The Power of Radiocarbon in Biogeochemical Studies of the Marine Carbon Cycle: Insights from Studies of Dissolved and Particulate Organic Carbon (DOC and POC)

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1. Introduction

In 1960, Willard F. Libby was awarded the Nobel Prize in Chemistry for developing the technique of radiocarbon (^{14}C) dating. The importance of this technique for scientific studies of the natural environment has only grown as technological advances have improved the ability to measure this isotope. Carbon is one of the most important elements in the biosphere, and the ability to trace its path and residence time in environmental reservoirs with a radioactive isotope enhances our ability to study biogeochemical cycles in the ocean.

This review focuses on radiocarbon in dissolved and particulate organic carbon (DOC and POC, respectively) in the open ocean. These marine reservoirs represent important sinks for atmospheric CO_2. For example, since sinking particles rapidly transfer material synthesized in the surface ocean, POC represents an important conduit for carbon transport from the surface (and, ultimately, the atmosphere) to the deep ocean or marine sediments, where it can be sequestered on long time scales. Dissolved organic carbon represents one of the largest exchangeable carbon pools on earth (~650 Gt C), containing as much carbon as is present in the atmosphere.[1] Therefore, small changes in the size of the DOC reservoir have the potential to significantly alter the concentration of CO_2 in the atmosphere. Due to the important role these carbon reservoirs may play in the global carbon cycle, many studies have used radiocarbon in marine DOC and POC to investigate the cycling of carbon through these pools. Therefore, we choose to focus this review on biogeochemical insights into these reservoirs offered by radiocarbon studies. To our knowledge, there are no comprehensive reviews addressing radiocarbon-based studies of DOC and POC in the open ocean, and we will discuss results from the entire history of the field, from 1966 to the present. There is one published review on the carbon isotope composition of DOC by Bauer,[2] but the current review is more comprehensive in scope and covers some important advances in the field since the time of that review.

We begin this review by describing the basic theory and history behind making natural abundance radiocarbon measurements (section 2) and briefly outlining temporal and spatial variations in the distribution of ^{14}C in various inorganic carbon reservoirs (section 3). Terminology in the radiocarbon field is very specific and sometimes confusing, and we feel it is important to summarize it here in some detail. Without the development of accelerator mass spectrometry (AMS), it would not have been possible to use radiocarbon to study the biogeochemical cycle of carbon in the oceans, and in section 2, we present a thorough review of AMS and where the technology is headed. Future advances in this field will continue to broaden the areas in which radiocarbon can help us understand the carbon cycle. Section 3 describes the distribution of radiocarbon in the environment, essentially describing the radiocarbon stage upon which biogeochemical processes occur. Our basic

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knowledge of radiocarbon in the ocean and atmosphere has been catalogued well in the past and, recently, in much more detail. Given the residence time of the pools of carbon in the ocean, it is important to understand the current and past distribution of radiocarbon in the environment well. These discussions provide the background necessary to understand the extent of the limitations posed by analytical techniques and interpret the DOC (section 4) and POC (section 5) data in the context of their biogeochemistry.

Section 4 details radiocarbon studies of DOC, a chemically heterogeneous reservoir of carbon which is present in ocean waters at concentrations between 40 and 100 μM C.[1] The ability to place limits on sources and residence times of the complex DOC reservoir with the use of radiocarbon is adding greatly to our understanding of it. The discussion presented in section 4 shows that the DOC reservoir in the ocean consists of a mixture of components with radiocarbon signatures ($DO^{14}C$) ranging from values similar to that of dissolved inorganic carbon (DIC) in surface waters[3] to values as depleted as −800‰.[4] The average $DO^{14}C$ values in surface waters are between −150‰ and −400‰, and the average $DO^{14}C$ value of the oldest water mass (North Pacific Deep Water) is −540‰.[5] Based on comparisons to the radiocarbon content of DIC ($DI^{14}C$), it is clear that the average residence time of marine DOC is several times longer than the time required for one ocean-mixing cycle, suggesting that a refractory DOC component exists well mixed throughout the water column (see, e.g., Williams and Druffel[6]). Despite the low radiocarbon values of the surface DOC reservoir, mass balance calculations indicate that DOC derived from recent photosynthesis accumulates in this reservoir.[5,7] However, it was not until the first compound-specific radiocarbon measurements were made that conclusive evidence in support of this hypothesis was presented.[3,8] These latter studies also provide evidence to suggest that while the bulk DOC reservoir may be distributed to deep ocean basins via water mass advection (similar to DIC), some components of DOC are added to the deep ocean during dissolution of rapidly sinking particles.[3] This "fresh" DOC may be vital in sustaining the communities of heterotrophic bacteria that have been identified in meso- and bathypelagic environments.[9,10]

Section 5 reviews radiocarbon studies of particulate organic carbon (POC). Radiocarbon studies of both the suspended (POC_{susp}) and sinking (POC_{sink}) pools demonstrate that POC cycles much more rapidly than DOC, as it contains bomb produced ^{14}C (see section 3) throughout the water column. The presence of bomb-^{14}C in POC reflects its source from the recent (post-1960, see section 3) synthesis of material from DIC in surface waters and the subsequent rapid transport to subsurface depths. Decreases in the radiocarbon content of POC_{susp} ($PO^{14}C_{susp}$) with depth are seen in all oceans and are thought to result from the absorption of ^{14}C-depleted DOC at depth. However, close to ocean margins, horizontal export of ^{14}C-depleted POC could also contribute to the observed decreased in $PO^{14}C_{susp}$.

2. Radiocarbon

2.1. Basics

Radiocarbon, ^{14}C, is the most abundant radioactive isotope of carbon and is generated in the upper stratosphere and lower troposphere by the reaction of cosmic rays with nitrogen in the reaction[11]

$$^{14}N + n \rightarrow {}^{14}C + {}^{1}H \quad (1)$$

The ^{14}C formed in eq 1 is rapidly oxidized to CO_2 and becomes a part of the global carbon cycle. The stable isotopes, ^{12}C and ^{13}C, are the most abundant isotopes of carbon; the approximate natural abundance of ^{14}C is 1 atom per every $10^{12}-10^{13}$ atoms of C. Radiocarbon decays with a half-life of 5730 years[12] and is ideal for the study of biogeochemical processes that occurred over the past 50,000 years. Suggestions that the half-life may be significantly in

error[13] do not appear to be substantiated by recent data (Roberts, M. L.; Southon, J. R. Personal communication). Studying radiocarbon requires the adoption of a new language, and it is important to understand the nomenclature and conventions before reviewing our current state of knowledge.

2.2. Terms and Definitions

Radiocarbon is measured as either a specific activity (A) or an isotopic ratio (^{14}R), where ^{14}R is the ratio of ^{14}C to either ^{13}C or ^{12}C, i.e., $^{14}R = {}^{14}C/{}^{13}C$ or $^{14}C/^{12}C$.[14−16] To use radiocarbon for dating purposes, a starting point for the time line had to be established, i.e., a theoretical time zero. The year 1950 was chosen as the base year for all radiocarbon measurements and is considered modern, or present. Although there is no *a priori* reason for choosing 1950 as time zero, it is convenient because of the history of radiocarbon in the atmosphere. Samples more recent than 1950 are likely to be influenced by bomb-produced ^{14}C, complicating the use of radiocarbon as a dating and source identification tool. Typically, the ^{14}C content of a sample is expressed as a deviation from a known standard (whose ^{14}C content represents modern/time zero). To avoid the influence of atmospheric radiocarbon fluctuations from burning of fossil fuel since the Industrial Revolution or nuclear weapons testing during the 1950s and 60s, the ^{14}C activity of "1890 wood" corrected to the activity it would have in 1950 was chosen as the absolute standard. This standard has since been replaced by NIST SRM 4990B (oxalic acid I, HOxI) and, subsequently, SRM 4990C (oxalic acid II, HOxII).[17] By definition, modern (A_m, R_m) is 95% of the activity or ratio of HOxI.[17] All sample measurements are reported relative to modern. For the remainder of this discussion, we will refer to isotopic ratios (^{14}R) rather than activities (A), as this is the quantity measured most frequently. Because specific activity is proportional to the ratio of ^{14}C to the total carbon in a sample, A can be substituted for R in eqs 2−6 listed below.

Radiocarbon is subject to isotopic fractionation during natural processes just as ^{13}C is (e.g., when atmospheric CO_2 is incorporated into organic matter during photosynthesis), and the ^{14}C isotopic ratios measured in a sample will reflect this fractionation as well as radioactive decay. Every ^{14}R is corrected to reflect the value it would have if its δ^{13}C were −25‰; that is, it is normalized to −25‰, the δ^{13}C value of the theoretical "1890 wood" standard. If this is not done, ^{14}R would reflect both aging and isotopic fractionation. Normalizing the sample allows the user to compare ^{14}C differences between carbon reservoirs due primarily to ^{14}C decay. To normalize the sample, fractionation between ^{14}C and ^{12}C is assumed to be approximately twice that between ^{13}C and ^{12}C.[15,16] Finally, for historical purposes, HOxI is normalized to a value of −19.0‰, its most likely actual value. The fractionation correction differs depending on whether $^{14}C/^{12}C$ or $^{14}C/^{13}C$ is measured.[18] These corrections are listed below.

For labs measuring $^{14}C/^{12}C$

$$R_{sn} = R_s\left[\frac{1 + 0.001 * (-25)}{1 + 0.001 * \delta^{13}C_s}\right]^2 \quad (2)$$

where

$$\delta^{13}C = \left[\frac{{}^{13}R_{sample}}{{}^{13}R_{standard}} - 1\right] \times 1000$$

For labs measuring $^{14}C/^{13}C$

$$R_{sn} = R_s\left[\frac{1 + 0.001 * (-25)}{1 + 0.001 * \delta^{13}C_s}\right] \quad (3)$$

where s refers to sample and n indicates R has been normalized.

Radiocarbon values are usually reported as fraction modern (fm), percent modern (pM), radiocarbon age (^{14}C yr), or Δ^{14}C. These terms are used as defined in Stuiver and Polach 1977[14] with the additions and amendments described in Stuiver,[19,20] Mook,[21] and Long[22] and as summarized here. Based on these definitions, we can express the terms used to report radiocarbon values as follows:

$$\text{fm} = 0.01(\text{pM}) = R_{sn}/R_m \quad (4)$$

$$^{14}\text{C yr} = -8033 \ln(\text{fm}) \quad (5)$$

where 8033 year is based on the Libby half-life of ^{14}C

$$\Delta^{14}\text{C} = 1000[\text{fm} \exp^{-\lambda(y-1950)} - 1] \quad (6)$$

where y is the year of sample collection or growth year of the sample and $\lambda = 1.201 \times 10^{-4}$ is the decay constant for ^{14}C based on the real half-life.[14]

The relationship of each of these terms is shown in Figure 1. fm and pM report the fractional amount of ^{14}C in a sample

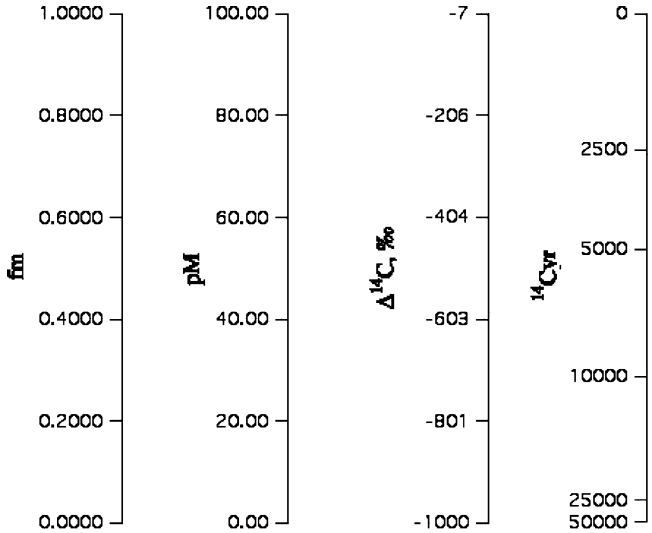

Figure 1. The relationship of four radiocarbon scales commonly used in ocean biogeochemistry. The Δ^{14}C scale is calibrated for a sample collected in 2006. Definitions of the terms appear in the text.

relative to that found in the standard. A radiocarbon age, ^{14}C yr, is not a calendar or chronological age and must be calibrated. In oceanography and carbon cycle studies, the concept of age is particularly problematic. The variety of carbon sources to the ocean and the mixing and movement of different water masses result in carbon with a variety of ages being used in all parts of the carbon cycle. Because of this, Δ^{14}C, which normalizes the radiocarbon content of a sample to the same δ^{13}C (−25‰) and time point (1950), is

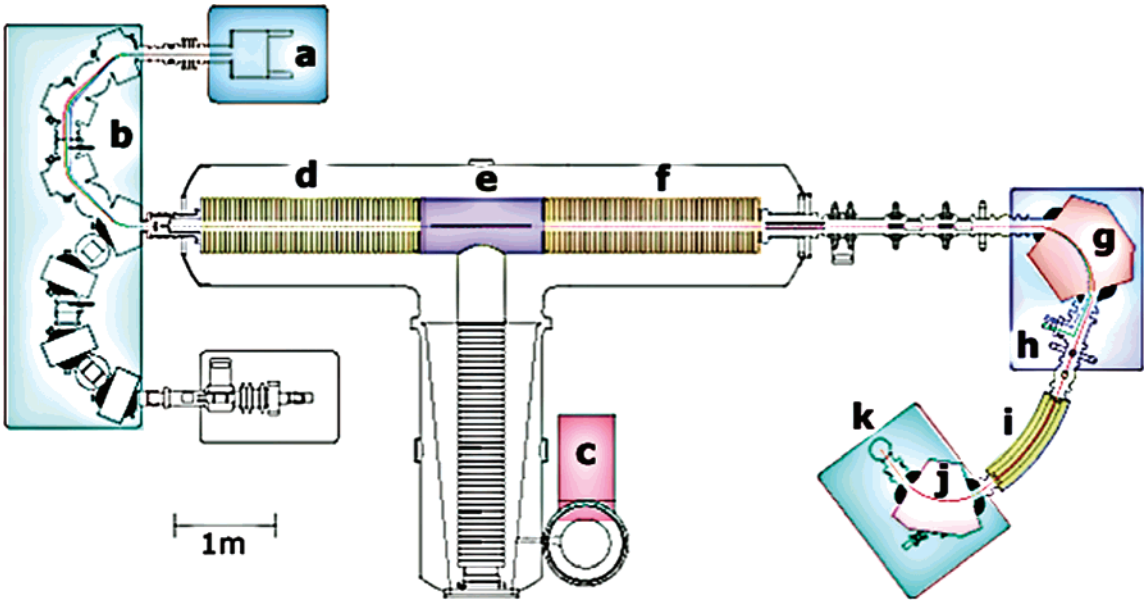

Figure 2. Schematic of a 3 MV AMS in operation at the National Ocean Sciences AMS Facility (NOSAMS). Detailed descriptions of the (a) ion source, (b) recombinator region, (c) power supply, (d and f) accelerator tubes, (e) stripper canal, (g and j) analyzer magnets, (h) Faraday cups, (i) electrostatic deflector, and (k) ^{14}C detector appear in the text.

a useful parameter. Further, it is a linear quantity and can be used in mass balances. In this review, when we report a radiocarbon value and its associated error, we refer to the 1 sigma error unless otherwise stated.

2.3. Decay Counting

Prior to the 1980s, all radiocarbon measurements were made by counting the radioactive decay products of ^{14}C, either with gas proportional or liquid scintillation counting. Comprehensive reviews of these techniques exist (e.g., Polach[23]), and they will not be covered in detail here. Decay counting techniques severely limited the scope of radiocarbon studies because of the size of the sample required (grams of carbon) and the time required to collect precise results (days to weeks). The heroic efforts of early researchers to collect and measure radiocarbon samples in the ocean using these techniques provided information that started to reveal the complexity of the carbon cycle and demonstrated the potential insight that could be gained if detection limits for ^{14}C could be improved. Although research is still conducted using counting methods, accelerator mass spectrometry (AMS), a much more sensitive technique, is eclipsing these studies with its tremendous advantages.

2.4. Accelerator Mass Spectrometry

In the 1970s and 1980s, AMS was developed to measure ^{14}C and other rare isotopes.[24] The marriage of middle energy physics with mass spectrometry allowed analysts to count the number of ^{14}C atoms in a sample rather than wait for a decay event to occur. This reduced the amount of time required to count a sample precisely to less than an hour and the amount of sample required to milligram quantities. This revolutionary development opened the world of radiocarbon to many more researchers. In its infancy, it was presumed that AMS could never achieve the same level of precision as decay counting. This has proven untrue, and laboratories routinely achieve precisions of 3−7‰ on modern samples of a standard size (>500 μg C). With abundant sample, a high-energy ion source, and an increased number of standards during analysis, even higher precision can be obtained (2−3‰).[25] For most biogeochemical studies, however, standard precision levels are more than adequate. A brief description of AMS as it applies to the study of radiocarbon follows.

A number of different accelerators are in use around the world for the analysis of radiocarbon, and we will not describe all the variations that exist. An example is shown in Figure 2, and the lettered sections of the accelerator shown in the figure are described in detail in the following text (marked in bold here). Currently, most radiocarbon laboratories prepare targets for AMS by converting the carbon in a sample to filamentous carbon generated on a metal catalyst. The solid carbon and metal sample, commonly referred to as a graphite target, is compressed into a target holder and transferred to the ion source (**a**). Here, a cesium (Cs) ion beam directed at the sample generates negative ions from the carbon in the target. Although the production of negative ions is inefficient, ranging from 3 to 10% depending on the ion source, this is an important step. Nitrogen, which has a mass of 14 and could overwhelm the detection of ^{14}C, does not form a negative isobar. Thus, it is not converted to an ion and is effectively removed from the system. The extracted beam is passed through a magnetic region, either a recombinator (**b**) or a bouncer system. In both systems, the beam is passed through a magnet region to isolate masses 12, 13, and 14 from higher and lower mass impurities. In the recombinator system, the three masses are then "recombined" and introduced to the accelerator, while in the bouncer system, each mass is introduced to the accelerator sequentially. Sequential systems measure masses 14, 13, and, sometimes, 12. The singly charged beam(s) are passed through an accelerating potential (**d**) of 0.5−10 MV depending on the accelerator. These ions are stripped of electrons in the stripper canal (**e**) to form positively charged ions that are then passed through a second accelerating potential (**f**). The stripping process also destroys most of the molecular ions, such as $^{13}CH^-$ and $^{12}CH_2^-$, which have masses that may interfere with the detection of ^{14}C. The charge state of the positive ions depends on the accelerator that is being

used and most commonly ranges from +1 to +4. At this stage, the beam is passed through an analyzing magnet (**g**) and ^{12}C and/or ^{13}C ion currents are measured with a Faraday cup(s) (**h**). The ^{14}C beam is passed through an electrostatic deflector (**i**) that discriminates particles based on their charge/mass ratio. Radiocarbon atoms can be counted using different detectors, the most common of which are gas ionization or solid-state detectors. The energy imparted by the accelerator facilitates the measurement because the natural abundance of ^{14}C is so low relative to those of ^{12}C and ^{13}C. The molecular fragments that have masses almost identical to that of ^{14}C are more efficiently destroyed by the high energy produced in an accelerator.

Current research efforts in AMS are aimed at reducing the operating energy of the accelerator and developing a gas ion source so that CO_2 gas can be directly introduced into the accelerator.[26] Lower energy machines are smaller, are less costly to purchase and maintain, and will make radiocarbon measurements more accessible. At present the lowest energy machines in use are 500 kV, but studies are investigating the utility of using energies as low as 200 kV.[26] Evidence indicates that the 500 kV instruments can provide the same range of precision and background as larger machines. The ultimate role of gas ion sources in the natural radiocarbon field is evolving at present. Simply converting a sample to CO_2 rather than reducing it to carbon and pressing the sample into a cartridge removes a number of steps where carbon may be added as a process blank and reduces the time required to process a sample. Additionally, the gas ion sources open the possibility of directly injecting samples from separation devices such as gas or liquid chromatographs and laser ablation systems. Early gas sources modified conventional sputter sources to accept the introduction of CO_2 and were limited by the observed background and the presence of memory effects.[27] The theoretical limits for the gas ion source developed at Oxford indicate the superiority of their source for very small samples ($\leq 1-2$ μg C),[28] but in practice, the most precise results and the best backgrounds on the smallest samples are measured on solid carbon targets.[29,30] Newer studies are developing ion sources specifically designed to handle gases and show promise for natural-abundance samples. Early results from a continuous-flow AMS system indicate the possibility of obtaining 10% precision on half-modern samples containing as little as 2.5 μg C.[31]

2.5. Sample Preparation

The adoption of AMS revolutionized the radiocarbon community by reducing the size of the sample required from grams to milligrams. Successful work at these levels has led researchers to clamor for even smaller sample sizes to be run, and the AMS community has been able to reduce the size requirement to micrograms.[32,29] This development is critical to the field of ocean biogeochemistry, since most studies are carbon-limited. However, the limitations imposed by the analysis of smaller samples must be recognized. Pearson et al.[32] demonstrate the successful analysis of samples containing as little as 20 μg C with a precision of 15−25‰. dos Santos[33] demonstrated the capability to measure samples as small as 2 μg on an accelerator with a precision of approximately 30‰. This is a tremendous development that Shah and Pearson[30] demonstrate has put the capability of the accelerator ahead of the ability of organic geochemists to isolate clean samples. Any handling, whether chemical or physical, can add carbon to a sample (referred to here as a process blank), and this carbon may or may not contain radiocarbon. Specialized sample preparations, e.g., solvent extraction and chromatographic isolation, will have process blanks that depend on the specific preparation, and these must be determined for each step and/or method. Determining the age of the carbon added is more problematic. In some cases, the quantity of sample carbon is too low to allow direct measurement of an individual sample and researchers resort to standard addition techniques or pooling of samples. In general, process blanks contain ^{14}C signatures that indicate the contaminating carbon is a mixture derived from modern and dead sources. When it is not possible to measure the fm value of the process blank, it is possible to calculate a range of expected fm values for a sample by assuming the process blank is either completely ^{14}C-free (fm = 0) or totally modern (fm = 1).[34]

A comprehensive study of the sources, magnitudes, and fm values of process blanks introduced during the isolation of lipids from marine samples indicates that each step adds measurable amounts of carbon with fm values that vary from dead to modern.[30,35] The amounts vary from very small, 0.03 μg m/L from an HPLC, to somewhat large, 1 μg C from closed-tube combustion. The latter value is in the range measured by others, approximately 0.5−1.5 μg C.[32,34,36−38] Currie et al.[36] demonstrated that the combustion blank could be reduced to 0.16 μg C using the cleanest chemical techniques available. In addition, Shah and Pearson[30] show that, until the magnitude of the error in the determination of the C amount and the ^{14}C content of process blanks can be reduced, samples containing less than 5 μg C can only be measured to precisions of hundreds of per mille units. Isotope dilution is another path to analyzing the smallest samples.[32,36] Currie et al.[36] increased the amount of carbon in small samples to 25 μg C by adding CO_2 from a source whose ^{14}C content was well-known. We refer to this technique here as dilution. The dilution ratio, i.e., total mass/sample mass, was measured accurately and precisely using a small quadropole mass spectrometer. The study's results indicate that this technique limits researchers to analyzing samples containing as little as 3 μgC in studies assessing the presence or absence of ^{14}C.[17,36]

3. Distribution of Radiocarbon in the Environment

Radiocarbon is a useful, but complex, tool for studying biogeochemical cycling in the oceans. Radiocarbon formed in the atmosphere is rapidly converted to CO_2 and enters the biogeochemical cycle through physical (e.g., dissolution in seawater) and biological (e.g., photosynthesis) processes (Figure 3). $\Delta^{14}C$ values of autotrophs, e.g., photosynthetic organisms, reflect the $\Delta^{14}C$ value of the inorganic carbon source. Therefore, terrestrial and marine plants have distinct $\Delta^{14}C$ signatures reflecting the difference in $\Delta^{14}C$ of atmospheric CO_2 versus DIC in the surface ocean. Heterotrophic consumers acquire carbon with essentially the same ratio as the source of their sustenance; that is, you are what you eat. While living, organisms maintain a ^{14}C content that reflects their source carbon. Upon death, carbon exchange between the organism and the environment ceases and starts the radiocarbon clock.

The use of radiocarbon as a chronological tool directly requires that the production of radiocarbon in the atmosphere be constant over time. However, since the flux of cosmic

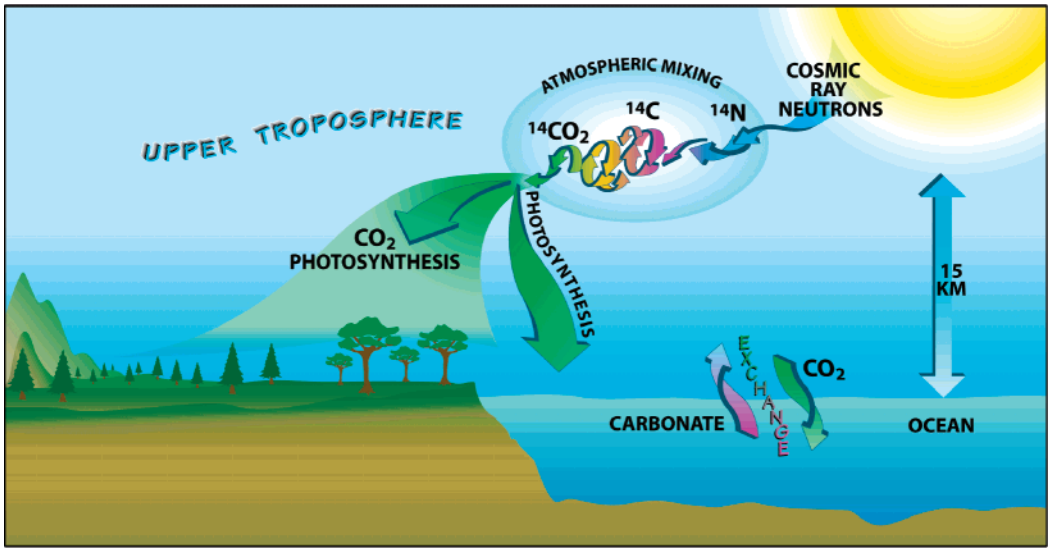

Figure 3. Illustration of the natural ^{14}C cycle (Reprinted with permission from Jayne Doucette, Woods Hole Oceanographic Institution).

rays that produce radiocarbon varies over time, the ^{14}C content of the atmosphere fluctuates. Figure 4 shows the

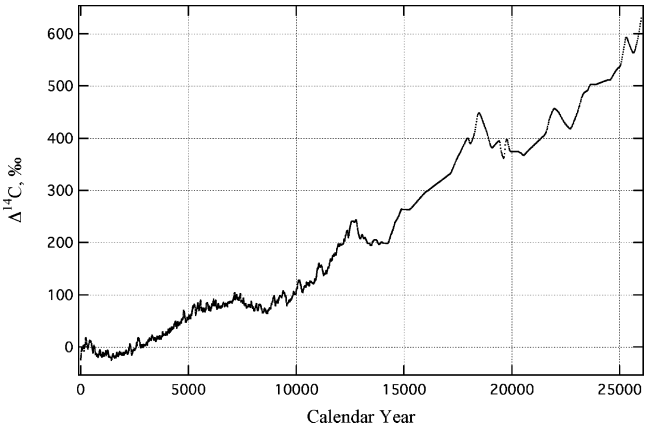

Figure 4. $\Delta^{14}C$ in the atmosphere as a function of calendar year; data obtained from INTCAL04 (references in text).

variation in atmospheric $\Delta^{14}C$ over the past 26,000 years.[39] Records of the atmospheric history of radiocarbon are stored in tree rings, and these have been used to calibrate the radiocarbon time scale.[40] Presently, the tree ring history extends back to 12,400 year, and other records are being used to extend the calibration further in time. Records preserved in corals, speleothems, varved sediments, and terrestrial cores have extended the record back to 26,000 year and are extending it to 40,000−50,000 calendar years.[13,41,42]

Anthropogenic disruptions in the atmospheric radiocarbon concentration started occurring in the 1800s. The use of fossil fuel as an energy source adds CO_2 with no ^{14}C, i.e., radiocarbon-dead, to the atmosphere and has led to an observable temporal decrease in $\Delta^{14}C$, commonly referred to as the Suess Effect.[43] From 1890 to 1950, $\Delta^{14}C$ observed in tree rings from the North American Pacific coast decreased about 20‰.[44] It was estimated that about 17‰ of this decrease was due to the addition of CO_2 from fossil fuel burning. A large ^{14}C spike was introduced into the atmosphere in the 1950s and 1960s as a result of above-ground nuclear weapons testing. This addition almost doubled the atmospheric inventory and slowly entered the surface ocean DIC reservoir through air−sea gas exchange. Figure 5 summarizes the atmospheric and surface ocean marine

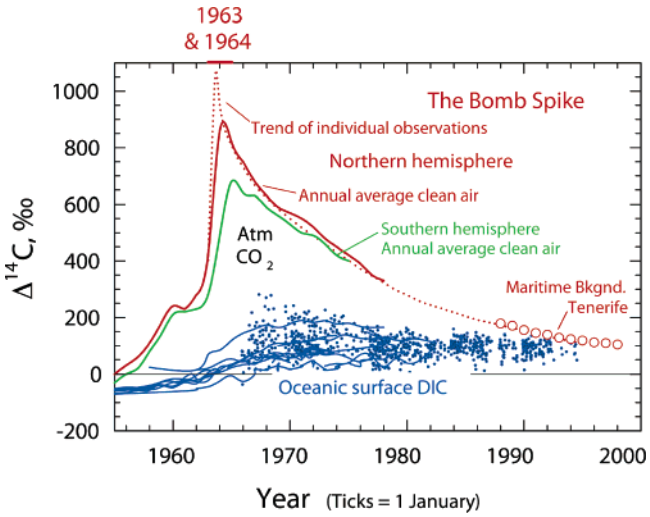

Figure 5. Radiocarbon levels ($\Delta^{14}C$) in atmospheric CO_2 and surface ocean DI^{14}C since 1955. The red dashes and circles represent individual measurements; red and green lines show annual average clean air; blue dots represent measurements of surface DI^{14}C; blue lines are ocean surface data reconstructed from coral measurements. References are cited in the text.

observations that have been made in recent times. Data for this figure were compiled from individual observations,[45−47] an annual average for clean air calculated by Tans,[48] surface water measurements collected in the Atlantic, Pacific, and Indian Oceans between 1965 and 1994,[49] and surface values derived from coral records[50,51] and accessible at http://www.ncdc.noaa.gov/paleo/coral/coral14c.html. The atmospheric spike in $\Delta^{14}C$ of CO_2 is clear and large. The appearance of the spike in surface ocean DIC is dampened and delayed due to the ocean reservoir size and to the relatively long time (approximately 10 years) required to reach isotopic equilibrium between the atmosphere and surface ocean. The hemispheric difference in the atmosphere arises because most of the weapons testing took place in the northern hemisphere and interhemispheric air mixing occurs on the time scale of 1 year. The large scatter observed in surface ocean measurements primarily reflects the complex circulation of the oceans, and not variability seen at individual locations. Although the introduction of this spike has complicated the use of radiocarbon as a strict dating tool,

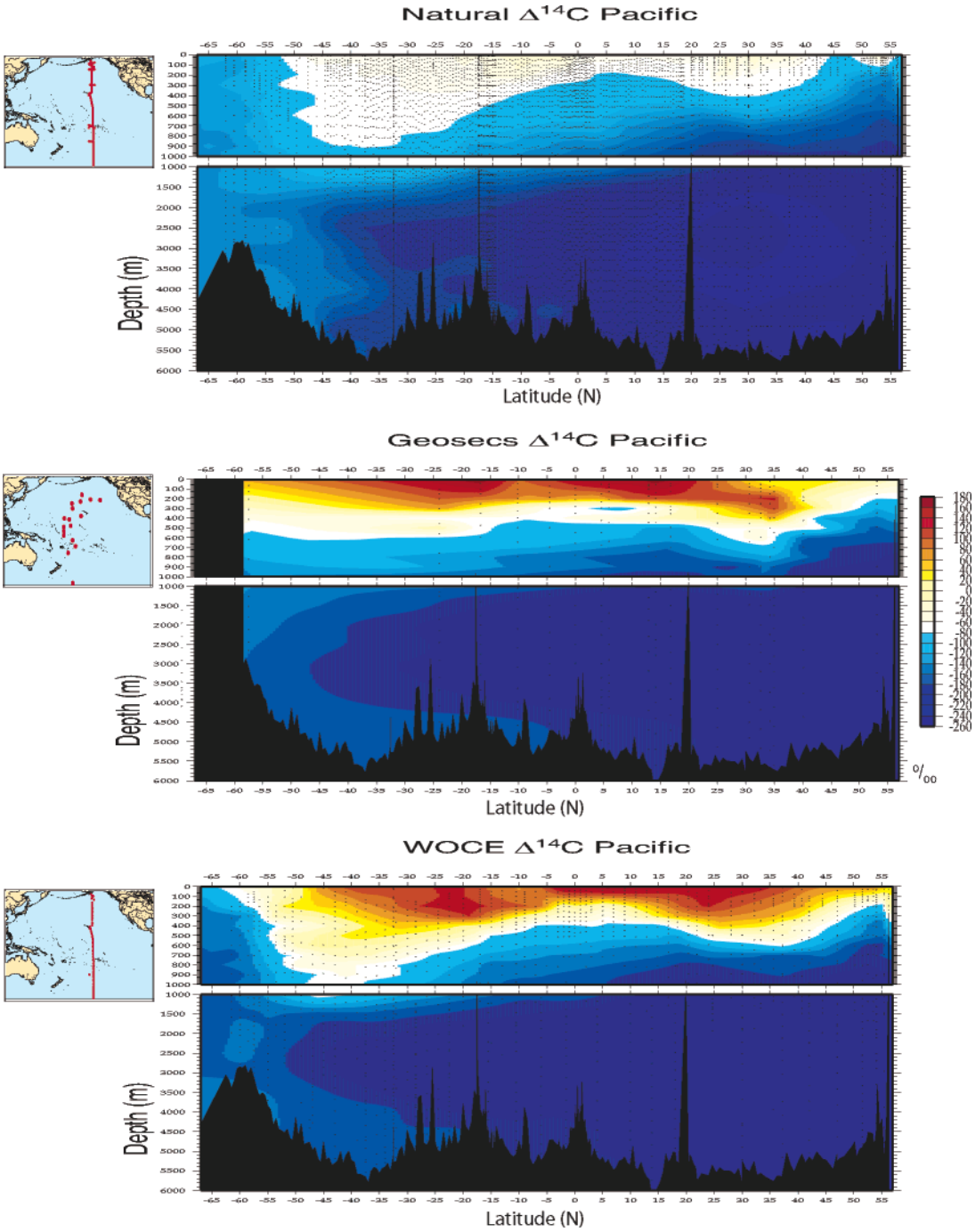

Figure 6. Vertical distribution of $DI^{14}C$ in the Pacific Ocean (a) prior to anthropogenic influence along 150°W, (b) in the 1970s in the western section from GEOSECS, and (c) in the 1990s along 150°W.

it has also acted as a useful natural experiment making it possible to trace the spike throughout natural carbon reservoirs that interact on time scales less than 50 years (i.e., time scales shorter than the time scale over which measurable decay-induced changes in $\Delta^{14}C$ occur).

3.1. Radiocarbon in the Ocean

Radiocarbon enters the ocean through many paths, but primarily through the equilibration of seawater DIC with atmospheric CO_2. Circulation of the ocean redistributes DIC, and the ^{14}C content of any parcel of water is related to both its ventilation history, i.e., the amount of time it has been isolated from exchange with the atmosphere, and its source water composition. Ocean surveys conducted in the 1970s (the GEOSECS program[52−54]), the 1980s (TTO[55] and SAVE[56,57]), and the 1990s (the WOCE program[58]) provide snapshots of the $DI^{14}C$ distribution in the world's oceans. Figure 6 shows some examples of $DI^{14}C$ patterns in the Pacific Ocean. In this figure, the top panel shows the distribution of $DI^{14}C$ prior to fossil fuel combustion and nuclear weapons testing, i.e., preindustrial, prenuclear (PIPN). The PIPN $DI^{14}C$ distribution is calculated from $\Delta^{14}C$ observations made in 1991/2 during the WOCE program and using the relationship between $\Delta^{14}C$ and potential alkalinity (PALK) observed by Rubin and Key[59] to correct for the uptake of ^{14}C introduced by anthropogenic activities. The second two panels show the distributions of $DI^{14}C$ measured during the 1970s GEOSECS program and the 1990s WOCE

program. Distinct patterns of high and low values of $DI^{14}C$ are evident and arise from the circulation patterns of the ocean. The uptake of bomb radiocarbon is most evident in the gyres (10°S−40°S and 5°S−40°N) where there is more time for equilibration with the atmosphere. The ^{14}C depletion resulting from radioactive decay in North Pacific Deep Water is seen in each figure; this is the oldest water mass in the ocean, and its $\Delta^{14}C$ values correspond to over 2000 ^{14}C yr. Different but similarly distinct patterns in $DI^{14}C$ are present in all ocean basins. General patterns that are evident in other regions are the transfer of ^{14}C to greater depths in regions of deep water formation and the transfer of ^{14}C-depleted waters to the surface through upwelling. Descriptions and data can be found in the literature (references above) and on Web sites (e.g., http://www-pord.ucsd.edu/whp_atlas/; http://cdiac3.ornl.gov/waves/). Based on Figure 6 (last panel), it is clear that bomb ^{14}C is present throughout the surface ocean DIC reservoir, but below approximately 2000 m in the Pacific, there is little evidence of bomb ^{14}C. If other reservoirs of carbon in the deep ocean and sediments contain bomb ^{14}C, it must be delivered via sinking inorganic and organic particles originating in the surface ocean.

Detailed time histories of $DI^{14}C$ in the surface ocean are recorded in ocean corals and long-lived mollusks. These histories augment the global snapshots obtained during the water sampling programs and provide a way to directly measure prebomb $DI^{14}C$ in the ocean. Marine prebomb $DI^{14}C$ values are required to accurately interpret the cycling of carbon through the various reservoirs. For example, estimating the time scale on which deep water masses circulate requires both the vertical $\Delta^{14}C$ distributions shown in Figure 6 (for example) and a measure of prebomb $DI^{14}C$ (i.e., the $\Delta^{14}C$ signature of these water masses at the time of last contact with the atmosphere). In the western equatorial Pacific Ocean, a high-resolution coral record collected near Nauru Island[60] (Figure 7) demonstrates the intrusion of the

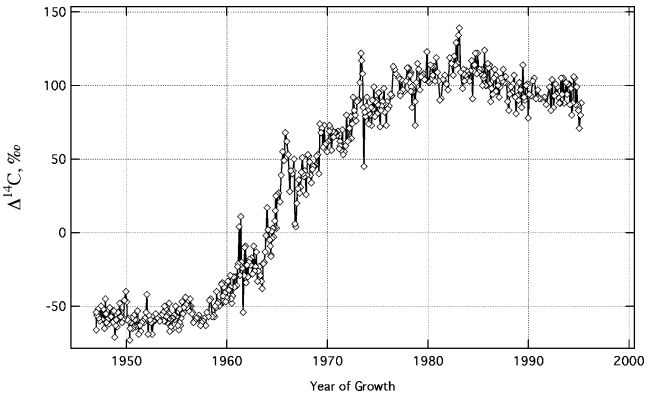

Figure 7. High-resolution record of $\Delta^{14}C$ in coral collected at Nauru Island in the western equatorial Pacific (references in text).

atmospheric bomb signal into the surface ocean and also points out the impact of regional ocean processes. Strong deviations from the general trend are correlated with El Nino−Southern Oscillation (ENSO) events, and the magnitude and direction of the deviation can be explained as ENSO-driven changes in the amount of upwelling at this site.[61] Records exist for corals collected in other Pacific locations,[50,51] the Atlantic,[62] and the Indian[63−65] Ocean. The $DI^{14}C$ history of regions where corals do not grow has been documented using other strategies. In the North Atlantic, for example, records have been obtained from Arctica Islandica, a long-lived mollusk,[66] and in the North Pacific, archived fish scales may provide a means of obtaining these records. In the ocean, the radiocarbon content of organisms and their organic molecules will depend heavily on the region and depth of the ocean where they were produced and, more recently, when they were produced.

3.2. General Biogeochemical Cycle of Radiocarbon

In addition to equilibration of the surface ocean with the atmosphere, radiocarbon enters the marine environment through other pathways. Radiocarbon signatures of bulk pools of organic carbon in the ocean and the pathways by which ^{14}C can be added to the ocean are summarized in Figure 8. Allocthonous carbon, with its burden of ^{14}C, enters from the terrestrial environment through river runoff, erosion, and atmospheric deposition from dust. This material can consist of fresh and pre-aged carbon from a variety of different sources with a full spectrum of chemical reactivity. Carbon can enter the water column from the subsurface as well, e.g., diffusion from sediment pore water, seeps from petroleum and gas reservoirs, hydrothermal vents, and resuspension of surface sediments. Biogeochemical processes in the ocean repackage and redistribute inorganic carbon and impact the observed radiocarbon distributions. Auto- and heterotrophy in the upper water column produce organic matter that can become a source of DIC, DOC, and POC throughout the water column. The majority of organic carbon within the ocean is derived from photosynthesis in surface waters, thus $DI^{14}C$ in surface waters is expected to have the greatest influence on the ^{14}C content of organic matter throughout the water column. As will be clear in the following sections (and as shown in Figure 8), the $\Delta^{14}C$ of some fractions of marine organic carbon deviates from this expectation. For example, the presence of DOC with depleted $\Delta^{14}C$ values despite delivery of fresh organic matter to the deep water column and surface sediments remains a mystery that is currently the subject of much study. Also, chemoautotrophic synthesis of organic matter in the deep ocean can produce some new organic matter with depleted radiocarbon signatures.

In general, carbon from a variety of sources has the potential to become actively involved in marine biogeochemical cycles. Distinct radiocarbon signatures of the many pools lead to the power of this tracer in studies of carbon cycling, yet the overlapping signatures of many of the reservoirs lead to great complexity, making it difficult to delineate the exact interactions between reservoirs and assign unique processes that contribute to the observed signal. It is usually upon this complex stage that biogeochemical processes take place. The following discussion will provide examples of both the strength and challenges associated with using this tracer while highlighting the unique insights into marine carbon biogeochemistry that it provides.

4. Dissolved Organic Carbon

4.1. Measurement/Isolation Techniques

Marine DOC is a complex pool of carbon and its collection, isolation, and preparation for radiocarbon measurement require careful consideration and definition in order to provide meaningful results for the oceanographic community. As shown in Figure 9, DOC is not a discrete and

caution researchers to carefully examine the available techniques, document the methods used, and realize that techniques appropriate for CN analyzers may not be appropriate for the sample size required for radiocarbon analysis.

5.2. Radiocarbon Studies of POC

The initial study of radiocarbon in POC was performed using β-decay counting methods on sinking particles collected in a sediment trap in the eastern sub-Arctic Pacific Ocean.[112] Results indicated that $PO^{14}C_{sink}$ was greater than $DI^{14}C$ in the ocean and suggested that there was a significant input of modern terrestrial organic matter to the traps through lateral advection. The advent of AMS led quickly to increased numbers of studies of the sinking as well as the suspended particulate pool.

The first study of the suspended pool demonstrated that its radiocarbon profile at both an oligotrophic site and a moderately eutrophic coastal basin was very different from that of either $DI^{14}C$ or $DO^{14}C$.[108] At a station in the North Central Pacific (NCP; Figure 13), $PO^{14}C_{susp}$ values ranged from 139 to 43‰ from the surface to 5700 m, decreasing throughout the water column. In the Santa Monica Basin, $PO^{14}C_{susp}$ showed similar values and trends with depth: from surface to 900 m, $PO^{14}C_{susp}$ decreased from 110 ± 13‰ at 100 and 200 m to approximately 0‰. These data confirmed that POC_{susp} has relatively short residence times (years to decades) in the ocean, even at depth, as bomb-^{14}C was present in this reservoir throughout the water column. $PO^{14}C_{sink}$ collected at approximately 4000 and 5000 m averaged 83‰ at the NCP site, greater than the $PO^{14}C_{susp}$ at corresponding depths, indicating that the sinking pool has a higher percentage of material from the surface than the suspended pool; these data further suggested that distinct processes must act on sinking versus suspended POC in the deep ocean.

Figure 13. Radiocarbon profiles of $\Delta^{14}C$ in DIC (open triangles), POC_{susp} (blue circles and red diamonds), and POC_{sink} (filled squares) in the (A) Atlantic and (B) Pacific Oceans. $PO^{14}C_{susp}$ profiles are shown at open ocean sites (filled blue circles) and shallow margin sites (red diamonds). Data from Druffel et al.[5,108] and Bauer et al.[73]

Figure 14 shows the processes that might be responsible for the decrease in $PO^{14}C_{susp}$ with depth. The similarity of the surface water $PO^{14}C_{susp}$ to the surface water $DI^{14}C$ coupled with the presence of bomb carbon in POC_{susp} throughout the water column indicates that most of the POC originates from recent primary production at the surface ocean. As only POC_{sink} can move through the water column rapidly enough to deliver bomb carbon to the deep ocean, measured $PO^{14}C_{susp}$ requires that sinking particles disaggregate during their transit through the water column, supplying the suspended POC reservoir. However, the decrease in $PO^{14}C_{susp}$ with depth was not expected based on concentration studies of POC and other studies of the residence time of POC in the water column. Druffel and Williams[108] speculated that older carbon was incorporated into the deeper POC_{susp} through either the sorption of old DOC from depth, chemosynthetic production of POC_{susp} using older DIC from depth, or, for sites near margins or slopes, incorporation of older carbon from resuspended sediments. Additional sources not discussed in this study include the incorporation of ^{14}C-dead material from hydrocarbon seeps and the possible effects of remineralization. POC_{susp} at the surface may be a mixture of a variety of types of organic matter,[126] each with its distinct radiocarbon content. Preferential remineralization of fresh/labile fractions could explain the decrease in $PO^{14}C_{susp}$ with depth. Alternatively, the residence time (i.e., replacement time) of POC_{susp} may be longer at depth if, for example, the supply of carbon to this reservoir from POC_{sink} also decreases with depth. Although the values and depth trends were similar at both open ocean and basin sites, it seemed likely that different processes were responsible. In the basin, episodic resuspension of slope sediments was likely to add older sedimentary material to POC_{susp}. This process seemed far less likely at the north Pacific site. Assuming that sorption of DOC was the only process responsible for aging of POC_{susp} in the North Pacific, using the average $\Delta^{14}C$ of POC_{susp} from samples below 1800 m and an average concentration of 0.1 μmol C/L, mass balance calculations indicate that 14% of the carbon comes from DOC, or only 0.25% of the DOC pool. If sorption of DOC is a major source of the older carbon, then it is possible that POC_{susp} can transfer old carbon from mid-depths of the ocean to the deep water. Rau (1991)[113] pointed out that the uptake of deep water $DI^{14}C$ onto POC by particle associated microorganisms could be another potential source for the decrease in $PO^{14}C_{susp}$ with depth.

Further studies of radiocarbon in POC at the North Central Pacific (NCP) site coupled with a study in the Sargasso Sea (SS) in the Atlantic Ocean revealed similar patterns to those described above.[5] $PO^{14}C_{susp}$ values were always similar to or greater than $DI^{14}C$ values at corresponding depths, confirming the predominant origin from surface-produced organic matter. In the NCP, $PO^{14}C_{susp}$ decreased from 147 ± 13‰ in the surface 100 m to 37 ± 17‰ between 4200 and 5720 m. The concentration of POC_{susp} decreased from 2.6 to 0.05 μM over the same depth intervals. $PO^{14}C_{sink}$ values collected at 4200 and 5120 m were 99 and 136‰, respectively, greater than $PO^{14}C_{susp}$ at the same depths. In the Atlantic, the average value of $PO^{14}C_{susp}$ in the surface 100 m was 124 ± 7‰, similar to that observed in the NCP, and the values at 3600, 4000, and 4450 m were −26, −92, and 76, respectively. The deep values showed far more variability than was observed in the NCP. The value for $PO^{14}C_{sink}$ at 3200 m was 66‰, greater than that measured in the suspended pool at the same depths. The overall decrease in $\Delta^{14}C$ values with increasing depth at both these sites was consistent with previous observations suggesting the incorporation of old carbon into POC_{susp} or the selective preservation of the older components of POC_{susp} as it cycles

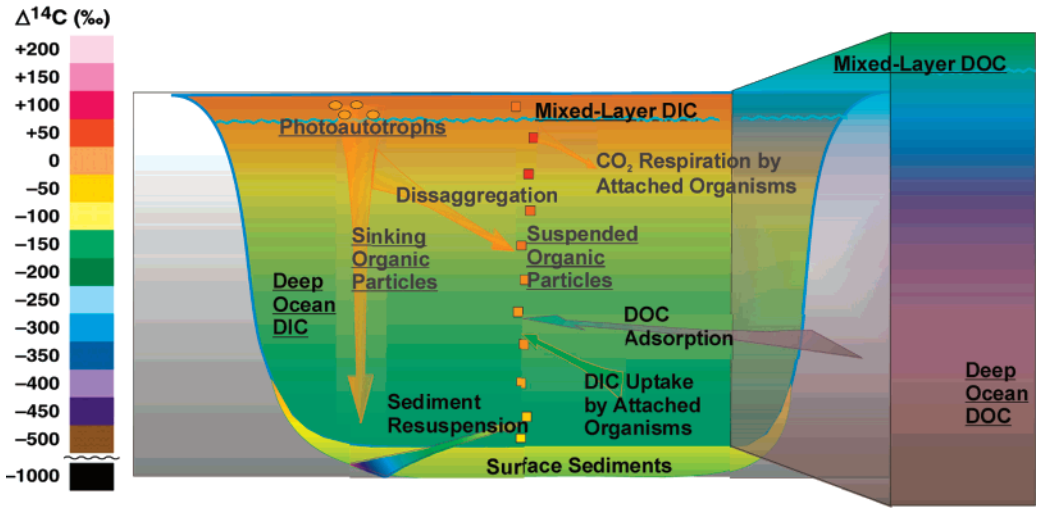

Figure 14. Processes potentially responsible for the decrease in $PO^{14}C_{susp}$ with depth in the water column. Adapted with permission from Pearson, A., Biogeochemical Application of Compound-Specific Radiocarbon Analysis. Ph.D. Thesis, MIT/WHOI: 2000; 00-01. Copyright 2000 A. Pearson.

down the water column. $PO^{14}C_{sink}$ was also greater than $PO^{14}C_{susp}$ at similar depths. Decreasing concentrations of POC_{susp} with depth lend further support to the theory that part of the observed decrease in $PO^{14}C_{susp}$ may result from a slower replacement time, from POC_{sink}, for this reservoir in the deep ocean.

The low concentration of POC and its likely rapid transport to depth imply that seasonal changes in $\Delta^{14}C$ may be reflected in POC_{susp} at depth. To address the issue of seasonality, $PO^{14}C$ measurements were made at four separate times at one site in the northeast Pacific Ocean (Station M): February, June, and October of 1992 and July of 1993.[114] This site showed seasonal variability in the magnitude of the POC flux with the highest pulses of 10−25 mg C m^{-2} day^{-1} seen in the late spring and early fall and the lowest fluxes of 1−3 mg C m^{-2} day^{-1} in the winter months.[115] Fluxes lower than normal were observed in spring 1992 due to the influence of an El Niño Southern Oscillation (ENSO) event.[114] At all times, $PO^{14}C_{susp}$ decreased with depth although the magnitude and profile of the decrease varied from one sampling period to the next. The overall universal decrease suggested a similar mechanism governed by the observed drop in $\Delta^{14}C$ with depth.[114] Values of $PO^{14}C_{susp}$ measured in the surface 100 m averaged 58 ± 16, 65 ± 7, 50 ± 10, and 75 ± 7‰ in February, June, October, and July, respectively. Compared to values from the deepest samples that were not influenced by resuspension of bottom sediments, gradients of 54, 105, 48, and 92‰ were observed in February, June, October, and July, respectively. Concentrations of POC decreased from values of 3.29−6.53 μM C at the surface to 0.1−0.2 μM C at depth. The most depleted profiles of $PO^{14}C_{susp}$ were observed in June and July. The most similar radiocarbon profiles were observed in February 1992 and October 1992, the times with the greatest disparity in fluxes (October had the highest flux). In general, this study revealed that measurable changes in $PO^{14}C_{susp}$ occur over relatively short time periods throughout the water column but that, despite the magnitude of the seasonal changes, $PO^{14}C_{susp}$ always decreases with depth. If sorption of old DOC were the primary mechanism for the decrease, 7−12% of the POC_{susp} below the surface must be from this source. $PO^{14}C_{sink}$ showed a negative correlation with flux; that is, the higher the $\Delta^{14}C$, the lower the flux of POC. This appeared counterintuitive given that the higher flux was presumed to arise from surface-derived organic matter during periods of high primary productivity. However, the coincidence of the lowest concentrations of DOC with the highest particle fluxes and the lowest $PO^{14}C_{sink}$ suggested that POC could strip DOC from the water column.[82,114] As this DOC has depleted $\Delta^{14}C$ values, sorption of DOC would lead to a decrease in $PO^{14}C_{sink}$ despite the higher flux of POC out of surface waters. This process also acts as a sink for DOC—transporting carbon from the DOC pool to the benthos.

Further studies of $PO^{14}C_{susp}$ at Station M, the abyssal site in the northeast Pacific, confirmed the patterns noted above.[116] Surface values of $PO^{14}C_{susp}$ were determined by the surface $DI^{14}C$; thus, changes observed in surface values of $PO^{14}C_{susp}$ at Station M over the course of almost a decade were related to the changes observed in $DI^{14}C$ due to the decrease in atmospheric ^{14}C content and the penetration of bomb ^{14}C deeper into the water column (Figures 5 and 6). The importance of $DI^{14}C$ in establishing the surface $PO^{14}C_{susp}$ is demonstrated particularly well in the Southern Ocean, where surface values of both $DI^{14}C$ and $PO^{14}C_{susp}$ (approximately 3 to 25‰ and −20 to −30‰, respectively) are much lower than those in the Pacific and Atlantic Oceans.[69] As demonstrated in Figures 6 and 10, the surface waters of the Southern Ocean have some of the most ^{14}C-depleted DIC in the ocean, although the deep water values are in between those in the Atlantic and the Pacific. At Station M, $PO^{14}C_{susp}$ values decreased by hundreds of per mille down the water column as the concentration of POC decreased by 2 orders of magnitude. A summary of the observations indicated that, at times of moderate flux, $PO^{14}C_{susp}$ values in the deep water column were less than that at times of low flux. Anomalously high values of $\Delta^{14}C$ at one time period appeared related to an anomalously high particle flux, different from what was seen during the seasonal study. It was suggested that, during this study, the flux of material was so great that the large amount of recently synthesized material passing through the water column contributed relatively larger amounts of modern carbon to the POC_{susp} pool and increased its $\Delta^{14}C$ value. This conclusion is consistent with studies showing that the suspended particulate pool turns over rapidly in the water column.[117]

Bauer and Druffel[82] investigated the transport of organic material from the margins to ocean gyres as a potential source of older carbon to deep POC. $PO^{14}C_{susp}$ at margin sites in

the western North Atlantic and eastern North Pacific Oceans was depleted relative to that measured in the central gyres of each ocean by greater than 100‰ in some cases. The carbon at these margin sites was more enriched in ^{13}C than that expected from studies of carbon supplied to coastal waters, indicating that it had a primarily marine source. The source of this older, marine carbon was speculated to be resuspended shelf and slope sediments. Using the margin data in an isotopic mass balance to constrain the sources of carbon to POC_{susp} in the ocean gyres indicated that up to 85% of the gyre carbon may have been advected from the margins. Studies of $PO^{14}C_{sink}$ support the transfer of older material from the margins. In the mid-Atlantic Bight, $PO^{14}C_{sink}$ in a trap at 1000 m was 120‰ lower than that in a 30 m trap, suggesting the lateral transport of POC at depth to this site from margin environments.[109] In the Okinawa Trough in the western Pacific, values of $PO^{14}C_{sink}$ less than surface $DI^{14}C$ were attributed to lateral transport of material from the East China Sea.[110]

At this stage, of the potential explanations suggested for the observed decrease in $PO^{14}C_{susp}$ with depth (Figure 14), sorption of old DOC seemed the most important with the advection of material from the shelf and slope temporally and spatially important. It is also clear that seasonal and secular events have a great influence on snapshot profiles in ways that are not always easy to predict and are more pronounced in POC than in DOC.

Temporal changes over time scales of 5 to 10 years are now evident in $DI^{14}C$ in the open ocean. Reoccupation of central gyre sites in the Atlantic and Pacific Oceans (NCP and SS) allowed Druffel et al.[118] to study the link between significant changes in $PO^{14}C_{susp}$ over a decade and the history of the bomb signal in the ocean. In the Pacific, there was a decrease of 32 ± 15‰ in $PO^{14}C_{susp}$ throughout the water column over a decade. In the Atlantic, there was a decrease of 26 ± 9‰ in the upper 200 m and a increase of 15 ± 8‰ between 600 and 3200 m over the same time period.[118] In the Pacific, it is likely that the change over time is due to the decrease in surface $DI^{14}C$ observed as the bomb signal is reduced in the atmosphere. A box model relating the observed differences was used to estimate the overall turnover time for POC_{susp} to be 8.5 year. This value is consistent with early thorium isotope studies which indicated residence times between 5 and 10 years for the suspended particulate pool.[104] The heterogeneous changes in $\Delta^{14}C$ seen at the deep Atlantic site made such calculations impossible and might be related to the episodic influence of lateral advection on POC_{susp}.

As more studies demonstrated the complexity of the influences on the radiocarbon content of POC, detailed studies of specific components of POC were undertaken. These studies focused on sinking POC because of sample size issues. Two samples of POC_{sink} collected at Station M in the Pacific Ocean in June 1993 were separated into four chemical groups.[119,120] The samples were collected at 3450 m and represented 9 day collections from the beginning and end of June. Organic matter was separated into total hydrolyzable amino acids (THAA), total carbohydrates (THCO), lipid, and acid-insoluble fractions. POC_{sink} was comprised of, on average, 26% THAA, 19% TCHO, 12.5% lipids, and 48% acid-insoluble material. Average radiocarbon values for the fractions were 56, 24, −1, and −23‰, respectively, and 15‰ for the bulk material. (A mass balance of the fractional amount of each chemical group and their radiocarbon values will not yield the bulk value because we are using average radiocarbon values that have not been mass adjusted.) The range of values observed in the different chemical fractions points to the complexity of the sources of POC_{sink} at depth and/or the mechanisms responsible for altering the biochemical composition of POC_{sink} as it passes through the water column. The values also confirm the influence of surface productivity on the entire pool of POC_{sink}. $DO^{14}C$ values at this site varied between −244 and −312‰ in the surface 85 m from 1991 to 1993 and averaged −540‰ between 1600 and 4050 m,[120,121] and so, fraction-specific sorption of a small amount of DOC could drive the observed decrease in $\Delta^{14}C$ of some chemical fractions. A more extensive study of the same compound classes isolated from POC_{sink} at the same depth and site showed the same general observations; that is, the lipids and an acid-insoluble fraction were depleted relative to the bulk POC_{sink}, and amino acids and carbohydrates had similar values.[122] Linear regressions of $\Delta^{14}C_{chemical\ group}$ vs $PO^{14}C_{sink}$ produced lines for each chemical group that intersected at the value of $DI^{14}C$ at the surface. This suggests that at least a fraction of the carbon in each chemical group was acquired as a result of surface ocean biological production.

To test whether sorption of old DOC to POC could explain the decrease in $PO^{14}C_{sink}$ with depth in the water column, Hwang et al.[123] incubated freshly collected, acidified, and dried plankton in freshly collected Sargasso Seawater for 13 days. In incubations with and without added poison, $PO^{14}C$ values decreased over time, with the greatest changes observed in the experiments that contained no poison. $\Delta^{14}C$ values decreased 96, 200, and 125‰ in the bulk, lipid, and acid-insoluble material in the unpoisoned experiment, respectively. Values decreased 30, 30, and 18‰ for the same classes in the poisoned experiment. Sorption of older DOC, enhanced by biological alteration of the surface of particles, was the most likely explanation for these results.

5.3. Summary

Studies of $PO^{14}C$ have greatly enhanced our knowledge of the cycling of particulate matter in the ocean. $PO^{14}C$ values throughout the water column, whether sinking or suspended, demonstrate that the primary source of this carbon is recent material produced at the surface of the ocean. As the surface ocean $DI^{14}C$ has changed over the past decade, so has the $PO^{14}C$. Decreases in $PO^{14}C$ values with increasing depth in the water column are universal: the global nature of these observations is summarized in Figure 15. In this figure, based on Druffel et al.,[118] we have plotted the difference between surface $DI^{14}C$ ($DI^{14}C_{sfc}$) and $PO^{14}C_{susp}$ values observed at depth as a function of the distance of each sampling location to the nearest continental shelf as well as a function of the water column depth at each site. Here, we calculate $DI^{14}C_{sfc}$ using the average of values measured in the surface 100 m and $PO^{14}C_{susp}$ using the value measured approximately 500 m above bottom. The differences for all but one site (a value of −390‰ was calculated for one mid-Atlantic Bight site and is out of the range of the graphs in Figure 15) range between approximately 50 and 200‰ and are not related to the proximity to the continental shelf or to the water column depth. It is also evident from Figure 15 that more radiocarbon data are needed to understand the processes affecting $PO^{14}C$. Studies of $PO^{14}C$ in a range of size fractions will provide more information about the sources and processes affecting this pool of carbon. The ability to measure smaller samples

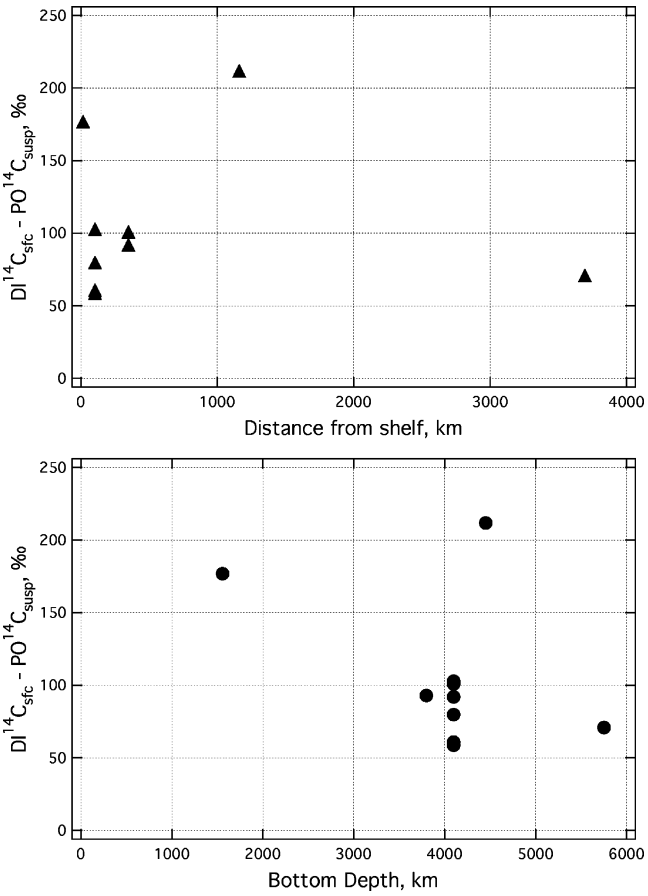

Figure 15. Difference between surface $DI^{14}C$ and $PO^{14}C_{susp}$ at depth as a function of distance from the nearest continental shelf and as a function of bottom depth.

accurately and precisely will make these types of studies easier. In general, however, coupled with evidence supporting both sorption of DOC and lateral advection of older material from the shelf and slope, the body of radiocarbon data discussed here suggests that both processes are equally important at all locations in the ocean.

Compound-specific radiocarbon analyses will also shed light on the nature and reactions of POC throughout the water column, although these studies are hindered by the ability to collect enough material for analysis. To date, only one study reports results on the radiocarbon content of specific compounds extracted from POC_{susp} in the mesopelagic ocean.[35] The study of archaeal lipids from the surface and 670 m in the subtropical North Pacific Gyre required the filtration of 100,000 and 200,000 L of seawater, respectively. Radiocarbon results on the individual archaeal lipids demonstrated that, at 670 m, the dominant metabolism of the archaea is autotrophy, yet some heterotrophy must be invoked to fully explain the observed $\Delta^{14}C$ values. These data also demonstrate that the uptake of local DIC by particle associated microorganisms must be considered when interpreting the $PO^{14}C_{susp}$ data. Studies targeting other biogeochemically relevant molecules will certainly lead to more insights into this dynamic pool of carbon although they will not be possible without the development of different methods for collection, isolation, and measurement.

6. Summary and Future Directions

The power of radiocarbon for studying the biogeochemistry of marine organic matter lies in its ability to provide unique information about the sources and residence time of carbon in different reservoirs. Analytical advances in both isolation and measurement capabilities have allowed more detailed isotopic investigations of the carbon in the ocean's reservoirs and are expanding our understanding of ocean biogeochemistry. This review has focused on two reservoirs, DOC and POC, but the next decade will see a great expansion in the application of radiocarbon to biogeochemical studies. Compound-specific radiocarbon analyses will expand, and radiocarbon will be studied in process-specific chemicals in the water column, just as it is now in sediments. This will expand our knowledge of the pathways of carbon transfer in the modern ocean. For example, application to problems in microbial ecology, as has occurred with ^{13}C, is likely to yield valuable and unique insights.

One poorly understood, but important, carbon reservoir in the ocean is that of black carbon (BC). BC has been recognized as an important link in the global carbon cycle for many years,[124] and it is a particular category of organic carbon in the ocean whose properties straddle the DOC/POC definition. Radiocarbon measurements of BC isolated in particles in the ocean will be critical for understanding the role of BC in the global carbon cycle. The supply of BC to the oceans from the atmosphere and the terrestrial environment is large enough to support the inventory found in the sediments, yet it is not known whether the BC that enters the ocean is transported rapidly to the underlying sediments or whether it is incorporated into pools of organic carbon that reside in the water column for significant periods of time prior to being removed to the sediments. The radiocarbon content of both the sources and the resident pool will help to answer this question.

The challenges for future researchers are many. As the capabilities of AMS and isolation techniques improve, the smaller samples that can be analyzed will require detailed and thorough assessments of process blanks and the implications of isotopic mixing and fractionation processes on ^{14}C measurements.[125] The realization of continuous flow AMS for natural-level measurements, now under development, will open the field to new ways of using ^{14}C to study biogeochemical processes. Completed research has demonstrated the power of radiocarbon, and the future holds promise for new and exciting applications.

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