GLOBAL OCEAN RADIOCARBON PROGRAMS

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ABSTRACT. The importance of studying the radiocarbon content of dissolved inorganic carbon ($DI^{14}C$) in the oceans has been recognized for decades. Starting with the GEOSECS program in the 1970s, ^{14}C sampling has been a part of most global survey programs. Early results were used to study air-sea gas exchange while the more recent results are critical for helping calibrate ocean general circulation models used to study the effects of climate change. Here we summarize the major programs and discuss some of the important insights the results are starting to provide.

KEYWORDS: dissolved inorganic carbon, ocean models, oceanography, radiocarbon.

Radiocarbon in dissolved inorganic carbon ($DI^{14}C$) in seawater has long been recognized as an important tracer for studying ocean processes. $DI^{14}C$ is reported as $\Delta^{14}C$ in per mille units as defined in Stuiver and Polach (1977). The earliest ocean measurements from the 1950s focused on deep ocean circulation rates (Bien et al. 1960; Broecker et al. 1960). Early studies of the surface ocean were thought to be complicated by the known lack of steady-state in the atmospheric radiocarbon content due to the atmospheric ^{14}C decrease since the Industrial Revolution (the Suess effect: e.g., Suess 1953; Keeling 1979; Stuiver and Quay 1981) and the sharp increase in ^{14}C since the atmospheric weapons tests in the 1950s and 1960s (the bomb spike, e.g., Rafter 1965; Nydal 1968). At the time, it was understood how useful the bomb spike would be for studying air-sea gas exchange in the future (Bien et al. 1960) and as a global carbon cycle tracer experiment. Reidar Nydal championed the collection and analysis of surface ocean radiocarbon starting in the mid-1960s (Nydal et al. 1984), amassing a data set of over 500 analyses between 1966 and 1981. The early work demonstrated the power of $DI^{14}C$ to study ocean processes but was limited in scope because of the challenges of collecting the samples and making the measurements.

Until the advent of accelerator mass spectrometry (AMS) in the early 1990s, up to 250 L of seawater was required to obtain a precise radiocarbon measurement, i.e., a measurement with a precision of ± 2–4‰ in the deep ocean. Two samplers in use until the early to mid 1990s were Gerard barrels (Bien et al. 1960; Broecker et al. 1960) and keg samplers (Young et al. 1969) (Figure 1). The former has a capacity of ~250 L, and the latter, repurposed beer kegs, had a capacity of up to ~60 L. Gerard samples were acidified on the ship using 40 mL of concentrated H_2SO_4 and sparged for about four hours (depending on sample temperature) using CO_2-free air or N_2. Extracted CO_2 was precipitated as either $BaCO_3$, $SrCO_3$, or dissolved in KOH or NaOH and transferred to shore-based laboratories for analysis and counting using specialized gas proportional (Östlund et al. 1962) or liquid scintillation (Tamers 1960) counters. The amount of time required to collect the Gerard samples coupled with the lengthy shipboard extraction procedure severely limited the numbers of samples that could be collected and

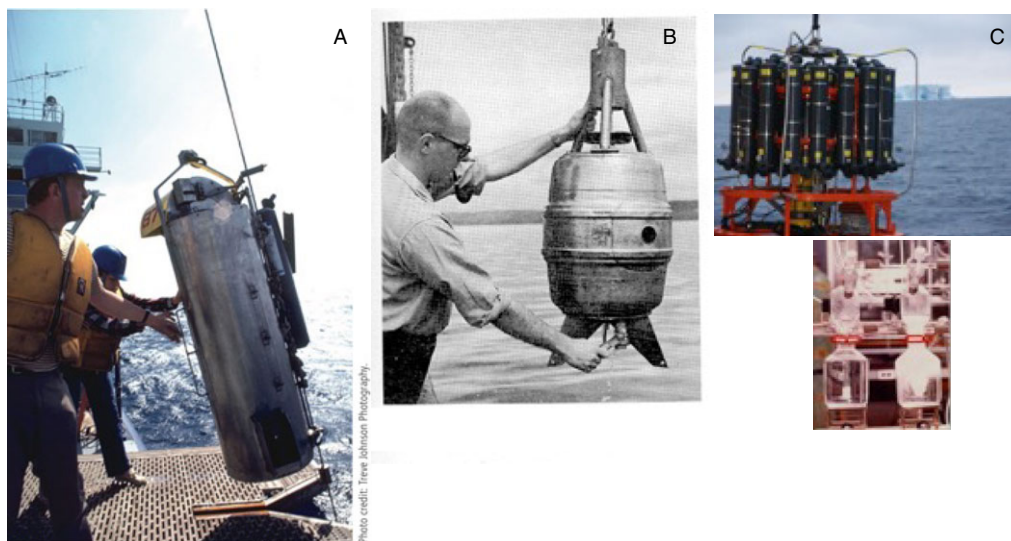*Corresponding author. Email: amcnichol@whoi.edu

Figure 1   Samplers used to collect water for radiocarbon analysis: A. Gerard barrel, B. Keg sampler, C. Niskin bottles. A and B use the entire volume of water for the analysis while only 500 mL are collected from the Niskin bottle.

analyzed. Regardless, the GEOSECS data collected during the 1970s provide an extraordinarily valuable baseline for the more extensive subsequent surveys.

The handling and difficulty of ensuring good recoveries also made it challenging to use these samples for $DI^{13}C$ measurements of adequate precision and accuracy to be oceanographically meaningful; therefore, separate samples were used for these analyses (Kroopnik 1985). The reduction in sample size afforded by AMS (from 250 L to 0.5 L) made it possible to collect samples at sea, preserve them with $HgCl_2$, and ship them back to laboratories for analysis. Until recently, the preferred extraction method for both $DI^{14}C$ and $DI^{13}C$ has been sparging with CO_2-free gases, usually N_2 (Bard 1987; Quay 1992; McNichol 1994). Newer methods include headspace analysis (Gao et al. 2014) and membrane transfer techniques (Gospodinova et al. 2016). Once the gas has been extracted, standard techniques are used for the analysis of radiocarbon (Vogel et al. 1987; Roberts et al. 2010; Longworth et al. 2015). Shipboard-based analysis using non AMS techniques to measure radiocarbon at sea, at least for waters containing bomb-produced carbon, allowing researchers to walk off the ship with data, will bring radiocarbon on par with chlorofluorocarbons (CFCs) for wider utilization within the oceanographic community. Much progress is needed but cavity-ring down systems similar to those in use for $DI^{13}C$ (Su et al. 2019) hold promise for the future (Galli et al. 2016; Fleisher et al. 2017).

The first global sampling program to include $DI^{14}C$ was the Geochemical Ocean Sections Study (GEOSECS) in the mid-1970s (Östlund and Stuiver 1980; Stuiver and Östlund 1980, 1983). A major force in the measurement of $DI^{14}C$ in the GEOSECS program and many of the programs that followed was Wally Broecker. As noted in a memoir (Broecker 2012), his interest was piqued during a conversation with Henry Stommel. Specifically, Broecker recalled, "Toward the end of the 1960s, two unique opportunities arose which led me to temporarily abandon my desire to plunge ever more deeply into paleoclimate. One was the

creation by the National Science Foundation of an initiative called IDOE (International Decade of Ocean Exploration) and the other was an invitation to participate in a limnological research program being launched in Canada. In 1968, during a visit to Woods Hole, Henry Stommel, a legendary figure in physical oceanography, took me aside and said, 'Wally, you guys measure radiocarbon here and there in the ocean, but if we are to properly use the results to pin down the rates of transport, we need a systematic survey along transects from one end of the ocean to the other.' I asked, 'how many stations along each transect and how many depths at each station?' He replied, '50 stations and 20 depths.' "

The GEOSECS goal was to increase the general knowledge of ocean geochemistry and to estimate the deep-ocean transport rates. Sampling consisted of a single section along the center of each major ocean basin. The GEOSECS Program introduction states, "As man [sic] becomes increasingly aware of the ocean as a source of food, a disposal area for nuclear and industrial waste products, a strategic realm for national security and a controlling factor in the earth's climatic regime, he also recognizes how very little he knows about the sea." Data from the early programs up through the original World Ocean Circulation Experiment (WOCE) occupations are stored in easily accessible internet locations (e.g., CLIVAR and Carbon Hydrographic Data Office [CCHDO], National Centers for Environmental Information [NCEI], Ocean Carbon Data System [OCADS]) and summarized in the Global Ocean Data Analysis Project (GLODAP) database (Key et al. 2004). Sample numbers cited here reflect those in GLODAPv2.2020 (Olsen et al. 2020) and include data reported through 2015 (mostly samples from the Climate Variability and Predictability [CLIVAR] and the Global Ocean Ship-Based Hydrographic Investigations Program [GO-SHIP] programs). During GEOSECS, 2218 DI^{14}C values from 125 stations were reported. Subsequent large programs were the Transient Tracers in the Ocean (TTO, 1981–1983, 937 values from 101 stations; Brewer et al. 1985; Östlund and Rooth 1990) and the South Atlantic Ventilation Experiment (SAVE, 1987–1989, 955 values from 77 stations) in the Atlantic Ocean, as well as the Indien Gaz Ocean (INDIGO, 1985–1987, 233 samples; Östlund and Grall 1991, 430 values from 20 stations) project in the Indian and Southern Oceans. The primary goal of these programs was to extend the two-dimensional description of the tracer distributions into three dimensions so that the properties could be mapped on density surfaces. Much of this earlier work used the fact that, in the 1960s and by GEOSECS in the 1970s, ocean DI^{14}C was controlled by air-sea exchange and had not penetrated deeply enough to be a good tracer analog for the uptake of anthropogenic CO_2.

During the 1990s the WOCE program was carried out "to survey the global distribution of ocean variables with a view to greatly improving estimates of the circulation of heat, water and chemicals around the world ocean, and their exchange with the atmosphere (Woods 1985)." The advent of AMS greatly increased the number of radiocarbon samples that could be collected and measured (see below) and 17,676 samples were measured as part of this program. Because the highest precision was needed in the deep water and the AMS technique was new, large volume samples were collected in the deep waters and small volume samples were collected in the surface and thermocline waters. The United States WOCE program collected and analyzed the majority of these samples at a laboratory funded and built primarily for this program (Jones et al. 1990) referred to as the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS). Other countries whose laboratories measured radiocarbon included Japan (primarily the Japanese Agency for

Marine-Earth Science and Technology) and Germany. WOCE was followed by the CLIVAR programs in the first decade of the 2000s. These programs were designed to better understanding climate variability and predictability on seasonal to centennial time scales, identifying processes responsible for climate change, and developing predictive capabilities (http://www.clivar.org). The most recent program is GO-SHIP, a program that has a goal of providing the measurements needed to understand and document large-scale ocean water property distributions, their changes, and their drivers in a changing global environment (http://www.go-ship.org). As of 2015, CLIVAR, GO-SHIP, and other smaller programs have added 14,085 measurements to the global database.

Results from these programs and sample analyses have contributed greatly to our understanding of the oceans. DI^{14}C is affected by biology and carbonate chemistry, but by normalizing to ^{13}C and time, the biological effect is minimized. This allows ^{14}C, reported as Δ^{14}C (or strictly Δ as per Stuiver and Polach 1977), to be used as a physical tracer for both anthropogenic carbon and as a water mass tracer to elucidate dynamics. Monitoring of the oceanic ^{14}C transient in the upper ocean has provided important metrics of surface-to-deep exchange rates predicted by ocean models, and, specifically, deep water formation rates and processes in key locations where continued penetration of anthropogenic CO_2 into the interior and abyssal ocean is occurring. Changes in ocean ^{14}C can now be used to track the arrival of anthropogenic CO_2 in the abyssal ocean (Graven et al. 2012), where the DIC changes are still small (< 2 µmol kg^{-1}) and difficult to detect using back-calculation approaches (e.g., ΔC* [Gruber et al. 1996] and variants thereof). The radiocarbon distribution and change have been used to study mixing, ventilation rates, rates of production of abyssal waters, shallow upwelling rates, and deep ocean residence times (Broecker et al. 1978, 1998; Broecker 1979; Toggweiler and Samuels 1993; Toggweiler and Key 2001; Matsumoto and Key 2004; Roussenov et al. 2004; Schlitzer 2007), deep ocean biogeochemistry and oxygen utilization rates (Broecker et al. 1991; Key 2001; Keller et al. 2002; Sarmiento et al. 2007), air-sea gas exchange (Broecker and Peng 1974; Wanninkhof 1992; Sweeney et al. 2007), thermocline ventilation rates (Gnanadesikan et al. 2004), as a proxy for anthropogenic CO_2 in the ocean (Broecker et al. 1980), to estimate deep water mass ages for anthropogenic CO_2 uptake and carbon studies (Sabine et al. 1999, 2002a, 2002b, 2004; Feely et al. 2002; Chung et al. 2003, 2004; Lee et al. 2003), and to evaluate ocean general circulation model (OGCM) performance (Maier-Reimer and Hasselmann 1987; Toggweiler et al. 1989a, 1989b; Guilderson et al. 2000; Key 2001; Orr et al. 2001; Key et al. 2004; Matsumoto et al. 2004).

An elegant example of the power of ^{14}C analyses is provided by Toggweiler et al. (2019a, 2019b). Their ^{14}C assessment combined surface water Δ^{14}C data from biogenic carbonate archives, primarily reef-building corals, and DIC samples from the WOCE/CLIVAR programs to place a constraint on the volume of water upwelled in the major upwelling centers of the global ocean and to provide insights on the mechanism of upwelling and forcing. The regional (and when combined, global) upwelling indicated by the spatial range of upwelling induced surface water Δ^{14}C deficits exceeds that which would be indicated by the surface wind (Ekman) forcing alone. In the Pacific, where the Δ^{14}C deficit stretches across the basin, Ekman-based forcing indicates an upwelling volume of ~2Sv off the coast of Peru and the Costa Rican Dome, whereas the Δ^{14}C budget indicates more than 10Sv. Similar differences occur in the other major upwelling regions. The Δ^{14}C surface deficit upwelling estimates are consistent with inverse modeling estimates in terms of the volume of water that upwells.

The inverse models, however, use large amounts of diapycnal mixing to transform relatively dense Antarctic Circumpolar Water (ACC) into lighter water. The newly formed "lighter" or less dense water can then be shunted to the surface by denser water pushing through the ACC into mode and interior water masses. In contrast, the $\Delta^{14}C$ data imply nearly direct exposure of interior water via upwelling of mode and intermediate waters at the western basin margins. If upwelling is geographically limited to these upwelling sources, less diapycnal mixing is needed to transform interior and mode waters to waters that are more easily mixed into the surface. Toggweiler et al. posit that the additional volume, beyond that required by Ekman forcing, upwelled in these regional locations and required to balance the surface water $DI^{14}C$ distribution is a "push" associated with the global thermohaline circulation: i.e., the classic "conveyor belt" initially coined by Arnold Gordon and made famous by Wally Broecker. The reduced impact of diapycnal mixing will require improved physics in ocean models that predict anthropogenic CO_2 uptake.

The Ocean Carbon Model Intercomparison Project (OCMIP) was one of the first major collaborative efforts between transient tracer experts and ocean modelers to explore $DI^{14}C$ in a coordinated, meaningful, and mechanistic way. The goal was to understand the processes that caused differences in model simulations, predictions and to improve model capabilities. Radiocarbon and CFC data were used as tracers. The OCMIP model predictions of the CFC distribution were much better than for $DI^{14}C$. This is largely because the CFC distribution is strongly dependent on surface ocean temperature that the models reproduce reasonably well, although biases in mixed layer depth propagate into CFC inventory biases (e.g., Long et al. 2013). Both natural and bomb radiocarbon provide model constraints not available from *any* other tracer. Figure 2 compares OCMIP results with WOCE ^{14}C data from section P16 (Key et al. 1996; Stuiver et al. 1996). Although all of the models reproduce the general shape of the contours, the concentrations vary widely. The model physics required to reproduce the ^{14}C distribution are much more difficult and involve the entire water column. Even cursory examination points out significant discrepancies in all model results, e.g., a too diffuse thermocline, and remarkable model to model differences. One conclusion was that some models could reasonably reproduce the sparse GEOSECS data, but none could adequately simulate the WOCE results (Orr et al. 2001): i.e., continued circulation and movement of $\Delta^{14}C$ showed flaws in model dynamics and their predictive transport skill.

In recent decades (post 1995), air-sea exchange exerts less influence on ocean $DI^{14}C$ because the air-sea ^{14}C gradients are now very small. In some regions such as the equatorial Pacific the flux is likely from the ocean back into the atmosphere (Figure 3a). This means that, for samples collected since mid-WOCE, the dominant control on oceanic $DI^{14}C$ has been surface-to-deep exchange, similar to the situation for anthropogenic CO_2 (Graven et al. 2012). In fact, in recent decades anthropogenic CO_2 uptake and oceanic ^{14}C uptake are strongly correlated in ocean models (Figure 3b). After the formal portion of OCMIP, model-data $\Delta^{14}C$ comparisons degenerated back to single model or at best two data-model comparisons (e.g., Galbraith et al. 2011; Graven et al. 2012), including eddy resolving models (e.g., Lachkar et al. 2007). OCMIP led to model specific developments and advancements. At Princeton, a series of sensitivity studies using a coarse model (Modular Ocean Model, or MOM) lead to the MOM model doing better at reproducing deep water radiocarbon in addition to a better understanding of thermocline ventilation processes (Gnanadesikan et al. 2002, 2004; Galbraith et al. 2011). Sensitivity experiments such as
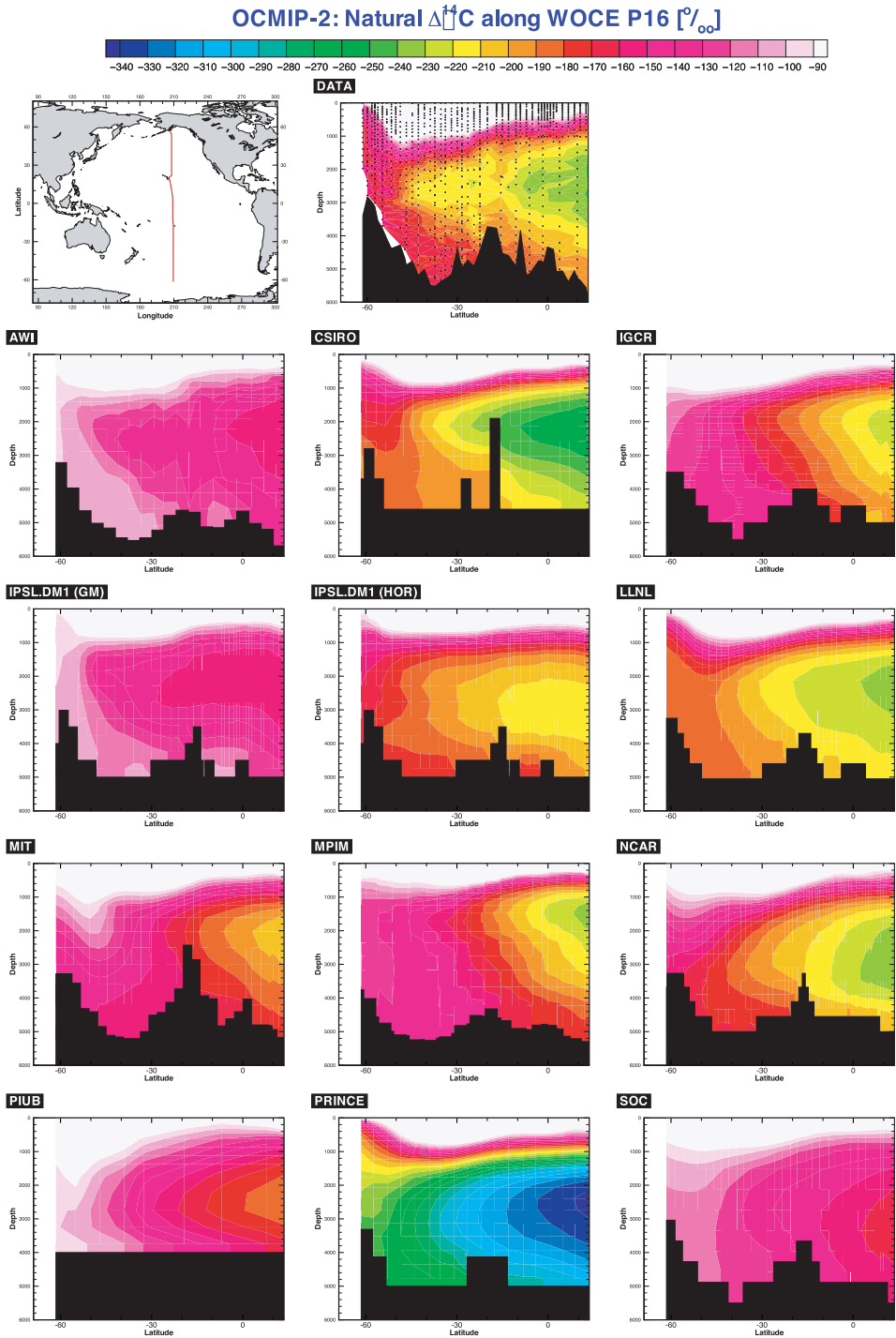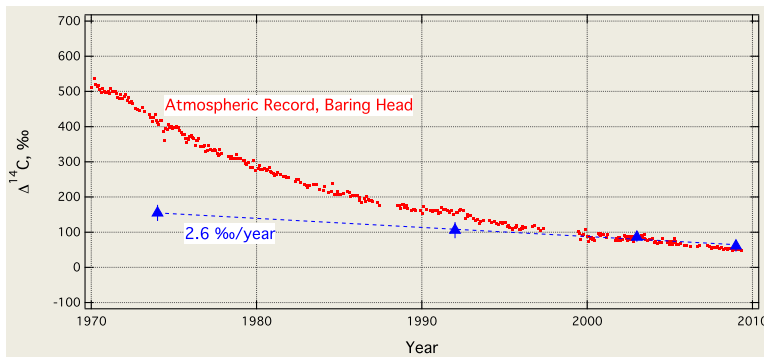
Figure 2   OCMIP-2 results. All of the model results and the data are colored and scaled identically and the portion of the section containing bomb radiocarbon has been masked.

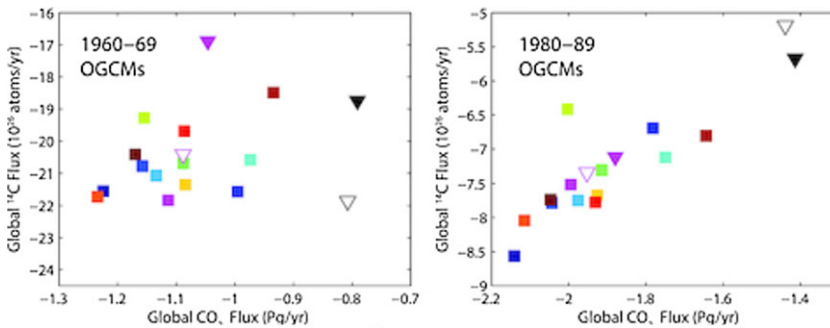Figure 3   A. Surface ocean DI^{14}C (blue diamonds) at 32°S in the Pacific at 4 time points compared to atmospheric record (red dots). B. Relationship between global ocean CO_2 and ^{14}C uptake in a collection of ocean models in the 1960s (left) and in the 1980s (right). (Figure adapted from Graven et al. 2012.)

these and data-model comparisons (e.g., Guilderson et al. 2000) have shed light on the challenges of accurately modeling ocean dynamics in regions with significant vertical fluxes.

Largescale coupled models have improved through the application of subgrid scale parameterization that impacts horizontal movement and mixing. Yet, issues remain with the models' representation of vertical dynamics as well as the incomplete understanding of the coupling with overlying wind-field and eddy-scale processes. This is slowly leading the modeling community away from "model democracy" where every model is equally viable, to focusing on models that achieve certain observation-based metrics better than others (e.g., Beadling et al. 2020). One metric that integrates atmosphere-ocean coupling, vertical dynamics, and the surface ocean's radiative balance is the model sea surface temperature (SST) field and how big and where any model-data bias occurs. SST bias in the Geophysical Fluid Dynamics Laboratory (GFDL) CM2Mc Earth System model (Figure 4) is representative of many earth system and OGCMs used in CMIP (c.f., fig 1 in Wang et al. 2014). The general statements that model cloud biases and a bias in the position and/or intensity of major wind systems (e.g., the Southern Ocean westerlies and western boundary wind systems) impact the surface radiative budget and are thus the cause of the observed model-data SST bias, although accurate, do not quite capture model failures. A cloud-forced radiative imbalance leading to SST biases does not directly explain the
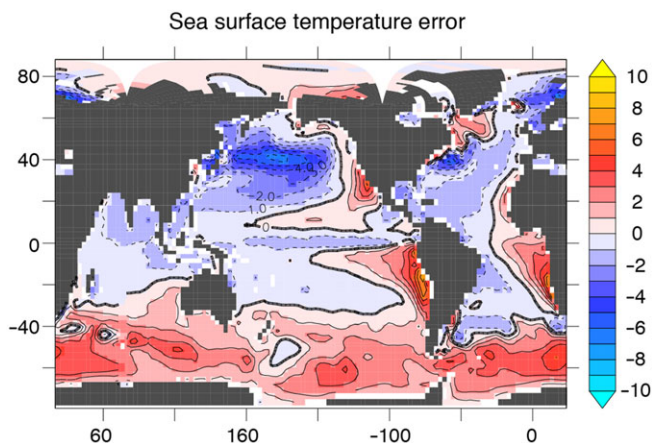
Sea surface temperature error

Figure 4   SST error or bias in the GFDL CM2Mc Earth System model relative to observations (after Galbraith et al. 2011). Similar biases in space and amplitude are observed in nearly all of the CMIP models (Wang et al. 2014). At the western boundaries, SST biases are accompanied by biases in upwelling volume. In the Southern Ocean the SST biases are accompanied by insensitivity of overturning rates with increased winds.

models' failures to accurately recreate the volume of water upwelling (and the $\Delta^{14}C$ values and "regional deficits") in these regions (c.f., Toggweiler et al. 2019a, 2019b). These regions are sources and sinks of nutrients and atmospheric CO_2, and have large impacts on ocean biogeochemistry. Model reproduction of decadal change is notoriously more difficult than reproducing a single snapshot of property distributions. Continued data-model comparisons using radiocarbon can lead to insights into inaccuracies in how mesoscale eddies are treated in the models and their effect on mixing as well as understanding the transfer of properties such as energy from the surface to the deep ocean. Small changes in the parameterization of mesoscale eddies can have a large impact on climate sensitivity (Fox-Kemper et al. 2019). Moving beyond "tuning exercises" the tracer data in the Repeat Hydrography Sections represent an opportunity to improve modeling of vertical dynamics and interior, deep circulation and, therefore, to increase models' ability to predict the sources and sinks of nutrients and carbon in surface water.

There is a recognition that the climate system has tipping or bifurcation points where the system can rapidly shift to an alternative state but will not return to the original state even when the forcing perturbation is removed (c.f., IPCC 2019). Acting much like a bath-tub drain, the Southern Ocean has been a significant modifier of anthropogenic atmospheric CO_2 and heat: the formation of interior and deep waters removes atmospheric CO_2 from the surface ocean (and thus from the atmosphere) and at the same time moves heat away from the surface (Purkey and Johnson 2013; Johnson and Lyman 2020). Largescale changes in the overlying wind (Ekman) forcing has the ability to alter the circulation in such a manner to decrease the uptake of heat and CO_2. However, teasing out natural multi-decadal variability associated with the Southern Annular Mode and its teleconnection to the Pacific Decadal Oscillation from changes directly forced by anthropogenic-induced climate change will be difficult in this sparsely sampled, yet incredibly important region.

The Southern Ocean Carbon and Climate Observations and Modeling Program (SOCCOM) is currently working to "unlock (sic) the mysteries of the Southern Ocean," at least in the upper 2000 m. Flexibility in the funding model for the radiocarbon portion of GO-SHIP has allowed the collection of DI^{14}C samples at selected SOCCOM float sites. The well-documented poleward movement and intensification of the southern hemisphere westerlies observed in 2000–2010s (e.g., Fyfe et al. 2007; Lin et al. 2018) have continued with an increase in the intensity of the 90th percentile winds (Young and Ribal 2019). This change has the potential to erode surface waters thus exposing subsurface or interior water with higher concentrations of CO_2. This will reduce the ability of these surface waters to take up anthropogenic CO_2 (e.g., Gray et al. 2018 Keppler and Landschützer 2019). Will deeper mixing associated with the winds and reduced salinity due to Antarctic glacial ice melting increase the stability of the Southern Ocean to yield a "new" mode of Southern Ocean circulation (e.g., Bronselaer et al. 2020)? This could have grave implication for the climate system as a whole and for future climate change scenarios.

Radiocarbon has a large dynamic range in the ocean. It is one of tools the oceanographic and modeling communities have to monitor changes in the structure of the Southern Ocean. In particular, the vertical and horizontal gradients of $\Delta^{14}C$ are sensitive to the competing effects of the air-sea ^{14}C disequilibrium isotope flux and the exhumation of low-Δ^{14}C interior water. Repeated meridional Southern Ocean sections frequent enough to distinguish sub-decadal variability associated with the Southern Annular Mode from secular changes across regions most important to upwelling, interior water formation, and air-sea CO_2 exchange will be a powerful diagnostic of the state of the Southern Ocean and a necessary model benchmark to elucidate biases.

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