first 3–4 days is similar. The divergence between the two time histories after that time is probably attributable to the fact that there were further additions of iron to the patch water on days 3 and 7 of Ironex II, but only the single initial iron enrichment during Ironex I, after which the disappearance of the added Fe, presumably by sedimentation, occurred very quickly. The simplest possible interpretation of the Ironex results is therefore that iron supply, when increased in the equatorial Pacific, allows diatoms to bloom and the chemistry of the water to change, providing that the iron concentration is elevated for several days at least.

## Conclusion

Several further applications of the tracer technique are presently under way. Two 'large scale' experiments in the open ocean are being actively monitored, in the Greenland Sea and the Brazil Basin. Numerous useful subsurface experiments can be imagined. However, because of the conflict between such subsurface release experiments and the use of  $SF_6$  as a transient tracer, there is a need to establish a forum by which the wider oceanographic community can have input into the planning of prospective release experiments.

Small-scale releases in surface waters should not normally compromise the transient tracer signal. One obvious application now under way is that of iron fertilization experiments to examine the extent to which 'high nutrient low chlorophyll' regions other than the equatorial Pacific are limited by iron availability. The recent Southern Ocean Iron Enrichment Experiment (SOIREE) has shown unequivocal evidence that iron supply does affect the biology of that region. This experiment was carried out during sometimes stormy weather, confirming that the patch-tracking technique works well in the open ocean under storm conditions. To summarize, experiments using  $SF_6$  tracer in the open ocean are now reduced to practice, if not routine. Three experiments at the 1000-km scale have so far been initiated, to measure ocean mixing on these scales. There have been more than twenty smaller scale experiments, of increasing sophistication, since they were first begun in 1986. For topics to which they are suited, such as iron limitation, biogeochemical budgets, gas exchange and diapycnal mixing rates, these experiments have enabled something of the precision of the land-based laboratory investigation to be brought to bear in at-sea oceanography.

## See also

Air–Sea Gas Exchange. Tracers and Large Scale Models. Tracers of Ocean Productivity. Long-term Tracer Changes.

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# **TRACERS AND LARGE SCALE MODELS**

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## Introduction

Geochemical tracers are included in large-scale models for a variety of applications. These include

(1) ocean model assessment, (2) the analysis of observed tracer fields, (3) simulation of the ocean carbon cycle, and (4) comparisons with paleoclimate measurements. This article reviews the use of tracers in large-scale ocean models, particularly in the context of ocean model assessment. Important information can be derived from chemical tracer simulations, such as how well models capture deep ocean ventilation. Tracer studies have revealed inadequacies in the model representation of certain water-mass formation processes, for example, convection, downslope flows, and deep ocean currents. This helps identify the need for model improvements, including better parameterizations of mixing and bottom boundary currents. The simulation of chemical tracers is important in model assessment and as a tool for analyzing water-mass mixing and transformation. For climate model validation, a cost-effective approach is to simulate natural radiocarbon to assess long timescale processes, and chlorofluorocarbon compounds (CFCs) for decadal to interdecadal ocean ventilation. Idealized scalar tracers, such as those tracking water-mass age and concentration, are also an important component of large-scale ocean modeling.

#### Large-Scale Models

Computational ocean models are a key tool in oceanographic and climate research. They can add to the knowledge gained from direct ocean measurements, which are often sparse in space and time. Ocean models are also incorporated into climate simulations, as the oceans play a vital role in regulating our climate. Ongoing model development is focused on improving existing simulations of the ocean's circulation, which involves the critical assessment of how well models represent the real system. An important aspect of this is the representation of water-mass formation, since this controls the removal of surface waters to greater depth, as well as determining poleward heat and freshwater transports. Model assessment relies on ocean measuring programs but is fundamentally limited in certain ways. For example, many dynamic processes that are linked with water-mass formation, such as convection, mixing, and deep currents, are extremely difficult to measure directly. Modelers can use temperature-salinity (T–S) to provide a 'proxy' means for assessment of the water-mass formation processes operating in models. In addition, seawater comprises dissolved chemical tracers, such as silicate, oxygen, phosphate, CFCs, and isotopes of carbon. The ocean influx of these tracers can be time-dependent and distinct for different locations, so they can provide detailed information on the pathways and rates of water-mass renewal beneath the surface mixed layer. In this way, tracers can be used to assess the simulated circulation in ocean models.

Geochemical tracers that have been used to assess ocean models include tritium. CFCs natural and bomb-produced radiocarbon, and, to a lesser extent, oxygen, silicate, phosphate, isotopes of organic and inorganic carbon compounds, and certain noble gases (e.g., mantle helium and argon). The choice of tracer depends partly on the timescales of interest. For example, natural carbon isotopes, particularly radiocarbon, are useful for examining old watermasses such as North Pacific and Circumpolar Deep Water. Anthropogenic tracers, such as tritium and CFCs, are best suited for analyzing model ventilation over decadal timescales, such as thermocline ventilation and the renewal of Antarctic Intermediate Water. Factors determining which tracer is best for a given problem include the atmospheric history or input function of the tracer, whether the tracer is involved in biological processes, and whether the tracer is easy to measure and indeed well observed in the region of interest. A summary of the main geochemical tracers used in ocean model assessment is given in Table 1.

#### Radiocarbon

Radiocarbon (<sup>14</sup>C) is created in the atmosphere both naturally and through human activities such as nuclear weapons testing. Its entry into sea water is

Table 1	The prine	cipal chemi	cal tracers	s used to	assess	large-scale	ocean	circulation	models
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Tracer	Chemical formula	Main source(s)	Properties	Applications
Natural radiocarbon	<sup>14</sup> C	Natural isotope of <sup>12</sup> C	5730 year half-life	Long time-scale ventilation
Bomb radiocarbon	<sup>14</sup> C	Nuclear bomb-testing	5730 year half-life	Transient and decadal
Tritium	<sup>3</sup> Н	Bomb-produced radionuclide	12.43 year half-life	Transient (favors NH)
Chlorofluorocarbons	CCI <sub>N</sub> F <sub>M</sub>	Refrigerants, foams, solvents	Stable, inert	Transient and decadal
Helium-3	<sup>3</sup> He	Seafloor volcanism, <sup>3</sup> H by-product	Stable	Deep water flows

Chemical formulae indicate the modeled isotope, compound or ion. Chlorofluorocarbons cover a variety of species (CFC-11 ( $CCI_3F$ ) and CFC-12 ( $CCI_2F_2$ ) are the most common). NH refers to the Northern Hemisphere. Natural radioactive isotopes are created by cosmic rays in the atmosphere, then radioactively decay once dissolved in sea water.

only via air-sea gas exchange with the surface mixed layer, from where its natural radioactive decay leads to a gradual differentiation of content in water masses. The longer a given water mass has been out of contact with the atmosphere, the more depleted the <sup>14</sup>C content becomes in proportion to the concentration of the main carbon isotope, <sup>12</sup>C. The half-life of <sup>14</sup>C is 5730 years, making it suitable for differentiating ocean ventilation rates over long timescales. In addition, bomb tests during the 1950s dramatically increased the atmospheric concentration of <sup>14</sup>C, and this can be used to study shorter timescale ventilation processes.

The distribution of natural radiocarbon provides the best measure of deep ocean ventilation rates over century timescales and beyond. Modern anthropogenic tracers (e.g., CFCs, bomb-produced tracers) only resolve the decadal to interdecadal timescale. Radiocarbon simulations, therefore, provide the most practical test of model ventilation in the deep Indian and Pacific Oceans, where renewal timescales are of the order of hundreds to thousands of years.

The <sup>14</sup>C content of the ocean is expressed as the deviation of the <sup>14</sup>C/<sup>12</sup>C ratio (in parts per thousand, %) from a reference atmospheric ratio. The notation used for this difference is  $\Delta^{14}$ C, which is normally negative since the <sup>14</sup>C isotope decays in the ocean. The more negative the value of  $\Delta^{14}$ C, the more time has elapsed since the water mass was last in contact with the atmosphere. The  $\Delta^{14}$ C ratio is the quantity normally simulated in ocean models, not the absolute concentration of <sup>14</sup>C. This means that biological conversion processes can be largely ignored because they affect <sup>12</sup>C and <sup>14</sup>C compounds in the same manner. In addition, because  $\Delta^{14}$ C simulations do not predict gas transfer on the basis of actual <sup>12</sup>CO<sub>2</sub> and <sup>14</sup>CO<sub>2</sub> concentration levels, isotopic fractionation between gaseous and dissolved  $CO_2$  phases can be neglected. This means that the prebomb cycle of  $\Delta^{14}$ C can be forced towards a time-independent atmospheric value of zero, typically at a rate that is wind-speed dependent and calibrated to match observed global mean gas exchange rates. Interior  $\Delta^{14}$ C is transported by the model circulation, convection and mixing processes, as well as undergoing natural radioactive decay with a half-life of 5730 years. When simulating bombproduced <sup>14</sup>C uptake, it is simply a matter of increasing the atmospheric reference value of  $\Delta^{14}C$ from zero to the estimated atmospheric concentrations resulting from nuclear bomb testing during the 1950s and 1960s.

An example of natural  $\Delta^{14}$ C simulations is shown in Figure 1, comparing the measured  $\Delta^{14}$ C in the western Pacific during 1974 with that simulated in two natural radiocarbon simulations. Experiment B is from a robust diagnostic experiment wherein the interior model T–S are continuously restored towards climatological data. Experiment P is identical to experiment B, except that there is no interior restoring of T–S, so they are free to drift towards



**Figure 1** Western Pacific sections of  $\Delta^{14}$ C (%) in observations (A) and in two natural radiocarbon experiments. (B) Experiment B is from a robust diagnostic experiment wherein the interior model T–S are continuously restored towards climatological data. (C) Experiment P is identical to experiment B, except that there is no interior restoring of T–S.

unrealistic values. Experiment P is therefore prognostic in its treatment of water masses; they form at the surface due to convection and vertical motions, and spread laterally due to interior currents and mixing. In contrast, case B has realistic values of T–S, although they may be generated by the artificial interior restoring terms. Which of the two model simulations determines the most realistic interior ventilation rates, can be distinguished by using radiocarbon.

Apparent in the upper kilometer of the observations is the penetration of high concentrations of radiocarbon due to bomb-produced levels of the <sup>14</sup>C isotope. This could be simulated by running the natural  $\Delta^{14}$ C simulations from 1950 onward, using the appropriate bomb-loaded atmospheric  $\Delta^{14}C$ concentrations. Below 1km, however, all of the observed  $\Delta^{14}C$  is derived from the prebomb atmosphere. Clearly apparent is the relative success of the prognostic experiment (P) in simulating the ventilation of North Pacific Deep Water in contrast to the robust-diagnostic experiment (B). Similar results have been obtained in the Atlantic Ocean; namely, that experiment P is superior to the robust-diagnostic case. This result is related to the way convection and vertical motions are suppressed in the diagnostic integration because water masses are created by the interior restoring of T-S to observations; they need not form at the sea surface. Indeed, water-mass formation is largely suppressed by the stable stratified water column, which is artificially maintained by the internal restoring terms. With reduced convection and vertical motion, insufficient <sup>14</sup>C is injected into the deep ocean, exposing a problem with the robust-diagnostic technique. One of the key conclusions here is that a robust-diagnostic simulation - in spite of a more realistic model T-S - is inferior to a prognostic run in representing important ocean ventilation processes. This finding also points directly to geochemical tracers as an important component of ocean model validation efforts, since a correct T-S field can theoretically support spurious circulation patterns.

#### Tritium

Tritium (<sup>3</sup>H) is a radioactive isotope (or radionuclide) of hydrogen that was produced by atmospheric nuclear bomb testing in the 1950s and 1960s in an amount greatly exceeding its natural abundance. Because of its time-dependent atmospheric history it is classed as a 'transient' tracer. It decays into <sup>3</sup>He with a half-life of 12.43 years. Its input function into the world oceans is rather complex as it depends on rainfall, air moisture, geographic location, and river input. Input from marine air-masses depends on latitude and rainfall/water vapor, the latitude dependence being weighted heavily towards those regions where nuclear bomb testing occurred  $(40^{\circ}-50^{\circ}N)$ . Air masses that move out over the sea from land have higher inputs for a given latitude than do marine air masses, because gas exchange over land is not as effective in removing tritium as it is over the ocean. Tritium concentrations are about four times higher in continental air as compared with marine air. Lastly, river input of tritium is significant since catchment areas over land can concentrate tritium-borne rainfall into single entry points into the ocean. Tritium has been measured and analyzed in several studies of oceanic circulation, particularly in the North Atlantic.

The main uncertainty in modeling ocean tritium uptake is in the estimation of the source function. Although global input climatologies have been constructed, the complex processes influencing tritium entry into the oceans renders these estimates a source of possible model error. However, the source function errors are typically smaller than those due to model circulation errors, so validation studies are still possible.

A model-observation comparison of tritium on a north-south section in the western Atlantic is shown in Figure 2. Apparent in the observations is the southward spreading of tritium-laden North Atlantic Deep Water (NADW) at around 2000-4000 m depth. In the model simulation, a stronger than observed signal of downslope flowing tritium is seen south of the Greenland-Iceland-Scotland Ridge. This is probably because the model has spuriously deep convective mixed layers, with nearuniform tritium concentrations of 4.0 TU reaching  $3000 \,\mathrm{m}$  at  $60^{\circ}\mathrm{N}$ . In the observed section, noticeable vertical gradients of tritium are seen in this region. As such, the model simulation of tritium has revealed a problem with excessive ventilation and overturn of surface waters in the North Atlantic. This could compromise the model's ability to predict climate change or  $CO_2$  uptake in the region.

#### Chlorofluorocarbons

The industrial release of chlorofluorocarbons (CFCs) began in the early 1930s, and accelerated greatly during the next three decades. Despite the discovery that CFCs destroy stratospheric ozone, the atmospheric concentration of these gases has continued to rise until very recently. Even though virtually all production and release occurs in the Northern Hemisphere, rapid mixing rates in the lower atmosphere and the chemical stability of CFCs ensure

relatively uniform distributions of these gases over the troposphere. Their input functions are therefore significant over the entire ocean, unlike some bomb-produced tracers (e.g., tritium) whose atmospheric concentrations favour the Northern Hemisphere.

Because CFCs are weakly soluble in sea water, they dissolve at the sea surface like most other atmospheric gases. However, relatively low solubility and negligible biological interaction ensure that the ocean uptake of CFC is only a small component of the global cycling of these gases (unlike, say,  $CO_2$ ). Upper level traces of CFC get redistributed vertically by convection and subduction, and then horizontally by interior ocean currents and mixing. Recently ventilated waters are therefore characterized by comparatively high concentrations of these anthropogenic gases.

Unlike the majority of ocean tracers, CFCs are not known to be influenced by biological processes and are very stable compounds; they therefore serve as relatively unambiguous tracers of the present day ocean circulation over decadal to interdecadal timescales. Direct measurements of the concentration of chlorofluorocarbons (CFCs) in the ocean are now routinely used to add information to conventional hydrographic surveys. With relatively well-known atmospheric histories and solubility properties in sea water, CFCs can be readily incorporated into general circulation models of the ocean.

An example of a CFC simulation is given in Figure 3, which shows observed and modeled CFC-11 along a transect in the South Atlantic near  $25^{\circ}W-35^{\circ}W$  during 1989. The observations were only taken as far south as  $55^{\circ}S$ , no CFC data can therefore be presented south of this latitude in the observed panel. The dashed contours included in the diagrams are locally referenced density surfaces in climatological observations as well as in two model experiments.

The two numerical experiments shown are identical global ocean models, only one case (ISOP) adopts simplified along-density surface mixing; whereas the other (GM) employs mixing that more realistically parameterizes the effects of subgrid scale eddies on the larger-scale transport of tracers. In the ISOP case extensive surface outcropping of deep density layers occurs in the Southern Ocean and Weddell Sea. In contrast, the observed deep ocean is much denser than in ISOP and deep ocean density layers do not outcrop at the surface. So in this model case there is an unrealistic pathway for penetration of CFC into the ocean interior. This translates to a strong vertical flux of CFC to relatively deep waters. In the GM case deep ocean density is greater, and deep-ocean density layers do not outcrop over the open ocean but instead only over the shelf in the southern Weddell Sea. This leads to less overturn of CFC-rich surface waters. In addition, a clear signal of CFC-depleted deep water is seen at 50°S in the GM model run. This corresponds to the upwelling of old Circumpolar Deep Water, as also noted in the observations. From this CFC model comparison, it is clear that the more sophisticated mixing scheme produces a superior simulation of Southern Ocean water-mass circulation.

#### **Ocean Carbon Cycle Tracers**

Models of the oceanic carbon cycle embedded in three-dimensional ocean models range in complexity from simple nonbiological CO<sub>2</sub> perturbation studies through to quite complex biogeochemical tracer cycles. The simpler variety of oceanic CO<sub>2</sub> uptake model assumes a perturbation approach, namely that the preindustrial ocean carbon cycle continues without being affected by anthropogenic influences, such as increasing levels of atmospheric  $CO_2$  or the resulting changes in ocean circulation. This enables these models to ignore biological processes, thereby greatly simplifying the seawater chemistry included in the model. Such simulations typically rely on other tracers (e.g., tritium and radiocarbon) to validate the simulated circulation fields before including anthropogenic CO<sub>2</sub> uptake.

More complex models incorporating biological cycles typically include the production of biogenic organic matter and nutrients at the surface, transport of biogenic material to the deep waters, and remineralization. This normally involves the ocean model carrying a number of chemical tracers as prognostic variables, including carbon compounds (such as total dissolved inorganic carbon and calcium carbonate), as well as phosphate, dissolved oxygen, particulate organic matter, and silicate. Often radiocarbon and CFCs also included for model validation purposes.

Unfortunately most natural biogeochemical tracers are not very useful for the purpose of largescale model assessment. This is because they are affected by both biological and circulation processes. A poor simulation of such a tracer might indicate either deficiencies in the model circulation fields or incorrect parameterization of a biological process, or both. In addition, biological cycles are difficult to model explicitly. As such, for validation purposes most ocean carbon cycle models rely on inert tracers (e.g., CFCs) or ones whose biological conversion processes can be ignored (e.g.,  $\Delta^{14}C$ ). Some natural biogeochemical tracers can, however, be used to assess model circulation fields. For example, the simulation of deep phosphate, silicate, and oxygen in ocean carbon cycle models primarily reveals the ocean's conveyor belt at depth. Younger waters have low concentrations of phosphate and silicate, and are enriched in oxygen and <sup>14</sup>C, whereas older waters show higher concentrations in phosphate and silicate, and are oxygen-depleted. This can be used to assess model water-masses in much the same way as in observational oceanography. For example, **Figure 4** shows the global distribution of  $PO_4^* = (PO_4 + O_2/177 - 1.95)$  at 3000 m depth in an ocean circulation model. The quantity  $PO_4^*$  can be regarded as a physical tracer at depth because the effects of remineralization have been cancelled out by combining  $PO_4$  and  $O_2$  in this way. The value 1.95 is arbitrarily subtracted in order to obtain similar numbers to those for phosphate, and  $O_2$  is scaled by 177 due to the Redfield ratio



**Figure 2** Tritium concentrations along a north-south section in the western Atlantic. (A) Measurements made in 1972; (B) a model simulation. Units are TU (1TU corresponds to a tritium/ $H_2O$  ratio of  $10^{-18}$ ).

for PO<sub>4</sub> and O<sub>2</sub>. The distribution of PO<sub>4</sub><sup>\*</sup> at 3000 m depth reveals the mixing effects between the source waters of NADW (PO<sub>4</sub><sup>\*</sup> = 0.7) and Weddell Sea Bottom Water (WSBW; PO<sub>4</sub><sup>\*</sup> = 1.8). In much of the Pacific Ocean, for example, PO<sup>\*</sup><sub>4</sub> is almost uniform at values between 1.35 and 1.4, indicating a model mixing ratio of 30:70 between NADW and WSBW.



**Figure 3** Vertical section of CFC-11 in the South Atlantic Ocean extending from the Weddell Sea northwards. (A) Observed, (B) in a model with simple isopycnal mixing, and (C) in a model including parameterized eddy mixing effects.



Figure 4 Global distribution of  $PO_4^* = PO_4 + O_2/177 - 1.95$  at 3000 m depth in an ocean model.

#### **Other Chemical Tracers**

So far we have looked at radiocarbon, tritium, chlorofluorocarbons, and standard biogeochemical tracers in analyzing circulation and water-masses in ocean models. There are enough measurements of these chemical tracers to enable meaningful ocean model assessment. There are several other chemical tracers that are present in sea water and have the potential for use in ocean modeling studies. Examples include argon, mantle helium, and cesium, as well as radioactive isotopes of common tracers such as silicon and oxygen. However, because of measurement difficulty - sometimes requiring largevolume seawater samples - there are generally not many observations of these tracers. Mantle helium is an exception in this context, with several transects made as part of the World Ocean Circulation Experiment.

The injection of mantle helium into the deep sea can be used to trace abyssal to middepth ocean circulation. Helium produced in hydrothermal fluids in seafloor volcanism has a distinct isotopic signature: it is highly enriched in <sup>3</sup>He relative to <sup>4</sup>He compared with atmospheric helium. Model simulations assume mantle helium injection along the mid-ocean ridge axes with different local spreading rates (Figure 5A). The forcing fields are based on observational studies of helium sources in mantle volcanism and some less direct estimates. Source functions of mantle helium are still under investigation, so the tracer is not ideal for direct model validation studies. Also, deep mantle simulations often ignore the atmospheric source of <sup>3</sup>He as a radioactive by-product of bomb-produced tritium, so simulations are then only valid away from recently ventilated waters, such as in the deep Pacific Ocean.

Results from a mantle helium simulation in the Pacific Ocean are shown in Figure 5. In comparison with observed <sup>3</sup>He, the model simulates a maximum in mantle helium that is too shallow and depleted in <sup>3</sup>He. Overall, insufficient mantle helium is apparent in the model section, a result of excessive loss of <sup>3</sup>He through abyssal to surface upwelling in the Pacific. Once upwelled into the surface layer, the mantle helium is lost by air-sea exchange to the atmosphere. This rapid flux of mantle-laden sea water from the abyssal Pacific into the upper ocean suggests the model removes too much Pacific Deep Water directly through equatorial upwelling. It should be noted, however, that uncertainties in the input source function for mantle helium remain, so the model-observed differences could in part be due to the assumed flux of <sup>3</sup>He at the Pacific Ocean seafloor.

Large-scale ocean model simulations have also been carried out using a number of natural and artificial radioisotope tracers. Examples include argon-39, silicon-32, krypton-85, thorium-230, and protactinium-231. However, there are relatively few measurements of these tracers' rendering model validation over large scales nearly impossible. Artificial radiotracers leaked from nuclear reactors, such as <sup>137</sup>Cs from the Chernobyl power station accident, can also be used to assess circulation models of nearby regional seas. Examples include the Black Sea and the Kara Sea, as well as parts of the Arctic Ocean.

In addition to the tracers described above, largescale model simulations have also been performed with stable isotopes, such as  $\delta^{18}$ O and  $\delta^{13}$ C. Direct oceanic measurements of these tracers are quite sparse and their concentrations are complicated by fractionation, so they are generally not used for ocean model assessment. They tend to be used to



**Figure 5** (A) Source function of mantle helium assuming <sup>3</sup>He injection along the midocean ridge axes with different local spreading rates. (B) Modeled section (Pacific Ocean, mantle source only). (C) Observed Pacific Ocean section of <sup>3</sup>He (mantle + tritium by-product).

study the role of fractionation in determining largescale ocean distributions. In addition, these tracers are important in paleoceanographic studies; they are measured in deep-sea cores and coral debris and used to infer past climate conditions, including oceanic T–S. As such, their simulation in large-scale models aids their interpretation in paleoclimate studies.

#### **Idealized Tracers**

Apart from incorporating chemical tracers into ocean simulations for model validation or carbon cycle studies, specialized nonchemical or 'idealized' tracers can be configured for other purposes. Examples include tracers of water-mass age, tracers tagging the spread of predetermined source waters, and particle (or 'Lagrangian' trajectory) tracers. The real world analogue of these tracers might be difficult to estimate, yet the model simulation can provide possible insight into ocean ventilation rates and watermass spreading pathways.

An example is given in Figure 6, which shows water-mass age near 2000 m depth in an ocean model. Here, the age is defined as the time taken for surface waters to reach each location, averaged for all source water types contributing to the watermass mixture. So, on average, it takes about 1000-1200 years for surface waters to ventilate the deep North Pacific in this model. This time-scale compares favorably with estimates using radiocarbon. Source waters for the deep Pacific comprise components of Antarctic Bottom Water and North Atlantic Deep Water. Contrasting the Pacific Ocean, relatively rapid ventilation rates are seen in the Atlantic, with NADW flowing in a deep western boundary current into the Southern Ocean. This water mass of relatively young age can be seen to flow into the Indian Ocean, giving that deep basin more rapid ventilation rates than the remote North Pacific.

#### Uncertainties

Incorporating a chemical tracer into an ocean model requires knowledge of the tracer's source function and a faithful representation of its seawater chemistry. Some of these issues have been discussed above. For some tracers, the seawater chemistry is well known whereas the input function is a source of uncertainty (e.g., tritium, mantle helium). For others, a complex seawater chemistry necessitates inclusion of other geochemical tracers and biological effects (e.g.,  $CO_2$ ,  $O_2$ , phosphate). In this section uncertainties in simulating chemical tracer uptake, particularly in the context of large-scale model assessment, are discussed.

Source function uncertainties remain for bombproduced tritium and mantle helium. Further studies in these areas are required. For CFCs and <sup>14</sup>C, uncertainties in the input function relate more to the parameterization of air-sea gas exchange, since atmospheric concentrations are relatively well known. Uncertainty in air-sea gas fluxes is related to the specification of the gas transfer speed or piston velocity. Several researchers have suggested bulk wind speed-dependent parameterizations for the gas transfer speed. However, the estimated value can vary by about a factor of two depending on the chosen formulation. This translates into uncertainty in the model simulation of gas uptake, most notably in slowly equilibrating gases such as CO<sub>2</sub>.

Tracer simulations are sometimes calculated in an 'off-line' model in which the steady-state fields of T-S and velocity from an ocean model are used to advect and mix the tracer. This is potentially useful in models of high resolution where the computational cost of an 'on-line' tracer model can be prohibitive. Although computational savings are made with such an approach, there are important factors that must be considered. For example, the tracer transport effects of convective overturn and internal variability (e.g., eddies) must be considered, including their full seasonal cycle. The 'off-line' tracer model needs to include all physical transport processes of the 'on-line' model.

Finally, it is of interest to consider how tracer simulations should be performed within coupled climate models. If the interest of the study is to simulate, for example, the oceanic carbon cycle during anthropogenic climate change, the air-sea flux of carbon should be simulated using the model-derived wind speed, sea ice, T-S, and so on. This is because these variables are likely to change during the climate change run, affecting the simulated carbon uptake by the ocean. Indeed, the very goal of such studies is to examine how changed climatic conditions will alter the oceanic uptake of CO<sub>2</sub>. If, however, the goal of the study is to validate the ocean model used within the climate system, an additional simulation needs to be performed. This second model run should employ observed wind speed, sea ice, and T-S to estimate the gas flux. This is because coupled models can simulate erroneous wind speeds and sea ice, which can bias the gas fluxes in some way. Then, compensating errors in model circulation can result in reasonable simulation of tracers. Using flux estimates derived directly from observations provides a less ambiguous test of climate model performance.



**Figure 6** Water-mass age (years) near 2000 m depth in an ocean model. The age is defined as the time taken for surface waters to reach each location, averaged for all source water types contributing to the water-mass mixture. Waters younger than 100 years are stippled.

#### Summary

A number of geochemical tracers can be used to assess the circulation and water-mass formation in ocean models. Tracers that have been used in this context include tritium, CFCs, natural and bombproduced radiocarbon, and, to a much lesser extent, mantle helium, stable isotopes of oxygen and carbon, and other less-measured radionuclides. Substantially more information can be derived from tracer experiments than that obtainable from T-S alone. For example, natural radiocarbon can be used to assess ocean models with regard to long time-scale circulation processes (centennial and beyond), such as deep-water ventilation. Anthropogenic tracers such as tritium, CFCs, and bombproduced <sup>14</sup>C are well suited for analysing model ventilation over interannual to decadal time-scales. It should be noted, however, that the ocean influx of tritium and bomb <sup>14</sup>C is less accurately known than

that for CFCs. As such, CFCs are presently the best available tracers for decadal to interdecadal ocean model validation.

The simulation of chemical tracers in ocean and climate model assessment is highly recommended. A cost-effective approach in large-scale models is to simulate natural <sup>14</sup>C to assess long time-scale processes, and CFCs for decadal to interdecadal ocean ventilation.

#### See also

Air-Sea Gas Exchange. Carbon Cycle. CFCs in the Ocean. Cosmogenic Isotopes. Deep-sea Fishes. General Circulation Models. Hydrothermal Vent Fluids, Chemistry of. Nuclear Fuel Reprocessing and Related Discharges. Ocean Carbon System, Modelling of. Ocean Circulation. Radioactive Wastes. Radiocarbon. Thermohaline Circulation. Volcanic Helium.

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## TRACERS OF OCEAN PRODUCTIVITY

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#### Introduction

Primary production is the process whereby inorganic carbon is fixed in the sunlit (euphotic) zone of the upper ocean, and forms the base of the marine food pyramid. It occurs when marine phytoplankton use sunlight energy and dissolved nutrients to convert inorganic carbon to organic material, thereby releasing oxygen. The total amount of carbon fixed during photosynthesis is called gross production, whereas the amount of carbon fixed in excess of internal metabolic costs is referred to as net production. It is understood that a significant fraction of the carbon fixed in this manner is rapidly recycled by a combination of grazing by zooplankton and in situ bacterial oxidation of organic material. New production is that portion of net production that is supported by the introduction of new nutrients into the euphotic zone. Traditionally, this has been regarded as production fueled by nitrate as opposed to more reduced forms of nitrogen, such as ammonia and urea. Some portion of the fixed carbon sinks out of the euphotic zone in particulate form, or is subducted or advected away as dissolved organic material from the surface layers by physical processes. This flux is regarded collectively as export production. The ratio of new (export) to net production, referred to as the f-ratio (e-ratio) can vary between 0 and 1, and is believed to be low in oligotrophic ('blue water'), low productivity regions, and higher in eutrophic, high productivity regions. Finally, net community production is the total productivity in excess of net community metabolic cost. On sufficiently long space- and time-scales, it can be argued that new, net community, and export production should be equivalent in magnitude.

Net production has been measured 'directly' by radiocarbon incubation experiments, whereby water samples are 'spiked' with radiocarbon-labeled bicarbonate, and the net rate of transfer of the radioisotope into organic matter phases determined by comparison of light versus dark incubations. Global maps of net productivity have been constructed on the basis of such measurements, and current estimates indicate a global fixation rate of order 50 GT C  $a^{-1}$  (1 GT = 10<sup>15</sup> g). Rates of export, new, and net community production are more difficult to determine directly, yet are of equal importance as determinants of biogeochemically important fluxes on annual through centennial timescales.

Geochemical tracer techniques have been used to make such estimates, and offer significant advantages in that they are fundamentally nonperturbative, and integrate over relatively large space-scales and long time-scales. Conversely, such determinations must be viewed from the perspective that they are indirect measures of biogeochemical processes, and have characteristic implicit space- and time-scales, as well as boundary conditions, and sometimes ambiguities and model dependence. Further, the specific tracer or physical system used to obtain production estimates determines the type of productivity measured. Thus any treatment of geochemical tracer estimates must include a discussion of these attributes.

## Measuring Oceanic Productivity with Tracers

Just a few approaches will be discussed here. Other techniques have been used with some success, parti-