MARINE ORGANIC CARBON AND RADIOCARBON—PRESENT AND FUTURE CHALLENGES

Ellen R M Druffel[1]* • Steven R Beaupré[2] • Hendrik Grotheer[3] • Christian B Lewis[1] • Ann P McNichol[4] • Gesine Mollenhauer[3] • Brett D Walker[5]

[1]Department of Earth System Science, UC Irvine, Keck Carbon Cycle AMS, Irvine, CA, USA
[2]School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY, USA
[3]Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Marine Geochemistry, Bremerhaven, Germany
[4]Department of Geology and Geophysics, Wood Hole Oceanographic Institution, Woods Hole, MA, USA
[5]Department of Earth and Environmental Sciences, University of Ottawa, Ottawa, ON, Canada

ABSTRACT. We discuss present and developing techniques for studying radiocarbon in marine organic carbon (C). Bulk DOC (dissolved organic C) $\Delta^{14}C$ measurements reveal information about the cycling time and sources of DOC in the ocean, yet they are time consuming and need to be streamlined. To further elucidate the cycling of DOC, various fractions have been separated from bulk DOC, through solid phase extraction of DOC, and ultrafiltration of high and low molecular weight DOC. Research using ^{14}C of DOC and particulate organic C separated into organic fractions revealed that the acid insoluble fraction is similar in ^{14}C signature to that of the lipid fraction. Plans for utilizing this methodology are described. Studies using compound specific radiocarbon analyses to study the origin of biomarkers in the marine environment are reviewed and plans for the future are outlined. Development of ramped pyrolysis oxidation methods are discussed and scientific questions addressed. A modified elemental analysis (EA) combustion reactor is described that allows high particulate organic C sample throughput by direct coupling with the MIniCArbonDAtingSystem.

KEYWORDS: CSRA, dissolved organic carbon, methodology, organic carbon, radiocarbon.

INTRODUCTION

Organic carbon (C) is reduced C whose molecular structure is formed on skeletons of C atoms. There are two pools of organic C in seawater, dissolved organic C (DOC) that passes a 0.2 to 1.0 micron filter, and particulate organic C (POC) that is retained on the filter (Figure 1). The pool size of DOC is 682 GtC (Hansell 2013), similar in size to the organic C present in the upper one meter of oceanic sediments (1000 GtC, Hedges et al. 2000); the POC pool is much smaller (30–40 GtC). Early studies demonstrated that bomb ^{14}C was incorporated into subsurface and deep organisms (technically a portion of the POC pool), such as decapods and fish, along with significant amounts of pre-bomb C, on decadal timescales (Williams et al. 1970; Williams and Linick 1975).

Organic C is primarily produced during photosynthetic reduction of dissolved inorganic C (DIC) by phototrophs in the surface ocean. The concentration of DOC in seawater is 2–4% that of DIC, which makes DOC more sensitive to changes in its sources and sinks than those for DIC. The processes controlling DIC in the ocean are CO_2 exchange with the atmosphere, photosynthesis, respiration and production and dissolution of carbonate. The processes controlling DOC in seawater are more complex, including river input, microbial production of recalcitrant DOC (Jiao et al. 2010), chemoautotrophy (Ingalls et al. 2006; Hansman et al. 2009), hydrothermal processes (McCarthy et al. 2011; Lang et al. 2006; Shah Walter et al. 2018; Estes et al. 2019), enhanced refractory DOC utilization by priming

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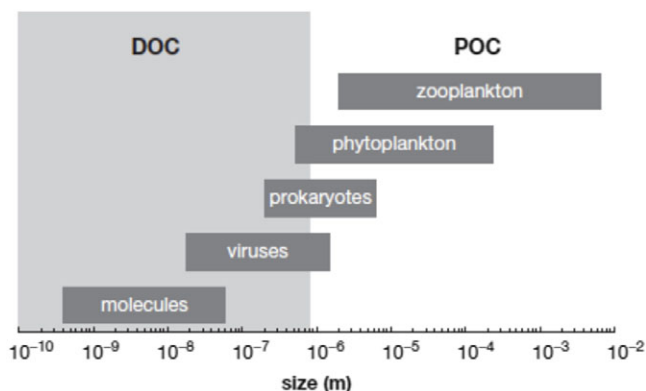*Corresponding author. Email: edruffel@uci.edu

Figure 1   Size ranges of organic matter constituents in seawater and their relationships to the operationally defined pools of DOC (gray background) and POC (white background). (After Beaupré 2019.)

(Bianchi et al. 2011; Fang et al. 2020; Shen and Benner 2018), gel formation (Verdugo et al. 2004) and dissolution/aggregation of POC (Smith et al. 1992; Druffel et al. 2016).

The introduction of ^{14}C analyses using AMS in the 1980s made it possible to study a broad range of organic C pools in the sea that were not possible with gas counting or liquid scintillation methods due to sample size restrictions. We discuss the present and developing advances for studying marine organic C using the mother of all isotopes, [14]C.

Bulk DOC [14]C

Methods for measuring bulk DOC Δ^{14}C in seawater were developed in the 1960s that required collection of 400–500 L of water in Gerard barrels (Figure 2), UV oxidation in 60 L batches, and gas counting of ^{14}C in the CO_2 (Williams et al. 1969). Improvements to the method required UV oxidation of 5 L of seawater using AMS measurements of [14]C (Williams and Druffel 1987). Beaupré et al. (2007) improved the method further by using UV oxidation of samples as small as 30 mL of seawater. Quantification of CO_2 lost during breakthrough of CO_2 from liquid nitrogen cooled traps during collection improved DOC concentrations reported with isotopic values (Walker et al. 2019). However, one day is required to process one sample, standard, or blank. New methods are critically needed to increase processing of DOC samples for ^{14}C measurement. Batch processing of bulk DOC in 100 mL reactors improves throughput of high [DOC] samples, such as freshwater and sediment pore water, to several per day (Xue et al. 2015).

Radiocarbon in DIC has been used to measure the timescale of global deep ocean circulation. Deep water is produced in the northern North Atlantic, flows south to the Southern Ocean where it flows eastward, and then northward into the Indian and Pacific oceans, taking ~1500 ^{14}C years to complete its journey (Broecker et al. 1960; Bien et al. 1965; Stuiver et al. 1983). This result agrees with pre-bomb bulk DOC Δ^{14}C values that decrease from the deep North Atlantic (–456‰, 4900 ^{14}C years), to the South Atlantic (–475‰, 5200 ^{14}C years), the Southern Ocean (–500‰, 5600 ^{14}C years), and are lowest in the North Pacific (–560‰, 6600 ^{14}C years) (Druffel et al. 2016, 2019; Bercovici et al. 2018; Druffel and Bauer 2000), increasing in ^{14}C age by 1700 years. This remarkable similarity between the deep

Figure 2   Peter M. Williams on the *R/V Melville* with a Gerard barrel, a 270 L steel vessel used to collect large volume seawater samples. The barrel is covered to protect it from particles coming mostly from the ship's stack. Circa 1989. (Photo by Ellen Druffel.)

cycling time of DOC and DIC suggests that DOC $\Delta^{14}C$ is controlled primarily by circulation, indicating that deep DOC is refractory on millennial timescales (Hansell 2013). Yet the DOC ^{14}C ages are much lower (~3000 ^{14}C years) than those of DIC.

There are significant correlations between DOC and DIC $\Delta^{14}C$ values for seawater taken from the same niskin bottle at numerous locations in the world oceans (Beaupré and Aluwihare 2010; Beaupré et al. 2020). Similar to DIC $\Delta^{14}C$ results in the central Pacific (<1,000 m) that contained bomb ^{14}C in the 1980s (Ostlund and Stuiver 1980) and >1990s (Key et al. 2004; McNichol et al. 2022), bomb ^{14}C is seen in the DOC $\Delta^{14}C$ values in the upper 1000 m in the Pacific Ocean (Figure 3). The highest surface values are found in the mid-ocean gyres around 20°N and 20°S (>–250‰), and lower values are near the equator and polar
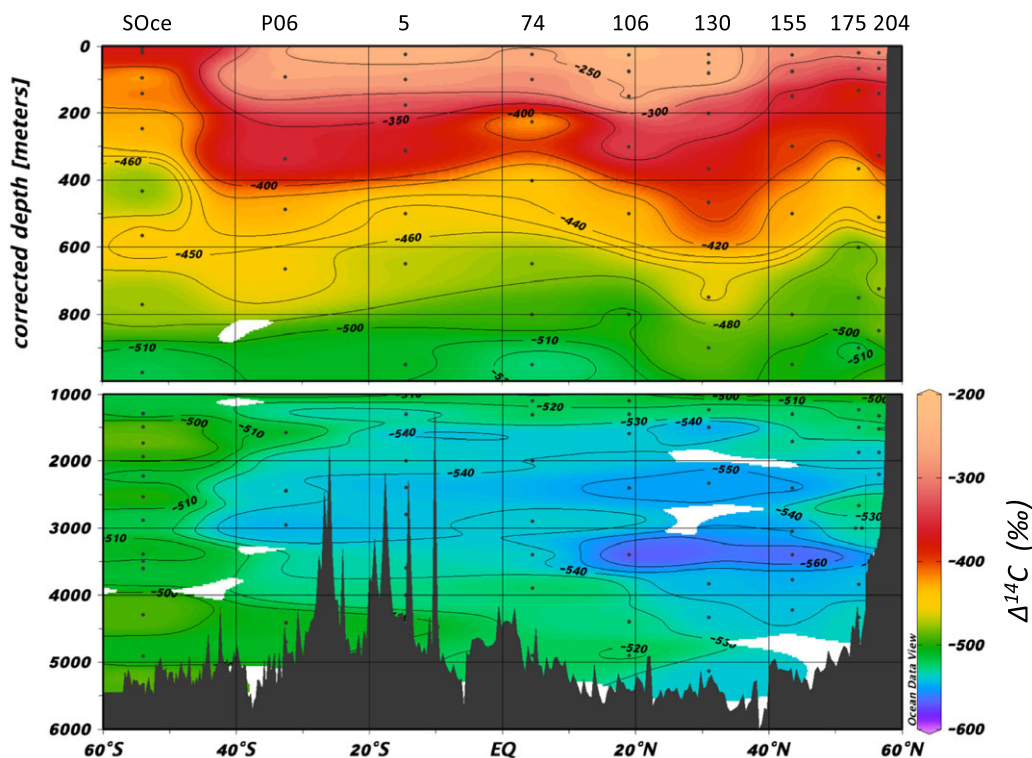
Figure 3   DOC $\Delta^{14}C$ values (‰) of water samples (indicated by black dots) collected from seven stations along 150°W on the P16N cruise in 2015 (Druffel et al. 2019), one station on the P06 cruise (stn 130, 32.5°S 144.7°W) in 2010 (Druffel and Griffin 2015) and one station from the Southern Ocean (SOce; 54.0°S 176.0°W) in 1995 (Druffel and Bauer 2000) using Ocean Data View (Schlitzer 2015). (After Druffel et al. 2019.)

regions (–260‰ to –400‰) where deeper waters upwell to the surface (Bercovici et al. 2018; Druffel and Bauer 2000). Subantarctic Mode Water, produced in the southwest Pacific, flows between 200 and 400 m to the Equatorial Undercurrent in the equatorial Pacific, and has $\Delta^{14}C$ values that range from –460 to –350‰ (Figure 3). Formed between 60° and 50°S, Antarctic Intermediate Water flows north at depths of ~700–1200 m and has $\Delta^{14}C$ values that range from –530 to –410‰ (Figure 3).

Questions that remain unanswered about marine DOC include the sources and sinks of DOC from hydrothermal systems, chemoautotrophy, sediment porewaters, interaction with POC, and photooxidation of DOC in the surface ocean and aerosols (Beaupré et al. 2020). ^{14}C and molecular identification methods (e.g., NMR and FT-ICR-MS) can help to determine the importance of these mechanisms.

SPE-DOC, and Size-Fractionated DOC

Solid-phase extraction (SPE) is a method of separating DOC (SPE-DOC) from bulk DOC using hydrophobic, silica or polystyrene resins. Seawater is acidified to enhance the relative abundance of protonated carboxyl groups, decreasing solubility and increasing sorption onto the resin (Mopper et al. 2007). XAD and C18 resins have been used to collect SPE-DOC and generally isolate humic substances from total DOC (Druffel et al. 1992; Green

and Blough 1994; Hedges 1992; Kieber et al. 1997; Peuravuori and Pihlaja 1997). C18 resins were especially effective in isolating chromophoric humic substances (Amador et al. 1990). More recently, styrene divinylbenzene polymer sorbents, such as PPL are more efficient at extracting DOC and leach less C than C18 resins. NMR analysis shows that SPE-DOC isolated using PPL is more representative of bulk DOC than that isolated using C18 resins (Dittmar et al. 2008). The ease of use, high recoveries, and ability to desalinate SPE-DOC samples have led to wide use of PPL resins in investigations of marine DOC. Subsequent methodological studies have compared PPL, C18, and other SPE resins in more detail, and show that DOC extraction can be increased up to 89% with the correct ratio of DOC/PPL (Li et al. 2016). Lewis et al. (2020) demonstrated that the optical and isotopic characteristics of SPE-DOC using PPL cartridges are heterogeneous during elution with methanol, which may be useful in further separation of compounds based on their relative polarities.

PPL has been used to isotopically and chemically characterize SPE-DOC in the east South Atlantic Ocean, the Bermuda Atlantic Time Series, Station ALOHA in the North Pacific, the Weddell Sea, and the deep North Pacific Ocean (Broek et al. 2020; Flerus et al. 2012; Hertkorn et al. 2013; Lechtenfeld et al. 2014; Zigah et al. 2017). SPE-DOC typically has lower $\Delta^{14}C$ and $\delta^{13}C$ values than those of total DOC (Broek et al. 2020; Coppola and Druffel 2016; Zigah et al. 2017; Lewis et al. 2021), is rich in aromatic C (Simjouw et al. 2005), and has elemental compositions indicative of thermogenic processes found throughout the water column (Dittmar and Koch 2006; Hertkorn et al. 2013). The presence of carboxyl-rich alicyclic molecules (CRAM), with low H/C and O/C ratios indicative of recalcitrance, is often found in SPE-DOC and tends to increase with depth in the water column (Broek et al. 2020; Hertkorn et al. 2013; Lechtenfeld et al. 2015). Lechtenfeld (2015) found that bacterial SPE-DOC isolated in laboratory experiments is similar in composition with natural marine DOC and the composition of recalcitrant molecules in the ocean. The link between SPE-DOC recalcitrance, low $\Delta^{14}C$, and low $\delta^{13}C$ may all be indicative of the influence of marine heterotrophic bacteria on DOC degradation, transformation, cycling, and the production of refractory DOC (Flerus et al. 2012; Lechtenfeld et al. 2015; Osterholz et al. 2015). Solid-phase extraction will likely continue to advance our knowledge of DOC molecular composition as techniques to isolate and further characterize DOC develop further.

For several decades, ultrafiltration (UF) has been used as a method to isolate DOC from abundant salts in seawater. The technique has shaped much of our understanding of DOC cycling and molecular composition, and samples material that can be isolated without the chemical bias inherent to all resin chromatography methods. Early UF studies have shown that, despite low DOC recovery (10–30%), ultrafiltered DOC (UDOC), also referred to as high molecular weight (HMW DOC), was generally representative of total DOC in terms of its bulk elemental (C:N) and isotopic ($\delta^{13}C$, $\delta^{15}N$) values (Benner et al. 1992, 1997; McCarthy et al. 1993). However, several studies have shown that UDOC differs from bulk DOC in molecular composition (Skoog and Benner 1997; Dittmar et al. 2001) and $\Delta^{14}C$ values (Santschi et al. 1995; Loh et al. 2004; McNichol and Aluwihare 2007). Further parameterization of UDOC $\Delta^{14}C$ values as a function of UF experiment concentration factor (CF) reconciled >250‰ variability in reported surface and deep Pacific UDOC $\Delta^{14}C$ values (Figure 4a; Walker et al. 2011). Further work suggested that changes in CF could be used for the targeted isolation of semi-labile or even bioavailable UDOC (Walker et al. 2016a). Robust, size-age-composition relationships within both the DOC pool and
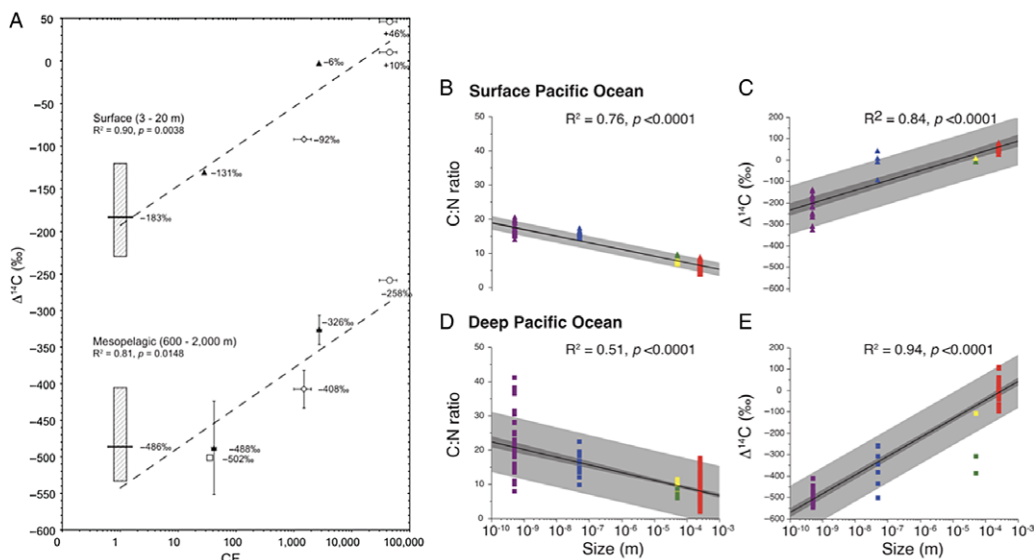
Figure 4   Size-Δ^{14}C and elemental composition (C:N) relationships of DOC in the Pacific Ocean. (A) DOC Δ^{14}C as a function of ultrafiltration concentration factor (CF) for the surface and deep Pacific ocean. Relationships between the C:N content of size-fractionated marine organic matter (B,D) and Δ^{14}C (C,E) in the surface and deep Pacific. (Figures adapted from Walker et al. 2011 and Walker et al. 2016b.)

total marine organic matter size continuum (Figure 4b,c,d) suggest a "precursor-product" relationship controlling the cycling (^{14}C age) and chemical composition (N-content) of marine organic matter. As a result, DOC C:N content and ^{14}C age can be generally predicted from molecular size (Walker et al. 2016b).

A recent advancement is the combination of UF and SPE techniques to view organic matter through various analytical windows simultaneously. By filtering out POC, then performing solid-phase extraction on UDOC permeate fractions, the comparison of up to three different sub-pools of DOC is possible (HMW-DOC, hydrophobic LMW-DOC, hydrophilic LMW DOC) (Broek et al. 2017; Zigah et al. 2017; Broek et al. 2020). This method has provided new insights regarding the cycling of hydrothermal vent DOC in the open ocean, the possible addition of high molecular weight DOC to the deep ocean, and the selective utilization of some LMW-DOC during meridional overturning circulation (Broek et al. 2017; Zigah et al. 2017; Broek et al. 2020).

Compound Classes and ^{14}C

Marine organic matter exists as molecules, some of which are characterizable. The characterizable organic C is made up mostly of amino acids/proteins, sugars/carbohydrates, lipids, and nucleic acids. However, more than half of the organic matter in seawater and sediments is not characterizable at the molecular level (Hedges et al. 2000). Whereas 85% of surface plankton and POC in the central Pacific is identified molecularly (Wakeham et al. 1997), less than 25% of deep POC is so identified, due to extensive remineralization as POC falls through the water column. The Δ^{14}C of sinking POC in the deep east North Pacific is lower than that of surface DIC that was photosynthesized to produce the organic C (Druffel et al. 1996). The surface sediment organic C has even lower Δ^{14}C values (Wang
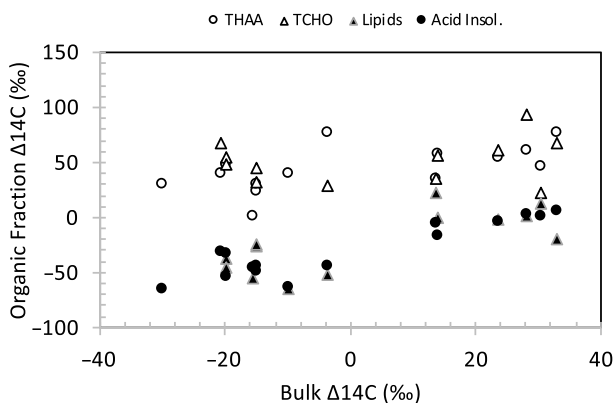
Figure 5 $\Delta^{14}C$ of organic compound classes (THAA, open triangles; TCHO, open circles; lipids, solid triangles; acid insoluble fraction, solid circles). The range of DIC ^{14}C values in surface waters at Stn M ranged from about 40 to 70‰. (After Hwang and Druffel 2003.)

et al. 1998). A correlation was found between $\Delta^{14}C$ and aluminum content of sinking POC, demonstrating that organic C associated with lithogenic material from sediment resuspension causes the observed low $\Delta^{14}C$ values (Hwang et al. 2010).

To understand these trends, separation of POC into four compound classes (or organic fractions), total hydrolyzable amino acids (THAA), total hydrolyzable carbohydrates (THCO), lipids and acid insoluble fraction were used to study ^{14}C (Wang et al. 1996, 1998; Hwang and Druffel 2003). Dried POC, zooplankton, phytoplankton, detrital aggregates on surface sediment and sediment from Stn M (34°50'N, 123°0'W, 4100 m depth) were extracted with methylene chloride:methanol to extract lipids. Half of the residue was hydrolyzed with 6M HCl under N_2 for THAA and the other half with 72% and 0.6M H_2SO_4. The hydrolyzates were eluted through ion exchange columns to separate the two fractions, and the organic C leftover from the THAA extraction was used for the acid insoluble fraction. All THAA and THCO fractions had higher $\Delta^{14}C$ values than those for the lipid and acid insoluble fractions (Wang et al. 1996, 1998; Hwang and Druffel 2003) (Figure 5). The proportion of acid insoluble fractions increased with depth in the water column, and was highest in sediment samples (49–69%) and lowest in zooplankton and phytoplankton (<10%) from the upper 100 m. These results implied that the acid insoluble fraction was composed of lipid-like macromolecules.

Compound classes have also been measured in HMW-DOC. Results similar to those obtained for POC and sedimentary organic C were obtained, where THAA and TCHO had higher $\Delta^{14}C$ values than those for lipid and acid insoluble fractions (Loh et al. 2004).

Dissolved black C (DBC) is incompletely combusted organic matter produced from fossil fuel and biomass burning. DBC was measured in HMW-DOC from 4 samples from the Pacific and Atlantic Oceans and found to have $\Delta^{14}C$ values that were 470–860‰ lower than those for bulk DOC from the same water (Ziolkowski and Druffel 2010). DBC was also measured in SPE-DOC from 6 samples in the Atlantic, Pacific and Arctic Oceans and DBC $\Delta^{14}C$ values were 0–560‰ lower than those of SPE-DOC (Coppola and Druffel 2016). They concluded that there

are two distinct pools of DBC, that in the surface ocean and that in the deep ocean. Coppola et al. (2014) measured black C in sinking POC and sediments and found that the main transport mechanism of black C to sediments may be sorption of ancient DBC onto POC. Further studies of DBC in marine systems are needed to understand more fully the sources and sinks of DBC and its residence time in the ocean.

Compound Specific Radiocarbon Analyses (CSRA)

Organic matter in the ocean consists of a complex mixture of different compounds, both of terrigenous and marine origin. Greater understanding of C cycling processes in the marine realm can be obtained by isolating specific fractions of marine organic matter that can be ascribed to a known source (biomarkers), by investigating the ^{14}C signature of individual organic compounds. Compound-specific ^{14}C analyses (CSRA) of marine biomarkers have been used to elucidate processes affecting the fate of marine organic matter during transport (e.g., Ohkouchi et al. 2002; Mollenhauer et al. 2003, 2007; Ausín et al. 2019), the reactivity of different types of marine organic compounds (e.g., Shah et al. 2008; Kusch et al. 2010, 2016), and C sources utilized for biosynthesis (Ingalls et al. 2006; Hansmann et al. 2009). Improvement of stratigraphies for sediments that are otherwise difficult to date have also relied on CSRA of marine organic compounds (Ingalls et al. 2004; Ohkouchi and Eglinton 2008). These studies have revealed the long-term residence of marine organic matter in continuous re-suspension loops (e.g., Mollenhauer et al. 2007, 2011), which has also been shown for terrigenous biomarkers (e.g., Bröder et al. 2018; Wei et al. 2021), its preservation in association with fine-grained lithogenic material resulting in long-distance lateral transport and the millennial scale duration of these transport processes (Ohkouchi et al. 2002; Mollenhauer et al. 2005, 2007). Chemoautotrophic metabolism has been shown to prevail among mesopelagic microbial communities (Ingalls et al. 2006). Steroids and pigments and their derivatives, biomineral occluded compounds and as nucleic acids (Cherrier et al. 1999) have been investigated. Recent developments use CSRA of amino acids to study their sources and cycling (Bour et al. 2016; Blattmann et al. 2020).

All applications of CSRA on marine organic compounds require extraction and purification of sufficient mass of the compound from samples where they are typically present in trace amounts. As a consequence, most CSRA studies are conducted using sediments that have sufficient material available. In most cases, CSRA of compounds isolated from POC or DOC sampled from the water column is not possible, unless dedicated sampling campaigns that collect several thousands of liters of water are conducted (e.g., Ingalls et al. 2006). An exception was sugars collected from HMW-DOC in surface waters of the North Pacific that had post-bomb $\Delta^{14}C$ values (Repeta and Aluwihare 2006).

Commonly used methods for extraction and purification targeting mostly lipid compounds have been summarized by Mollenhauer et al. (2019). Often, a sequence of wet-chemical and chromatographic techniques is applied, and typically samples of 100 µg C or less are obtained. The samples need to be combusted prior to ^{14}C analysis and in many cases will be graphitized. AMS analyses of small samples are conducted using size-matched standards and blanks for normalization. For such small samples, accurate determination of the amount and $\Delta^{14}C$ value of extraneous C added to the sample during the various steps of sample preparation is of critical importance (Santos et al. 2010). Recently, isotope dilution techniques are increasingly used to obtain reliable estimates of this extraneous C
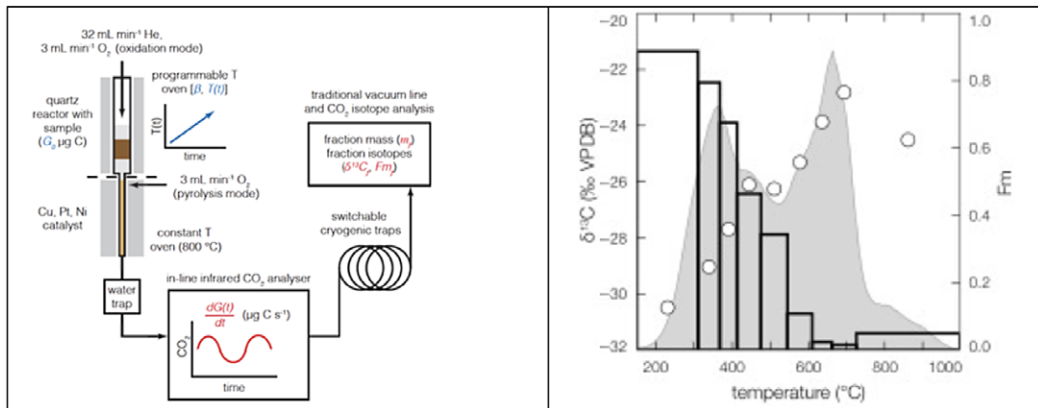
Figure 6   Schematic of the RPO reactor (left) and the results (right) from a POC sample collected from the Narayani River, Nepal (Hemingway 2017). The top half of the quartz reactor heats the sample while the gases are swept into a CO_2 analyzer before passing through a cryogenic trap. The gray shaded region is the thermogram, the variation in ppm CO_2 vs. temperature (units not shown), white circles show the $\delta^{13}C$ values, and bars show the fraction modern values for each temperature interval (Hemingway 2017). The data show that the high temperature, more refractory, fractions have dramatically less ^{14}C, i.e., are older than the lower temperature fractions.

contribution and its ^{14}C content, which can subsequently be used to correct CSRA results (e.g., Haghipour et al. 2019; Sun et al. 2020).

Taking advantage of the elemental-analyzer-accelerator-mass-spectrometer (EA-AMS) setup, recent methodological developments allow for direct injection of CO_2 gas produced from combustion of purified compounds into a gas accepting ion source (Haghipour et al. 2019; Mollenhauer et al. 2021). Purified compounds are transferred into small tin cups, dried and combusted in the EA (Elementar Elemental Analyzer) coupled to the AMS. Thereby, the graphitization step is omitted, and high-precision ^{14}C data can be obtained for samples containing 50 µg C or less. For samples younger than approximately 5000 years, precise ^{14}C analyses can be achieved for samples as small as 10 µg C (Haghipour et al. 2019).

Ramped Pyrolysis Oxidation (RPO) and ^{14}C

In the mid-2000s, attempts to understand the chronology of Antarctic sediments led John Hayes to develop the Ramped Pyrolysis Oxidation system (RPO) at the National Ocean Sciences AMS facility, a system that separates organic matter based on thermochemical properties. RPO ^{14}C analysis involves the controlled step heating of samples containing organic C, with or without oxygen, typically at a heating rate of 5°C/minute (Figure 6). As heating proceeds, the most reactive organic components become volatile and are swept into an oxidizing reactor by a helium stream, allowing separation of CO_2 from other pyrolysis/ combustion components and collection of CO_2 over discrete temperature intervals for analysis of both stable and radiocarbon isotopes. A major advantage is the ability to analyze all of the organic matter in a sample, not just an isolated fraction. In sediments, the thermal separation allows the isolation of fresh detrital matter from eroded bedrock. The initial goal of improving the chronologies of Antarctic sediments was realized (Rosenheim et al. 2008) and has been expanded upon (Rosenheim et al. 2013; Subt et al. 2016).

Building on this success, RPO has since been applied to a wide variety of biogeochemical questions in many environments including the oceans. It is being used to study the nature of the organic material transported to the oceans from rivers (Hemingway et al. 2019). Hemingway et al. (2017) developed an inverse method to calculate organic C reactivity from RPO results. They used the method on RPO results from 62 sediment organic C, riverine POC, soil organic C, and DOC samples to indicate that mineral interactions are more important for the preservation of organic C than selective preservation (Hemingway et al. 2019). RPO has been applied to studying the fate of petroleum hydrocarbons, both natural and pollutant, in marine and coastal ecosystems (Pendergraft et al. 2013; Pendergraft and Rosenheim 2014; Adikhari et al. 2016; Rogers et al. 2019). A time series study of the impact of the Deep Water Horizon oil spill on sediments from four sites demonstrated the range of impacts and the time evolution of the oil spill. RPO and C isotope analysis allowed the separation of the spilled petrocarbon from natural hydrocarbon seep C. Emerging work is using the technique to explore the nature of DOC, particularly the high molecular weight fraction.

EA-AMS for Suspended POC [14]C

During oceanographic expeditions, suspended POC (POC_{susp}) for radiocarbon analysis is typically collected using in-situ water pumps with GF/F filters that are lowered to water depths where up to 1000 L are pumped (Griffith et al. 2012). Because water pumps are expensive, multiple casts per station are required to obtain full-depth water column ^{14}C POC_{susp} profiles, a time consuming process that is also expensive.

Utilizing the EA-AMS setup can overcome in-situ water pump limitations, because the MICADAS (MIniCArbonDAtingSystem) allows routine, high precision analysis of small samples (> 100 µgC). For EA-AMS, seawater is processed onboard directly from CTD-ROS (Conductivity Temperature Depth-Rosette) niskin bottles, where 2–40 L of water are collected to obtain sufficient C on GF/F filters, depending on the POC_{susp} concentration. It is possible to sample up to 24 depths during one deployment and generate high resolution depth profiles of POC_{susp} [14]C (Figure 7). POC_{susp} is concentrated on pre-combusted GF/F filters using a vacuum supported glass filtration device that allows the sampling of filtrate to obtain the corresponding DOC fraction. In the lab, the filters are acidified, packed into tin capsules, and combusted in the EA. The generated CO_2 is measured in the MICADAS via direct injection into the gas ion source (Mollenhauer et al. 2021).

The conventional CuO oxidation reactor of the EA operating at 950°C is prone to cracking, due to halogen radicals reacting with CuO that attack the quartz reactor. Recently, a modified EA reactor has replaced the CuO with WO_3 and changed the position of the Ag wool. The WO_3 does not react with halogen radicals and Ag wool is positioned at low reaction temperatures further preventing unwanted side reactions. The reaction temperature is lowered to 850°C, and an Inconel liner and ash fingers are used to further protect the quartz reactor. This reactor setup withstands 150–200 samples, whereas a typical CuO reactor processing saline POC_{susp} filters cannot withstand more than 50 samples.

The disadvantage of this setup is that the C content of the blank increases significantly. The C content of a typical blank for a pre-combusted ½ 45 mm GF/F analyzed on a CuO reactor is ~10 µg C, but for the modified WO_3 reactor it is ~20 µgC. The higher blank C originates from the WO_3 and can be reduced by carefully inspecting the material and removing incompletely

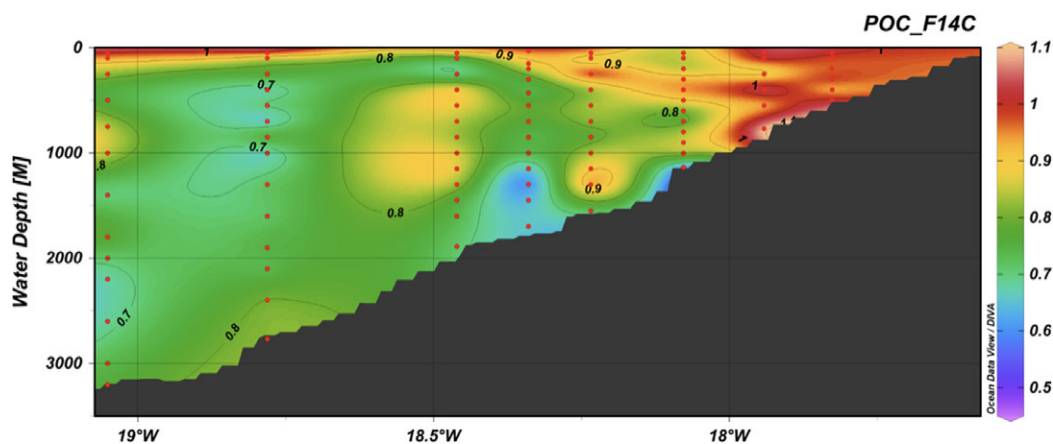Figure 7   Preliminary $F^{14}C$ POC_{susp} values of samples collected along a shelf to open ocean transect off Cape Blanc (NW Africa, ~21°N) collected in November 2018 during research cruise MSM79 onboard the German R/V *Maria S. Merian* and processed according to the EA–AMS method described above (H. Grotheer unpublished data). Red dots indicate sampling depths. (The map was generated using Ocean Data View; Schlitzer 2015).

oxidized tungsten particles and foreign objects. Nonetheless, pre-combusted GF/F filters contain a significant amount of blank C and appropriate blank determination and subsequent correction is critical. The high blank C content has further implications for the minimum amount of seawater that needs to be filtered per sample in order to acquire an optimum blank C to POC_{susp} ratio.

In the first example of a high-resolution $F^{14}C$ (Fraction modern ^{14}C) POC_{susp} profile (Figure 7, H. Grotheer unpublished data) was generated for a transect from the shelf to the open ocean off Cape Blanc (NW Africa, ~21°N). The Cape Blanc region is located in the southern part of the Canary Current Eastern Boundary Upwelling system off northwest Africa. Here, the Cape Blanc upwelling filament transports cold, nutrient-rich, upwelled waters for hundreds of kilometers offshore towards the oligotrophic ocean (Van Camp et al. 1991; Gabric et al. 1993; Àlvarez-Salgado et. al. 2001) and is an important transport pathway for particles (Karakas et al. 2006).

Fresh POC_{susp} ($F^{14}C$ 1.0) produced by primary production on the shelf is transported along the continental slope within the bottom layer and travels offshore at ~500 m water depth. Further offshore, underneath the photic zone, $F^{14}C$ POC_{susp} decreases to ~0.8 at 500 m depth. Below 500 m, $F^{14}C$ values show a heterogeneous distribution with pre-aged POC_{susp} ($F^{14}C$ ~0.6) separated by layers of POC_{susp} with intermediate $F^{14}C$ values, suggesting the presence of a refractory POC_{susp} pool, potentially originating from sediment resuspension. These preliminary data highlight the potential of the EA-AMS method to generate high-resolution, $F^{14}C$ POC_{susp} profiles that will advance our understanding of POC cycling, transport and sequestration processes in the ocean.

FUTURE WORK

Studies of marine organic C have benefitted from research conducted outside of the marine scientific community. Effort to continue this strong communication and collaboration is important to maintain and to nurture. New ways to unlock the secrets of the

biogeochemistry of the marine system will benefit humanity as we chart a course through the Anthropocene.

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