increased catches in areas where the teleost fishes have been heavily exploited (Saharan Bank).

Role in the Oceans

Combining data from commercial harvest fisheries with crude estimates of total consumption by predators, the global biomass (standing stock of adults and sub-adults) of cephalopods in the oceans has been variously estimated to lie between 193 and 375×10^6 t. These figures have been derived by tentatively accumulating the estimate ranges for mesopelagic squid $(150-300\times10^{6}t)$; oceanic epipelagic squid $(30-50\times10^{6} t)$; slope/shelf-edge squid $(8-15\times10^{6} t)$; and shelf sepioids and octopuses $(5-10\times10^{6} t)$.

Whether or not these apparently massive estimates of biomass are realistic, their compatibility with other global estimates of marine productivity and consistency with the productive potential of cephalopods is uncertain. Overestimation of cephalopod frequency in predator diets could arise because cephalopod remains persist longer than those of other prey. Another source of uncertainty is the scaling up of limited predator and fishery data to ocean basin scales and the low carbon content (watery tissues) of many mesopelagic cephalopods. Some studies suggest the cephalopod biomass in the open sea (nektonic) to be about half that of fish and the mismatch between direct sampling with nets and indirect sampling from higher predators in this environment is well known.

Conclusions

Cephalopods are undoubtedly one of the most charismatic groups of marine animals. Sharing a basic body with the other molluscs they have evolved very distinctive biological characters, advanced behavior, and life cycle patterns. Cephalopods comprise a major sector of marine biomass, having central signiRcance to higher tropic levels and global fisheries. Little is understood about the biology of the oceanic and mesopelagic species and, consequently major uncertainties remain surrounding the quantitative role of cephalopods in the world's oceans.

See also

Bioluminescence. Molluskan Fisheries.

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CFCs IN THE OCEAN

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Introduction

The oceans, atmosphere, continents, and cryosphere are part of the tightly connected climate system. The ocean's role in the climate system involves the transport, sequestration, and exchange of heat, fresh water, and carbon dioxide $(CO₂)$ between the other components of the climate system. When waters descend below the ocean surface they carry with them atmospheric constituents. Some of these are gases such as carbon dioxide and chlorofluorocarbons (CFCs). The CFCs can serve as a physical

analog for $CO₂$ because they are biologically and chemically inert in oceans. In the oceans the distribution of CFCs provides information on which waters have been in contact with the atmosphere in the past few decades. The CFCs also give information on the ocean's circulation and its variability on timescales of months to decades. The timescale information is needed to understand and to assess the ocean's role in climate change, and its capacity to take up anthropogenic constituents from the atmosphere. Thus, the advantage of using tracers like CFCs for ocean circulation studies is the added dimension of time; their time history is fairly well known, they are an integrating quantity and an analog for oceanic anthropogenic $CO₂$ uptake, and they provide an independent test for time integration of models.

Tracers serve as a 'dye' with which to follow the circulation of ocean waters. There are conventional ocean tracers such as temperature, salinity, oxygen, and nutrients. There are stable isotope tracers such as oxygen-18, carbon-13, and there are radioactive tracers both naturally occurring (such as the uranium/thorium series, and radium), and those produced both naturally and by the bomb tests (such as tritium and carbon-14). The bomb contributions from the latter two are called transient tracers, as are the CFCs, because they have been in the atmosphere for a short time. This implies an anthropogenic source and a nonsteady input function.

Atmospheric Source

The chlorofluorocarbons, CFCs, are synthetic halogenated methanes. Their chemical structures are as follows: CFC-11 is CCl_3F , CFC-12 is CCl_2F_2 , and CFC-113 is $\text{CCl}_2\text{FCCIF}_2$. For completeness the compound carbon tetrachloride, $CCl₄$, is also included in this article as its atmospheric source, measurement, and oceanic distribution are similar to those of the CFCs. The CFCs have received considerable attention because they are a double-edged environmental sword. They are a threat to the ozone layer, and a greenhouse gas. The CFCs are used as coolants in refrigerators and air conditioners, as propellants in aerosol spray cans, and as foaming agents. These chemicals were developed over 50 years ago when no one realized that they might cause environmental problems. When released CFCs are gases that have two sinks, the predominant one being the atmosphere, and to a lesser extent the oceans. Most of the CFCs go up into the troposphere, where they remain for decades. In the oceans and in the troposphere the CFCs pose no problem. However, some escape into the stratosphere where they are a threat to the ozone layer. Due to their role in UV absorption they have been correlated with the increased incidence of skin cancers. Since the recognition of the CFCs as an environmental problem in the 1970s and the signing of the Montreal Protocol in 1987, the use of CFCs has been phased out. The atmospheric concentrations have just started to decrease. This is an important international step toward correcting the dangerous trend of stratospheric ozone depletion.

The atmospheric CFC concentrations became significant after the 1940s. The concentrations increased exponentially until the mid-1970s, and then increased linearly until the 1990s at a rate of about 5% per year. The production and release data for CFCs tabulated by the Chemical Manufacturers Association (CMA) were used (**Figure 1**) to reconstruct the atmospheric time histories for the Northern and Southern Hemispheres. Since 1979 the atmospheric concentrations have been based on actual measurements at various sampling stations around the globe, and these are checked against the CMA production and release estimates. The curves in **Fig** $ure 1$ show all CFCs including $CCl₄$ increasing with time, with CFC-11 leveling off and actually decreasing in the late 1990s. The atmospheric increase of all the CFCs slowed markedly after the Montreal Protocol. The uncertainties in the reconstructed pre-1979 atmospheric histories depend on the atmospheric lifetimes of the compounds. The range of lifetimes for the compounds are $29-76$ years for CFC-11, 77-185 years for CFC-12, 54-143 years for CFC-113, and 21-43 years for Cl_4 . The uncertainties are a few percent, and they are highest for the early period. The continuous direct atmospheric measurements, which began in the late 1970s, are uncertain to within $1-2\%$. It is important to evaluate the uncertainties in the atmospheric source function, because they translate into uncertainties when used to put timescales on ocean processes. Because of their long atmospheric residence times, the CFCs are homogeneously distributed in the Northern and Southern Hemisphere, with the Northern Hemisphere about 8% higher than the Southern Hemisphere.

CFCs in the Oceans

Analytical Techniques

Water samples collected from the ocean are measured for CFCs and CCl_4 using an electron capture detection gas chromatography system. Analysis of water samples is done onboard ship, usually within hours of collection. The unit of measure is pmol

Figure 1 Northern Hemisphere atmospheric time histories. (Atmospheric data from Walker et al., 2000.)

 kg^{-1} or 10^{-12} moles kg $^{-1}$. These are extremely low level concentrations that are easily susceptible to contamination from shipboard refrigerants, solvents, lubricants, etc.

Chemical Stability

Under oxygenated oceanic conditions both CFC-11 and CFC-12 are believed to be chemically stable. CFC-11 has been shown to be unstable in anoxic marine waters; both CFC-11 and CFC-12 have been shown to be unstable in anoxic sediments. The compound CCl₄ undergoes temperature-dependent hydrolysis, which limits its usefulness in the ocean when sea surface temperatures exceed $\sim 18^{\circ}$ C. CFC-113 also has some stability problems at higher temperatures.

Gas Flux and Solubility

The CFCs are gases, and like other gases they get into the ocean via air-sea exchange. There is a direct correlation between gas exchange rate and wind speed, and the direction of the gas flux between the air and ocean is from high to low concentration. For CFCs the atmospheric concentrations generally exceed those in the ocean. The concentration of CFCs dissolved in the surface layer of the oceans is dependent upon the solubility, atmospheric concentration, and other physical factors affecting the gas saturation including upwelling, entrainment due to mixing, ice cover, etc. The solubility of CFCs and Cl_4 has been measured in the laboratory. The accuracy of the measurements is about 1.5% and precision is about 0.7%. The solubility increases with decreasing temperature, at a rate of about 4% for 1° C. Therefore, the colder the water the higher the CFC concentration. At a constant salinity the temperature effect is about two times greater for CFCs than for oxygen. The solubility is only slightly dependent on the salinity, and it decreases with increasing salinity.

Surface Saturation

The approach to equilibrium condition or the saturation state is dependent on the mixed layer depth and air-sea transfer rate. It takes from days up to a few weeks after a change in temperature or salinity for 'normal' (not very deep) oceanic surface layers to come to equilibrium with the present atmosphere. While the surface waters of the world's oceans are close to equilibrium with the present day atmospheric concentration of CFCs, there are exceptions. At times of rapid warming, such as in the spring, the surface waters will tend to be a few percent supersaturated with the gas due to lack of time to equilibrate with the atmosphere. Likewise at times of rapid cooling the surface waters will be a few percent undersaturated with the gas. Typically there are undersaturations within a few degrees of the equator due to upwelling of deeper less saturated waters. In high latitudes, where there are deep convective mixed layers that do not readily equilibrate with the atmosphere, there are likely to be undersaturations of as much as 60%. These have been observed in the Labrador Sea. The undersaturations in the high latitude water mass source regions need to be taken into account when using the CFCs to put timescales on oceanic processes.

Oceanic Distribution

The compounds CFC-11 and CFC-12 were first measured in the oceans in the late 1970s. The first systematic and intensive survey was carried out in the tropical North and South Atlantic oceans starting in the early 1980s. Since then CFCs have been part of the measurements made during physical oceanography field work. A global survey was conducted as part of the World Ocean Circulation Experiment during the 1990s. Typical vertical profiles versus pressure for stations in the North Atlantic and North Pacific oceans are presented in Figure **2** along with other properties. Although CFC-12 has higher concentrations in the atmosphere, CFC-11 is more soluble in sea water, so its concentrations are about twice that of CFC-12. Note that there are measurable concentrations of CFCs in the western North Atlantic that reach to the ocean bottom, while they reach to only 1000 m in the North Pacific. The difference between the CFC concentrations of the North Atlantic as compared with the North Pacific, reflects the formation of deep waters in the North Atlantic and the absence in the North Pacific. Concentrations generally decrease as the ocean depth increases. However, there may be subsurface concentration maxima due to the lateral intrusion of water that has been in more recent contact with the atmosphere (see applications below). The concentrations of CFCs and oxygen should behave similarly except where the biological effects on the oxygen distribution cause the differences, for example, the oxygen minimum at mid-depth.

Combining a series of vertical profiles, as in Fig**ure 2**, will give a slice or section through the ocean. Sections through the eastern Pacific and Atlantic are shown in **Figure 3**. The absence of CFCs in the deep waters of the Pacific Ocean shows the relative isolation of the deep Pacific from contact with the atmosphere on timescales of decades. In contrast, the North Atlantic north of 35° N has CFCs in deep and bottom waters, because these waters form in the high latitudes of the North Atlantic and easily spread equatorward on timescales of 10-20 years. As part of the density-driven, thermohaline circulation some of these waters will eventually be transported into the Pacific, but it will take hundreds of years. The upper waters of both oceans are in contact with the atmosphere on much shorter timescales. These upper waters are part of the winddriven circulation.

CFC Ages in the Ocean

Age Calculations

One of the main advantages of using CFCs as tracers of ocean circulation is that the time-dependent source function permits the calculation of timescales for these processes. A tracer age is the elapsed time since a water parcel was last exposed to the atmosphere. The tracer-derived age is the elapsed time since a subsurface water mass was last in contact with the atmosphere. Two estimates of 'age' can be calculated, one from the CFC-11/CFC-12 ratio and one from the partial pressure of either dissolved CFC. In both cases, the atmospheric value of either the ratio or partial pressure with which the water had equilibrated is compared to the atmospheric source function to determine the corresponding date.

To normalize the concentrations for the effects on the solubility of temperature and salinity CFCs are expressed in terms of their partial pressures, pCFC, where the pCFC is the concentration divided by the solubility of the gas. This value is then adjusted for what the percent surface saturation is thought to be based on the measured temperature and salinity, then matched to the atmospheric time histories, and a corresponding year is assigned to the water mass. This age is an average of the water parcel. The pCFC is used to calculate the age of upper ocean waters, because at low concentrations the effects of dilution will bias the age toward the older components of a mixture.

The age can also be calculated using the ratio of two CFCs; instead of using one pCFC the ratio of two pCFCs are used. In this case no assumptions are needed about surface equilibrium saturation at the time of water mass formation. Since the atmospheric changes in the ratio of CFC-11/CFC-12 have remained unchanged since the mid-1970s, this restricts the application of the ratio age for CFC-11 and CFC-12 to waters dating back further than 1975. However, either CFC-11 or CFC-12 can be combined with CFC-113 to extend age estimates to the present. Similarly they can be combined with CCl4 to extend age estimates further into the past. Unlike the pCFC age, the ratio ages are actually the

Figure 2 Vertical profiles of oceanographic data. (A) North Pacific salinity and potential temperature, (B) North Pacific CFC-11 and CFC-12, (C) North Pacific oxygen, (D) North Atlantic salinity and potential temperature, (E) North Atlantic CFC-11 and CFC-12, (F) North Atlantic oxygen. North Pacific World Ocean Circulation Experiment cruise P17C station 20, 33^oN, 135^oW, June 1991; North Atlantic Subtropical Atlantic Climate Studies cruise station 7, 26.5°N, 76°W, June 1990. (North Atlantic data from Johns et al. (1997) Journal of Physical Oceanography 27: 2187-2208; Pacific data from Fine et al. (2001) Journal of Geophysical Research.)

ages of the CFC-bearing components. **Figure 4** shows sections of CFC ratio ages from the eastern North Atlantic and North Pacific oceans. Note that the intermediate and deep waters of the eastern North Atlantic (between 2000 and 4000m) have CFCs younger than 30 years north of 45° N, because of their proximity to the formation regions, whereas this is not the case in the North Pacific. In the Pacific below 2000 m the water column has been isolated from interaction with the atmosphere on similar timescales (except for the far western South Pacific).

Caveats For Using CFC Ages

There are several caveats to the use of CFC ages. Both ages $-$ partial pressure and ratio $-$ may be subject to biases when there is mixing of more than one water mass component. Because of nonlinearities in the source functions and solubilities, neither age mixes linearly in multicomponent systems over the entire concentration range observed in the ocean. The atmospheric source function is nonlinear for much of the input history; however, it can be approximated as being linear between the late

Figure 3 (A) Sections versus pressure of CFC-11 concentrations (pmol kg⁻¹) in the eastern Atlantic (latitude 65°N-5°S) along 20°W in summer 1988. (B) Sections of CFC-11 concentrations (pmol kg⁻¹) in the eastern Pacific (latitude 54°N-32°S) mostly along 135°W in summer 1991. (North Atlantic data from Doney SC and Bullister JB (1992) Deep-Sea Research 39: 1857-1883; Pacific data from Fine et al. (2001) Journal of Geophysical Research.)

1960s and 1990. The solubilities are nonlinear functions of temperature, but they are approximately linear over ranges of a few degrees. Thus, for some regions of the ocean, these nonlinearities are not significant.

The different types of ages are appropriate for putting timescales on different processes. For thermocline ventilation, where equilibrated water is subducted and mixed isopycnally along extensively outcropping density surfaces, the water subducted within a given year mixes with water subducted in previous years. In this situation, a water parcel is a mixture of water that has left the surface over a period of several years. The average age of this water parcel can be represented by the pCFC age if the change of CFC concentration in the source region is constant with respect to time. This has been confirmed for the North Atlantic thermocline in the eastern basin by comparing pCFC ages to tritium/He-3 ages.

In regions where surface waters are converted to deep and bottom waters which then spread into a background of low-tracer water, the high CFC concentrations of the cold surface water are diluted by entrainment and mixing. The resulting pCFC age is much too young for the average age of the mixture and much too old for the CFCbearing component. However, a tracer ratio is conserved in this situation, and the corresponding ratio age represents that of the youngest component of the mixture, not the average age of the water parcel. Thus, there are different estimates of ages that can be derived from CFC-11 and CFC-12, and the associated timescales can be expanded in regions where CFC-113 and $CCl₄$ data are available.

Figure 4 (A) Sections of CFC-11/CFC-12 ratio ages (years) in the eastern Atlantic (latitude $65^{\circ}N$ -5 $^{\circ}S$) along 20 $^{\circ}W$ in summer 1988. (B) Sections of CFC-11/CFC-12 ratio ages (years) in the eastern Pacific (latitude $54^{\circ}N-32^{\circ}S$) mostly along 135°W in summer 1991. (North Atlantic data from Doney SC and Bullister JB (1992) Deep-Sea Research 39: 1857-1883; Pacific data from Fine et al. (2001) Journal of Geophysical Research.)

In most high latitude intermediate and deep-water source regions the age clock is not reset to zero due to lack of time to equilibrate deep mixed layers with the atmosphere. Thus, water masses will start out with an age of a few years (rather than zero), that is, they are not completely renewed during formation. This additional age is called a relic age which can be estimated from observations of the tracers at the water mass formation regions. The relic age can then be subtracted from the tracer ages calculated downstream from the water mass formation regions.

Applications of CFCs to Ocean Processes

Examples of the application of CFCs to understanding oceanographic processes are divided into four subjects: the thermohaline circulation, upper ocean circulation, model constraints, and biogeochemical processes.

Thermohaline Circulation

There is a close coupling of the surface waters in high latitudes to the deep ocean through the densitydriven thermohaline circulation. During the process of deep-water formation, atmospheric constituents such as CFCs are introduced into the newly formed water. In recent years, major advances in our knowledge of the thermohaline circulation can be attributed to information derived from transient tracer data, particularly for two reasons. First, the development of analytical techniques so that oceanographers can easily produce large quantities of high quality data. Tracer oceanographers have benefited from multi-investigator programs like the World

Ocean Circulation Experiment. The following highlights some of the advances that have come about in our understanding of the thermohaline circulation to which observations of CFCs have contributed:

- Discovery of a new water mass component of North Atlantic Deep Water (NADW), called Upper Labrador Sea Water, location of its formation region and contributing processes, and timescales of eastward spreading along the equator.
- Identification of Denmark Straits Overflow Water as the primary source of bottom water of the western subpolar basin.
- Confirmation of the structure and continuity of the Deep Western Boundary Current throughout the western North Atlantic Ocean, and extension into the South Atlantic.
- Extension of the CFCs well into the interior of the western North Atlantic show the importance of deep recirculation gyres in ventilating the interior basins, and in slowing the equatorward transport to timescales of $<$ 30 with effective spreading rates of $1-2 \text{ cm s}^{-1}$.
- Contribution to quantifying formation rates and decadal climate variability in the Arctic, Greenland and Labrador Seas.
- Estimates for the formation rates of Weddell Sea Deep and Bottom Waters, production rate of Antarctic Bottom Water and pathways and timescales for spreading into the North Atlantic.

Upper Ocean Circulation

The use of CFCs for upper ocean processes has involved the application of concentrations to deduce sources and circulation pathways, and application of pCFC ages. The following highlights some of the advances that have come about in our understanding of the upper ocean circulation to which observations of CFCs have contributed:

- \bullet Identification of the Sea of Okhotsk and Alaskan Gyre as important location for the ventilation of North Pacific Intermediate Water, these waters then spread into the subtropics on a timescale of $<$ 20 years.
- Quantification of the flux of water from the mixed layer into thermocline and intermediate layers of the North and South Pacific.
- Contribution to the description of sources and pathways of water masses transported from the Pacific through the Indonesian Seas into the Indian Ocean.
- \bullet Quantification of the sources of northern and southern water and the processes needed to venti-

late the tropical Pacific and Atlantic, including advection, diapycnal and vertical mixing.

- Observation that pathways of the most recently ventilated Antarctic Intermediate Waters are into the eastern South Indian Ocean, while at that level there appears to be flow of older waters from the South Pacific into the western Indian Ocean.
- Quantification of subduction and formation rates for subtropical underwaters and in the North Atlantic its interannual variability that is negatively correlated with intermediate waters of the eastern subpolar gyre.

Model Constraints

In general CFC concentrations and inventories have been used in comparison with model simulated concentrations and inventories. The time-dependent nature of the CFCs provides a stringent test of a model's ability to integrate property distributions over time. The following highlights some of the advances that have come about in our ability to put constraints on models from the use of CFCs in models:

- Dilution of CFCs transported by the Deep Western Boundary Current and effect on tracer ages.
- Testing the sensitivity of a model for correct simulation of formation rates, pathways, and spreading rates.
- Testing the sensitivity of a model for correct simulation of ocean model velocity fields.
- Determining the model sensitivity to subgrid scale mixing for purposes of estimating ventilation rates.
- The importance of considering seasonal variations in the upper oceans as part of the tracer boundary conditions when trying to simulate subduction processes.
- Demonstration in a model simulation that eddy transport is required to transport South Indian subtropical gyre waters across the equator along the western boundary.
- Use of CFCs to validate model parameterizations of gas fluxes.

Biogeochemical Processes

The tracers provide a method for calculating rates of biogeochemical fluxes that is independent of direct biological measurements. Again the age information from the CFCs is used to calculate rates for these processes. (*see* **Nitrogen Isotopes in the Ocean**). The following highlights some of the advances that have come about in our understanding of biogeochemical processes to which observations of CFCs have contributed:

- Apparent oxygen utilization rates from the central Arctic that are so high, they need to be balanced by transport of high production water from over the continental shelves.
- Quantification of moderate biological consumption and initially low oxygen concentrations in the Arabian Sea are needed to maintain the low oxygen layer.
- Calculation of denitrification rates for the Arabian Sea and Bay of Bengal.

Conclusions

The advantage of oceanic tracers like CFCs is that they can be used to provide timescale information for oceanographic processes. Direct application of the timescale information from the CFCs is used to calculate fluxes of atmospheric constituents, such as $CO₂$. The oceans have taken up a considerable portion of the anthropogenic $CO₂$ released to the atmosphere. A large part of the uptake involves water mass formation in high latitudes. The rate at which these waters are transported into the interior will have an effect on the rate at which anthropogenic $CO₂$ is taken up.

See also

Abyssal Currents. Air+**Sea Gas Exchange. Carbon** Dioxide (CO₂) Cycle. Current Systems in the Atlan**tic Ocean. Current Systems in the Indian Ocean. Current Systems in the Southern Ocean. Nitrogen Isotopes in the Ocean. Ocean Subduction. Thermohaline Circulation. Tracers and Large Scale Models. Tritium**+**Helium Dating. Water Types and Water Masses. Wind Driven Circulation.**

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CHLORINATED HYDROCARBONS

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Introduction

These chemicals are considered in a pollution category because both deliberate and accidental release to the environment of several of these types of compounds, for example the industrial chemicals such as PCBs (polychlorinated biphenyls) and the chlorinated pesticides p, p DDT (dichlorodiphenyltrichloroethane; formal chemical name 1,1-(2,2,2 trichloroethylidene)-bis (4-chlorobenzene)), have had unintended adverse environmental effects on diverse plants and animals and on people. Initially, chemicals such as PCBs and DDT were beneficial to human civilization: PCBs as industrial chemicals allowing economical, safe delivery of electricity, and DDT as a pesticide eradicating vector pests of human health concern and agricultural crop pests. Only after these chemicals had entered widespread use did it become apparent that there were environmental problems, although in hindsight there was evidence of potential problems early in the history of their manufacture and use.

Chlorinated hydrocarbons are chemicals made up of the elements carbon (C) and hydrogen (H) of the combine for the 'hydrocarbon' part of the molecule, and chlorine atoms (Cl) substituted for hydrogen where a hydrogen atom was normally bonded to a carbon atom. Examples of structures of chlorinated hydrocarbons are given in **Figure 1**.

Chlorinated hydrocarbons have a wide range of molecular weights (related to size), and complexity, i.e., there are various distinct configurations or