP in marine systems to date. In this study, a combination of ultrafiltration and enzymatic techniques were used in coastal waters off of Japan. Two enzymes, alkaline phosphatase and phosphodisterase were added to the HMW fraction of SNP (>10 kDa, 14–36% of total). Tests by these researchers using specific P compounds suggests that alkaline phosphatase only hydrolyzes monoesters, whereas phosphodisterase, hydrolyzes diesters as well. Within the HMW fraction, $\sim 10\%$ were found to be monoesters, whereas diesters, presumably dominated by nucleic acids, DNA and RNA, comprised 25%. The remaining 65% of the HMW SNP was unreactive.

This remaining unreactive HMW SNP fraction was further extracted with chloroform (to identify the solvent soluble hydrophobic fraction of SNP), such that 46–68% remained in the aqueous phase. Chloroform extraction substantially changed the reactivity of the compounds, as 87–92% of the aqueous phase material was hydrolyzed by enzymatic treatment after extraction. A secondary treatment of the HMW fraction using polymyxin B, a detergent that can disrupt phospholipids (membrane structures of all marine microorganisms), reduced 38–46% of the non-reactive HMW SNP fraction to <10 kD. The results of the HMW SNP treatments led Suzumura et al. (1998) to hypothesize that HMW SNP contains protective structures dominated by phospholipid containing macromolecules that prevents hydrolysis of labile mono- and diester-P compounds.

Although the above analyses are hampered by many analytical questions, they have begun to pro-

vide a basis for understanding the composition of P within marine systems. Low molecular weight compounds dominate both the inorganic and organic pools. The SNP fraction consists of a wide variety of compounds, but is predominantly comprised of monophosphate esters, nucleotides, nucleic acids, and phosphonates. All of these compounds are of biological origin. It is clear that new, easily utilizable techniques still need to be developed to study the P composition in marine systems. Only in this manner will we truly be able to understand the processes that govern P composition in the ocean.

4.4. P bioavailability

By far the majority of research on P bioavailability has been conducted in freshwater regimes (e.g. Cembella et al., 1984a,b). Marine studies have been much more limited. In natural systems, phosphate is the most readily utilizable form of P (e.g. Björkman and Karl, 1994). Although, several studies have demonstrated the presence of other inorganic P compounds, these compounds appear to typically be only a small fraction of TDP in marine regimes (Solorzano and Strickland, 1968; Doemell and Brooks, 1975; Langowska, 1982). SNP, on the other hand, could provide a substantial and ubiquitous source of P to marine organisms. The above studies on the composition of SNP have provided indirect evidence that there are components of this pool that are preferentially utilized and eliminated from the water column.

The study by Chu (1946), using non-axenic cultures, was one of the first investigations to try and directly demonstrate that under low phosphate conditions, organisms, such as *Phaeocystis poucheti*, were able to utilize phospholipids (lecithin) and sugar phosphates (glucose-6-phosphate). Since then, a number of studies have provided evidence that remineralization of SNP primarily occurs through enzymatic reactions at the cell surface of prokaryotic and eukaryotic organisms (Ducklow, 1983; Ammerman and Azam, 1985, 1991a,b; Flynn et al., 1986; Martinez and Azam, 1993; Azam, 1998).

Bacteria are ubiquitous in both the coastal and open ocean, and numerous studies have demonstrated their importance in the biological food web (e.g. Ducklow, 1983; Azam, 1998). Alkaline phosphatase and 5′ nucleotidase are two of the major enzyme classes found within these marine organisms (Hassan and Pratt, 1977; Bengis-Garber and Kushner, 1981; Ammerman and Azam, 1985; Martinez and Azam, 1993; Rath et al., 1993). Thus, based on diagnostic enzymatic studies, between 10% and 100% of the SNP found in marine environments is potentially bioavailable (Strickland and Solorzano 1966; Taft et al., 1977; Kobori and Taga 1978; Chrost et al., 1986). The presence of alkaline phosphatase and 5′ nucleotidase in natural systems has been inferred from field studies (Kobori and Taga, 1978; Ammerman and Azam, 1985, 1991a,b; Azam, 1998). By far, the most ubiquitous and studied enzyme is alkaline phosphatase. Its presence in the water column has been hypothesized to be directly related to the phosphorus deficiency found within the bacterial cell (Perry, 1972; Karl et al., 1992). Perry (1972) determined that the addition of 5 μM of phosphate decreased the alkaline phosphatase activity by greater than 75% in just 2 h. Furthermore, it was determined that alkaline phosphatase activity was either low or absent in regions with higher concentrations of SRP, and tended to be detected only during algal blooms under low SRP conditions (Perry, 1972; Karl et al., 1992). The relationship between low phosphate and alkaline phosphatase activity has been confirmed in laboratory studies, which have demonstrated end-product inhibition by phosphate (Bengis-Garber and Kushner, 1981, 1982).

A secondary enzyme, 5′nucleotidase, has only been recently identified as being potentially significant in SNP remineralization in aquatic systems (Ammerman, 1991; Ammerman and Azam, 1985, 1991a,b; Tamminen, 1989). Unlike alkaline phosphatase, 5′nucleotidase recognizes the carbon moiety of the nucleotide. Furthermore, this enzyme is not inhibited at high cellular P levels. Ammerman and Azam (1985) hypothesized that the hydrolysis of SNP by 5′nucleotidase could supply as much as 50% of the phosphate required by plankton in coastal California waters.

Björkman and Karl (1994) studied the relative bioavailability of SNP compounds in coastal waters of the Hawaiian Islands. Two SNP compound mixtures, one containing monophosphate esters, the other nucleotides, were added to natural microbial assemblages. The monophosphate esters always demonstrated lower bioavailability and less than 25% of the compounds accumulated as SRP. In contrast, the

nucleotides were much more bioavailable and 65–95% of these compounds accumulated in the SRP pool. Thus, Björkman and Karl (1994) suggested that 5′nucleotidase was the major enzyme being utilized by bacteria in the system. The lack of SRP consumption further suggested that these organisms were carbon limited, and only using the carbon–nitrogen portion of the nucleotide. Carbon limitation of bacteria has been found in several environments (Azam et al., 1983; Jurgens and Gude, 1990; Benitez-Nelson and Buesseler, 1999a). The idea that 5′nucleotidase activity may tend to release large amounts of SRP into marine systems, has an enormous impact on the role that bacteria may play in phytoplankton production and export.

It is currently unclear as to what fraction of SNP hydrolyzed by enzymatic processes is released into the water column. A number of studies have found that heterotrophic bacteria out-compete phytoplankton for SRP under P limited conditions (Currie and Kalff, 1984; Tamminen, 1989; Jurgens and Gude, 1990; Bentzen and Taylor, 1991). A few studies, however, have found the reverse to be true (Tarapchak and Moll, 1990; Cotner and Wetzel, 1991). Differences are most likely related to environmental conditions and the time scales over which each study occurred. If bacteria do out-compete phytoplankton in the uptake of SRP, then any SRP released during enzymatic hydrolysis will be immediately consumed by the surrounding bacterial population. On the other hand, if bacteria are limited by other elements, such as C or N, then bacteria and phytoplankton could exist in a co-dependent relationship, with bacteria releasing enough SRP during SNP hydrolysis to support phytoplankton production (e.g. Ammerman and Azam, 1985).

Regardless, bacteria themselves may be a substantial contribution to SRP. These organisms constitute a large fraction of the diet of heterotrophic protozoa (Sieburth, 1984; Sherr and Sherr, 1994). Laboratory studies have demonstrated that through feeding and egestion, protozoa can convert and release between 20–90% of the P within the bacterial biomass to soluble forms (Anderson et al., 1986; Jurgens and Gude 1990; Ferrier-Pages and Rassoulzadegan, 1994; Eccleston-Parry and Leadbeater 1995). The dissolved P produced from these processes is dominated by inorganic P, although organic P is also released (Anderson et al., 1986; Jurgens and Gude 1990). The efficiency of P regeneration does appear to be dependent on nutrient-limitation conditions and the phase of protozoan growth (Anderson et al., 1986; Jurgens and Gude 1990). Controversy still exists over the specific role that protozoans play in nutrient regeneration in natural systems. There is little direct evidence of the magnitude of bacterial and heterotrophic protozoa remineralization processes and their effect on phytoplankton production.

Viral lysis of bacteria may provide another source of P to marine systems (e.g. Scanlan and Wilson, 1999). Middelboe et al. (1996) noted that both bacterial DOC uptake and alkaline phosphatase activity increased when viruses were added to P limited cultures of natural microbial assemblages. This suggests that the resulting products constitute a significant new source of readily bioavailable P to larger plankton. In fact, Gobler et al. (1997) found that P produced from viral lysis decreased diatom P limitation. However, viruses may also be P limited, or at least behave differently depending on the regime (e.g. Scanlan and Wilson, 1999).

The term ‘bioavailability’ is relative, and depends on the time scales that are being discussed. SNP concentrations decrease with depth in the water column, such that below 1000 m very little is detectable (e.g. Romakevich, 1984). Hence, these compounds must undergo dephosphorylation to SRP over time. Based on ocean mixing rates, it is highly likely that this remineralization occurs in less than several hundred years (e.g. Broecker and Peng, 1982). The studies discussed above, however, have focused on the potential remineralization of SNP over significantly shorter time periods (<1 day to months). In order to truly understand the importance of SNP in primary production and particulate matter export, we must also identify the P recycling rates within all of the dissolved and particulate biological P pools.

4.5. P turnover time

4.5.1. Artificial tracer estimates

It has been only recently that the study of nutrients in marine systems has begun to focus on turnover times (Table 3). The driving force behind this transition is the idea that high nutrient flux and regeneration rates could increase primary production to levels

Table 3
SRP and SNP turnover rates

P turnover rates	Coastal	Open ocean	References
SRP	< 1 h–10 days (> 1000 days in Bedford Basin)	Week to several months	Pomeroy, 1960; Duerden, 1973; Taft et al., 1975; Harrison et al., 1977; Perry and Eppley 1981; Smith et al., 1985;Sorokin, 1985; Harrison and Harris, 1986; Björkman and Karl, 1994; Björkman et al., 1999; Benitez-Nelson and Buesseler, 1999a
Total SNP	3–> 90 days	50–300 days	Jackson and Williams, 1985; Orrett and Karl, 1987; Lal and Lee, 1988; Lee et al., 1992; Karl and Yanagi, 1997; Björkman et al., 1999; Benitez-Nelson and Buesseler, 1999a
Bioavailable SNP (model compounds)	2–30 days	1–4 days	Ammerman and Azam, 1985; Nawrocki and Karl, 1989; Björkman and Karl, 1994; Björkman and Karl, 1999
Microplankton (< 1 μm)	> 1–3 days	NA	Benitez-Nelson and Buesseler, 1999a
Phytoplankton (> 1 μm)	< 1–8 days	< 1 week	Waser et al., 1996; Benitez-Nelson and Buesseler, 1999a
Macrozooplankton (> 280 μm)	14–40 days	30–80 days	Lal and Lee, 1988; Lee et al.,1991, 1992; Waser et al., 1996; Benitez-Nelson and Buesseler, 1999a

that are much greater than those predicted from inorganic nutrient concentrations alone. Turnover times, unfortunately, are difficult to quantify and there are few techniques available for investigation.

One method of elucidating the time scales over which nutrient recycling occurs is through the use of radioisotopes. In essence, radioisotopes behave as a 'clock' enabling one to trace processes that have occurred over a well-defined time interval. There are three isotopes of P, one stable, ^{31}P, and two radioactive, ^{32}P ($t_{1/2} = 14.3$ days) and ^{33}P ($t_{1/2} = 25.3$ days). Using ^{32}P and ^{33}P one can monitor the movement of P throughout various biological reservoirs and determine a net age of P within each particular pool. Although fractionation may occur, it is unlikely that the magnitude of such a process would significantly effect results. For example, an improbable fractionation of 100‰ between ^{32}P and stable P (twice that observed for ^{14}N and ^{15}N), results in only a 10% change in the ratio of ^{32}P to stable P (20% for ^{33}P to stable P) (Waser et al., 1996).

^{32}P and ^{33}P have been used to investigate the recycling rate of P within a number of aquatic regimes (Cembella et al., 1984a). In general, the use of these isotopes has been restricted to incubation experiments in which artificially produced ^{32}P and ^{33}P had been added. The difficulty with such types of research is that they involve significant perturbations to the system of interest. For example, samples are first separated from the ecosystem before incubation. Bottle incubations will, at best, miss sporadic bloom events and provide rate estimates that are only valid for discrete depths and times. Nonetheless, these studies have provided much needed insight into the cycling of P in both coastal and open ocean regimes (Harrison et al., 1977; Smith et al., 1985; Perry and Eppley 1981; Sorokin, 1985; Orrett and Karl 1987; Björkman et al., 1999).

In coastal regimes, SRP turnover times are typically rapid, ranging from < 1 h to just over a week (Pomeroy, 1960; Taft et al., 1975; Harrison et al., 1977; Smith et al., 1985; Harrison and Harris, 1986;

Björkman and Karl, 1994). Bedford Basin, however, is one exception to this trend with turnover times greater than 1000 days (Duerden, 1973). In contrast to most nearshore settings, SRP turnover times in open ocean environments are generally longer, on the order of a week to several months (Perry and Eppley, 1981; Sorokin, 1985; Björkman et al., 1999). Differences in turnover times between environments are most likely related to low rates of biological assimilation and/or seasonally high P concentrations (Perry and Eppley, 1981).

SNP turnover times, unfortunately, are a bit more complicated to measure. Unlike SRP studies, where one can monitor the consumption of $^{32}PO_4$ or $^{33}PO_4$ and the production of radiolabeled SRP directly, SNP turnover times are often determined using specific radiolabeled compounds, such as AT^{32}P. Thus, only a part of the SNP pool is investigated in any detail. As a result, SNP turnover times found in this manner are often referred to as the biologically available SNP pool. Using a number of radiolabeled organic P compounds, several studies have demonstrated that the biologically available SNP pool has similar turnover times to the phosphate pool, ranging from a day to as long as a month (Ammerman and Azam, 1985; Nawrocki and Karl, 1989; Björkman and Karl, 1999).

There are other, indirect methods of elucidating the turnover rate of the entire SNP pool within the upper ocean. The first involves monitoring the utilization rate of radiolabeled SNP from radiolabeled $^{32}PO_4$ and assuming steady state (Orrett and Karl, 1987; Björkman et al., 1999). A second similar method involves monitoring the accumulation rate of SNP based on ^{14}C primary production rates and assuming Redfield ratios (Jackson and Williams, 1985; Karl and Yanagi, 1997). Not surprisingly, both methods tend to give significantly longer SNP turnover times, 50–300 days, than that found from measuring bioavailable SNP alone (Jackson and Williams, 1985; Karl and Yanagi, 1997; Björkman et al., 1999). The large range in estimates is most likely due to seasonal/interannual differences and particular aspects of the turnover time calculation, as all of these studies were conducted in the Central North Pacific. In contrast, it should be noted that there is little difference between the total and bioavailable turnover times of SNP found in coastal areas, 3–10 days (Jackson and Williams, 1985; Orrett and Karl, 1987). This indicates that either coastal organisms have the ability to utilize a larger suite of SNP compounds, or that the composition of coastal SNP is dominated by more bioavailable forms.

4.5.2. Natural tracer estimates

All of the above studies have relied on incubation experiments in one form or another. In order to circumvent the inherent difficulties associated with such methods, several researchers have used naturally produced ^{32}P and ^{33}P to directly investigate marine P cycling (Lal and Lee, 1988; Lal et al., 1988; Lee et al., 1991, 1992; Waser et al., 1996; Benitez-Nelson and Buesseler, 1999a). The major advantage of using naturally produced radioisotopes is that they enable one to examine the net recycling of P without disturbing the regime of interest. Furthermore, results will integrate over all of the processes that have affected the distribution of ^{32}P and ^{33}P over the prior 20 to 35 days, thereby decreasing short-term variability effects. The difficulty, however, lies in the amount of water which needs to be processed for measurement of ^{32}P and ^{33}P in the dissolved and particulate phases, >4000 l. Thus, biological pools are only separated by size classes typical for each level of the food web. It is only recently that new techniques have been developed to measure both ^{32}P and ^{33}P in both coastal and open ocean environments consistently (Benitez-Nelson and Buesseler, 1998).

^{32}P and ^{33}P are naturally produced in the atmosphere via cosmic ray interactions with atmospheric argon nuclei. Once produced, these isotopes quickly scavenge onto particles and enter the oceans predominantly in rain (e.g. Benitez-Nelson and Buesseler, 1999b). In situ production of ^{32}P and ^{33}P has been estimated to be less then 5% and 1%, respectively, of the total cosmogenic input within the top 5 m of the ocean. While the magnitude of ^{32}P and ^{33}P concentrations will vary dramatically from one rain event to another, studies have shown that the ratio of $^{33}P/^{32}P$ remains constant and varies by less than 15% around a mean of 0.88 (Waser and Bacon, 1995; Benitez-Nelson and Buesseler, 1999b). This lack of variance has been demonstrated to hold regardless of the magnitude of precipitation and is

consistent throughout a precipitation event. Higher $^{33}P/^{32}P$ ratios in rain, however, can be observed following stratosphere/troposphere exchange (STE) events. Fortunately, STE events are limited and appear to only occur during severe storm (Benitez-Nelson and Buesseler, 1998b), or during tropopause folding at mid-latitudes (Waser and Bacon, 1995). By measuring the $^{33}P/^{32}P$ ratio in rain and in various marine pools, and determining the relative change in the $^{33}P/^{32}P$ ratio between various marine pools (caused by the differential decay rates of ^{32}P and ^{33}P), one can determine the net age of P in any particularreservoir of interest.

Several studies have provided evidence that the use of natural P radioisotopes has enormous potential for understanding P cycling in marine systems (Lal and Lee, 1988; Lal et al., 1988; Lee et al., 1991, 1992; Waser et al., 1996; Benitez-Nelson and Buesseler, 1999a). Lal and Lee (1988) were the first to measure naturally produced ^{32}P and ^{33}P in a marine system. Although their results were limited, they found that the turnover rate of SRP off the coast of California (Santa Catalina Island) was 20 days. A specific turnover rate was not defined for the SNP pool, however, it was hypothesized that it must be rapid due to measurable amounts of ^{32}P (^{33}P was not determined). Using a modified technique for the collection of radioactive P, Lee et al. (1992) measured equal activities of ^{32}P in both SRP and TDP, suggesting that the residence time of P in the SNP pool exceeded 6 weeks. A TDP residence time of 30 days was determined from ^{32}P mass balance estimates. Waser et al. (1996) measured both ^{32}P and ^{33}P in suspended particles off Bermuda. In general, they observed little difference between the $^{33}P/^{32}P$ measured in suspended particles and in rain. This suggested that at least a fraction of the open ocean TDP pool had rapid turnover times of less than a week (<1 week) (Waser et al., 1996).

The use of ^{32}P and ^{33}P suffered in these past experiments due to the requirement of large sampling volumes and difficult extraction and analysis techniques. However, recent developments in seawater chemical extraction and in the measurement of the low energy beta emitter, ^{33}P, have alleviated many of the prior difficulties (Benitez-Nelson and Buesseler, 1998). It is now possible to conduct comprehensive measurements of dissolved and particulate concentrations of both ^{32}P and ^{33}P in the water column, regardless of stable P concentration.

Benitez-Nelson and Buesseler (1999a) was the first group to measure ^{32}P and ^{33}P in both SRP and SNP. In the Gulf of Maine throughout the spring and summer, SRP turnover times were rapid (<1–8 days) and variable, with the longest turnover times occurring in July. SNP turnover times were substantially longer and increased from 28 days in July to greater than 100 days in August. This increase in turnover rate, coupled with a large decrease in P activity, was much greater than that possible from radioactive decay alone, indicating preferential removal of a small fraction of the SNP pool. High ^{32}P and ^{33}P activities and low $^{33}P/^{32}P$ ratios within bacteria (0.2–1.0 μm) during August indicated that this size class was both the primary consumer and regenerator of dissolved P within the ecosystem. In the late summer, when SNP concentrations were detectable (>0.05 μM), it was hypothesized that marine bacteria were consuming a portion of the SNP pool directly, even though SRP (~ 0.2 μM) was also present. This implies that SNP remineralization is independent of the inorganic nutrient concentration, a hypothesis that has since been confirmed in temperate lake studies (Hudson et al., 1999). While the bacterially consumed SNP was only a small fraction (5%) of the total SNP, it appears that this material was younger than the rest of the SNP pool. Mass balance estimates suggested that the remaining SNP fraction had a turnover rate longer than 100 days, similar to that found in incubation experiments (Jackson and Williams, 1985; Karl and Yanagi, 1997; Björkman et al., 1999).

The study by Benitez-Nelson and Buesseler (1999b) provides the first in situ evidence that SRP has rapid turnover times in the upper ocean, which suggests that low P concentrations could support relatively high levels of primary production. In addition, SNP appears to be made up of a chemically diverse group of compounds that cycle over very different time scales. Furthermore, the observation that bacteria were rapidly consuming SNP in the presence of SRP, suggests that bacteria were remineralizing SNP for other nutrient requirements, such as for carbon or nitrogen. This finding, along with those mentioned previously (see Section 4.4), gives greater support for 5′nucleotidase activity as being a

significant component in the regeneration of SNP in marine systems. Interestingly, there was no evidence that heterotrophic protozoa were consuming bacteria, or were significantly involved in the P remineralization process. Thus, at least in this regime, bacteria, and not protozoa, are the major regenerators of SNP.

Measurement of ^{32}P and ^{33}P in the larger particulate size classes indicated that the age of P generally increased as one moved up through the food chain. Larger phytoplankton had turnover times that were typically less than 2 weeks, whereas macrozooplankton turnover times were not only longer, but exhibited more variability (Lal and Lee, 1988; Waser et al., 1996; Benitez-Nelson and Buesseler, 1999a). In the North Atlantic Ocean, the recycling rate of P in zooplankton ranged from 60–70 days (Waser et al., 1996). Off the coast of California and in the Gulf of Maine, rates ranged from 30 to 80 days (Lal and Lee, 1988; Lal et al., 1988; Lee et al., 1991; Benitez-Nelson and Buesseler, 1999a). These rates are slightly higher than the 19 days found in copepods by Marshall et al. (1961) using ^{32}P radiolabeled phytoplankton and the 12–21 days (Gulf Stream) determined by Pomeroy et al. (1963) using mass balance estimates.

The rapid turnover and temporal variability of P turnover within the dissolved and small planktonic pools demonstrates the dynamic nature of P in marine systems. The short turnover times of SRP suggest that studies of inorganic nutrient concentrations alone are insufficient for determining either nutrient limitation or maximal primary production. The potential for a substantial fraction of SNP to also have rapid turnover times, indicates that organic P pools must be considered as well. The implication of these findings suggests that the microbial food web plays an essential role in nutrient remineralization and primary production. A better understanding of the effects of bacterial remineralization on nutrient availability in both coastal and open ocean regimes is necessary for further understanding primary production in the world's oceans.

5. Conclusions and future outlook

It is clear that elucidating the cycling of all nutrients in marine systems is extremely important if we are to understand current controls on primary production and particulate carbon export in the world's oceans. The intensity of upper ocean P cycling, in particular, can have a direct impact on the magnitude of particulate matter exported from the euphotic zone to underlying sediments. Hence, long-term changes in P cycling will effect the residence time of P over geological time scales.

The many unanswered questions regarding the oceanic P pool will continue to cause debate within the oceanographic community. The studies discussed in this treatise only scratch the surface of what appears to be an adaptable and dynamic P cycle. The most studied aspects of P, the oceanic sources and sinks, are still ambiguous in many key areas. P sinks could be much larger than current estimates as more information concerning the distribution and magnitude of phosphorite deposits is brought forth. The impact of such a finding would result in a substantial decrease in the residence time of P in the ocean, and thus its role in nutrient limitation over geological time scales. In contrast, the total inputs from atmospheric, riverine, and regional P sources, such as volcanoes, are still based on only a few measurements. Hence, it is entirely possible that the reverse is true and that P residence times may be even longer than modern estimates. Regardless of whether or not P limits primary production, man has significantly altered the flux of P containing material into the oceanic reservoir. The interplay between the anthropogenic addition of P versus other elements, such as N and iron, remains uncertain. For example, hypothesized ecosystem shifts from N to P limitation in the open ocean (e.g. Karl et al., 1997) may in fact only be due to natural oscillations, rather than anthropogenically induced climate change.

The analytical definition of inorganic and organic P has hampered efforts to investigate P composition and the role of organic P compounds in supporting primary production. New techniques need to be developed and, more importantly, employed by the oceanographic community in order to fully understand the subtle differences between organic P and SNP. The SNP pool appears to be dominated by a number of biologically derived compounds, such as nucleotides, nucleic acids, monophosphate esters, and phosphonates. However, other compounds such as phospholipids have also been identified and may be

responsible for a large percentage of HMW P compounds.

It is clear that constituents of the SNP pool can be directly utilized by bacteria, and in some cases, over extremely rapid timescales. Thus, elucidating the relative components of SNP may have a dramatic impact on the potential of this pool to satisfy the nutrient requirements of phytoplankton in P limited habitats. Unfortunately, the percentage of SRP released into the water column during bacterial remineralization remains vague. It may be primarily due to microflagellate grazing rather than via direct bacterial exudation. This information is key for current ecological models of the food web in the upper ocean, especially since many of these models rely on inorganic P concentrations alone. Thus, primary production and particulate export rates could be much higher than currently estimated.

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