TRACER RELEASE EXPERIMENTS

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Introduction

Since the mid 1980s, analytical and engineering techniques have been developed to enable the compound sulfur hexafluoride (SF_6) to be used as a tracer for oceanographic experiments. SF_6 is a stable and inert substance with an exceptionally low level of detection, and its use enables large bodies of water to be unambiguously marked, allowing the investigator to keep track of a particular parcel of water. Three kinds of experiment have thus far made use of this technique: (1) measurement of mixing and transport integrated over large regions; (2) estimates of gas transfer velocities at the surface of the sea; (3) open ocean iron enrichment experiments. This article briefly describes the techniques used, and the major results from each of these types of process study.

The Tracer

Sulfur hexafluoride is an inert perfluorine, routinely detectable in sea water at ~ 0.01 fmol kg^{-1} by electron-capture gas chromatography (1 fmol $= 10^{-15}$ mol). At room temperature and pressure SF_6 is a gas, but it forms a dense ($\rho = 1880$ kg m^{-3}) liquid at pressures exceeding 20 bar. It is extremely stable in the environment and, other than being an asphyxiant, the pure compound has no known toxic effects. It is produced commercially largely ($\sim 80\%$) for use as a gaseous insulator in high-voltage installations. Much of this industrial production eventually finds its way into the atmosphere. The atmospheric mixing ratio was about 4×10^{-12} in 1999, and is growing at about 7% per year. Its solubility is very low, so that the surface concentrations in equilibrium with the atmospheric concentration are on the order of 1 fmol kg^{-1}. The combination of very low detection limit, nontoxicity, low marine background concentration, ease of analysis and inertness make SF_6 a nearly ideal tracer.

SF_6 is included in the Kyoto Protocol because, molecule-for-molecule, it is a powerful greenhouse gas with a long (>1000 years) lifetime in the atmosphere. The signatory nations are thus committed to controlling the rate of its production. However, for any realistic future emission scenario, SF_6 will remain insignificant ($<1\%$) as a contributor to the anthropogenic greenhouse effect for the foreseeable future.

Mixing Experiments in the Deep Ocean

To measure diapycnal mixing (i.e. mixing across-density surfaces) by tracer release, the tracer is released, as near as possible, onto a single, well-defined density surface, and its subsequent spread onto neighboring surfaces is monitored. If the mixing occurs in accordance with Fick's law, the square of the mean width of the concentration distribution increases linearly with time, the rate of increase being a direct measure of the diffusivity. The advantage of this strategy compared to the documentation of temperature or velocity microstructure, is that it gives an unambiguous measurement integrated over a substantial time and space scale. In practice, in the open ocean these scales are of order months or years, and hundreds or thousands of kilometers – hence also the method's main disadvantage, which is that it must be done on a large scale.

At the time of writing, five experiments of this kind have been initiated in the open ocean. The first two, relatively small-scale releases, were made in the ocean-floor basins off the coast of Southern California and the remaining three in the thermocline of the North Atlantic, the deep Brazil Basin and the central Greenland Sea. Below we describe the release method used in most of these experiments, and the results of the North Atlantic experiment in more detail. Mixing rates from all five experiments are then compared.

Release Method

Sulfur hexafluoride is very insoluble; for small-scale experiments it can be dissolved by presaturating drums or tanks of water with the gas. However, the practical limit for the amount which can be injected in this way is a few moles, sufficient for tracer experiments on the 10–100 km scale only. For large open ocean releases, we designed an injection package which releases liquid SF_6 into water by pumping it through fine orifices at high pressure, so that it

breaks into an emulsion of fine droplets on contact with the sea. These droplets are sufficiently small that they dissolve before they have settled an appreciable distance. The apparatus is designed to allow the accurate delivery of SF_6 at rates of up to 3 kg h^{-1} onto a given 'target' density surface at any depth greater than 200 m in the ocean, when towed behind a ship on a conducting cable.

In use, the injector was controlled by a computer in the laboratory of the ship. The output of the CTD was used to calculate in real time the density of the water at the package, and compare it to the 'target' density. The computer issued commands to the automated winch to haul in wire if the density was higher than the target, or pay out if it was significantly lower. During the North Atlantic Tracer Release Experiment (NATRE) this system was able to deliver tracer with an overall RMS accuracy of ± 2 m from the target surface. With such an injection system, it is practical to initiate experiments using several hundred kilograms of tracer, sufficient to enable investigations at the ocean-basin scale.

NATRE: Overview of Results

The tracer results from NATRE have been reported in detail. Major findings were that the diapycnal diffusivity was 0.12 cm^2 s^{-1} for the first 6 months, and then 0.17 cm^2 s^{-1} for the subsequent 24 months. The mean vertical profile for each survey was nearly Gaussian, and as a set they illustrate an approximate solution of the diffusion equation in one dimension (**Figure 1**).

The result that the diapycnal diffusivity in the pycnocline is of order 0.1 cm^2 s^{-1} confirms estimates based on internal wave dynamics and on measurements of turbulent dissipation rates. Some analyses of the penetration of transient tracers into the deep pycnocline also have implied diffusivities on the order of 0.1 cm^2 s^{-1}. Values of diffusivity of 1 cm^2 s^{-1} were inferred by Munk's classic 'abyssal recipes' analysis, but this was for depths between 1000 and 4000 m and included boundary processes as well as interior processes. It is now clear that 1 cm^2 s^{-1} is an overestimate for the interior pycnocline.

The lateral dispersion of the tracer revealed surprisingly efficient mechanisms of stirring at scales from 0.1 to 30 km. The lateral diffusivity setting the width of tracer streaks at 6 months was found to be about 2 m^2 s^{-1}. The mechanism is not well understood, but may be due to shear dispersion by vortices generated during the adjustment to diapycnal mixing events. The experiment did confirm the predictions of C. Garrett, that a tracer patch remains streaky only for a year or so, after which time the exponential
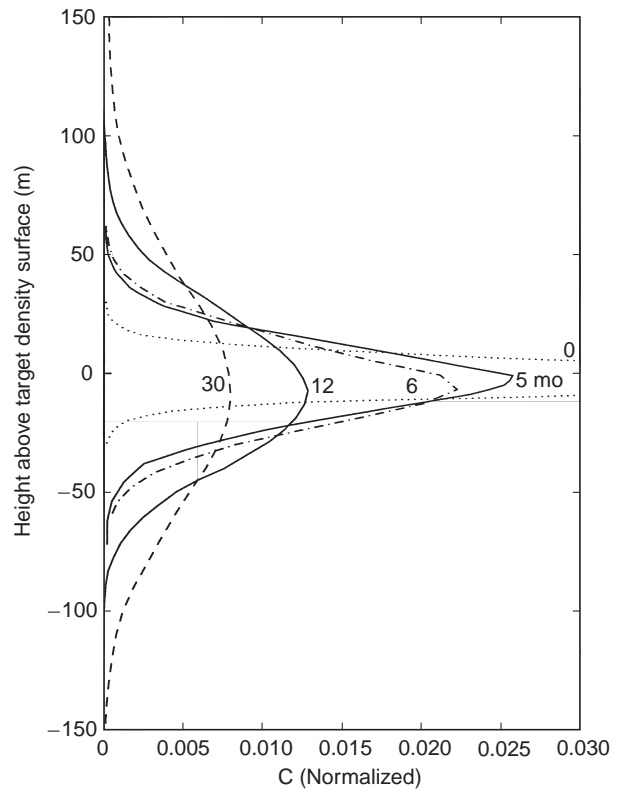

Figure 1 Mean vertical profiles from NATRE at 0, 5, 6, 12 and 30 months after the initial survey. The SF_6 concentration has been averaged on isopycnal surfaces, approximately, and plotted versus height above the target isopycnal surface using the mean relation between depth and density for the 12-month survey. The profiles are normalized to have equal areas. The initial profile (... .) is allowed to run off the graph so that the others are clear.

growth of the area actually tainted by the tracer streaks catches up with a power-law growth of the overall area occupied by the tracer patch.

It is important in a tracer study of mixing in the ocean to measure the hydrodynamic forcing, and also to measure hydrodynamic parameters that are believed to be useful for estimating diffusivities, so that existing theories can be tested. Several groups were involved in profiling fine structure and microstructure during NATRE. Dissipation of turbulent kinetic energy and temperature variance measured by profiling instruments gave estimates of diapycnal diffusivity which agreed closely with the tracer results. Measurements of the fine structure have helped reveal the roles of shear and double diffusive gradients in driving the mixing.

Dependency of Diapycnal Mixing and Buoyancy Frequency from Tracer Release Experiments

Figure 2 shows diapycnal diffusivities as a function of buoyancy period for the deep ocean tracer release
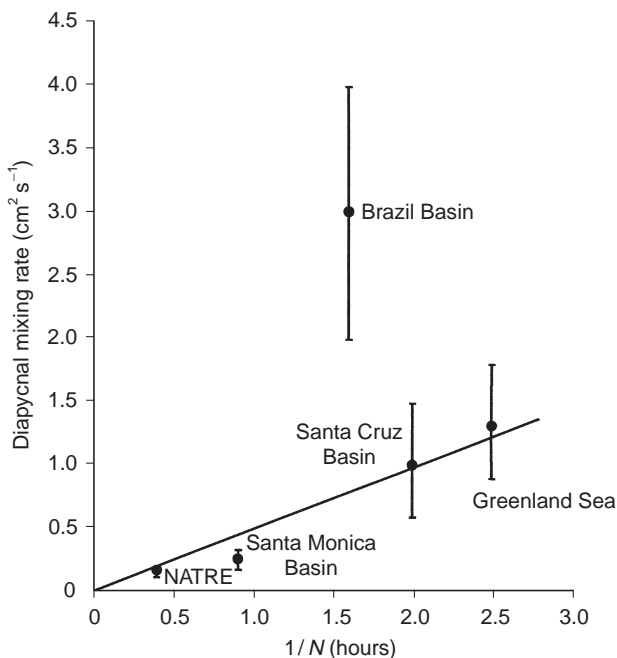
Figure 2 Vertical mixing coefficients for five tracer release experiments in the open ocean, plotted as a function of $1/N$ where N is the buoyancy frequency. For discussion see text.

experiments so far published. Except for the recent Brazil Basin experiment, the data indicate correlation between the two, as would be expected if the forcing were in some sense held constant. However, the reader should beware of such relationships, as the Brazil Basin result shows. There is evidence from internal wave phenomenology and energy dissipation measurements that the diffusivity in the interior of the ocean, when driven only by the background internal wave field, is independent of the buoyancy period with a value of approximately $0.05 \ cm^2 \ s^{-1}$. The only one of our experiments that has been conducted in the interior of the ocean, well away from boundaries, was NATRE, and that was probably influenced by salt fingering. The measurements shown in **Figure 2** are those made before the tracer-containing water had time to contact the boundaries; mixing increased dramatically in the California basin experiments once such contact occurred. Nevertheless, the energy input for all but the NATRE site may have been enhanced by the proximity of the boundaries. If this is the reason why most of these experiments show elevated values, it is evident that in many situations of interest, the diffusivity, and presumably the energy flux through the internal wave field, must be enhanced even at considerable distance from boundaries.

Gas Exchange Experiments

The rate of air–sea gas transfer is a parameter which is needed in a wide range of biogeochemical studies. Gas exchange is dependent on environmental conditions that affect the near-surface turbulence in the sea and which are not easily reproduced in laboratory facilities, such as wind speed, sea state, and the chemical state of the air–sea interface. In laboratory wind-wave facilities for example, a strong dependence on wind speed is observed, but the functional form depends on the experimental set-up. As a consequence, though substantial theoretical understanding has been gained from experiments in laboratory facilities, there has also been a need to assemble a body of gas transfer measurements made at sea.

The first aqueous use of SF_6 as a tracer was the measurement of gas exchange in lakes by R. Wanninkhof, in 1985. Lake experiments are comparatively easy to set up and perform, and give absolute estimates of gas exchange. The basis of the technique is to keep track of the total amount of gas in the lake. The results of the first experiment gave unambiguous evidence in a field situation, for a strong dependence of gas exchange on wind speed, and the data form the calibration for the 'Liss–Merlivat' formulation of gas exchange. However, the gas exchange rates found in that experiment, when scaled and applied to carbon dioxide, are lower by about a factor of two than might be expected from an analysis of the global ^{14}C budget of the ocean. This uncertainty in marine gas exchange rates remains unresolved up to the present. In recent years, many investigators who need to parameterize gas exchange as a function of wind speed, have bracketed the uncertainty by applying both the Liss–Merlivat relation (scaled to agree with the lake SF_6 experiment), and a relation due to Wanninkhof that is scaled to agree with global ^{14}C values.

The Dual Tracer Technique

This long-standing uncertainty in marine gas exchange rates provided a good reason to adapt the lake SF_6 technique to the measurement of gas exchange at sea. However, whereas in a lake it was easy to determine the total amount of tracer present and the area over which it is spread, in the open ocean the tracer release is unenclosed and dilutes into a constantly larger volume of water. A means must be found to account for this dilution. Theoretically, this could be accomplished by releasing a nonvolatile conservative tracer with the gaseous one, and then use the change in ratio between the two to define gas exchange rates. In practice, no such ideal conservative nonvolatile tracer is

available, so instead SF_6 and ^3He were released, two volatile tracers having very different molecular diffusivities. When the water column is well mixed and of constant depth H, the ratio $r = c_2/c_1$ of the concentrations of the tracers (in excess of any concentration in equilibrium with the atmosphere) evolves according to the equation:

$$\frac{1}{r}\frac{dr}{dt} = -\frac{1}{H}(k_2 - k_1)$$

where k_1 and k_2 are the gas transfer velocities appropriate to each tracer. This suggested that in the right environment, that is a shallow sea, well-mixed and with a constant depth, measurement of the tracer ratio could be used to define the difference between the two gas transfer rates. If another relation between the gas transfer rates could be defined, the 'dual tracer' technique would enable absolute values for k_1 and k_2 to be derived.

For this second relation, dual tracer experimenters have used a power law dependence of gas transfer velocities on Schmidt number (the ratio of kinematic viscosity of water to the diffusivity of the gas):

$$\frac{k_1}{k_2} = \left(\frac{Sc_1}{Sc_2}\right)^n$$

For most conditions in which bubbles and spray are not affecting gas exchange, $n = 0.5$. This result is derived from models and supported by measurements, in the laboratory and on lakes. At very low wind speeds when the sea is glassy smooth, this relation does not hold and $n = 0.67$ is the theoretical result, but this condition is very rarely met at sea. In rough seas where substantial bubble-mediated gas transfer may occur, the theory is more complex and different assumptions have been made to derive absolute values under these conditions. Recent theoretical work suggests that the square-root assumption is reasonably accurate even in the presence of bubble-mediated transfer, though care is needed in scaling the results obtained using these insoluble tracers to more soluble gases such as carbon dioxide. In one experiment, a third tracer, bacterial spores specially treated to be suitable for this purpose, were used as a nonvolatile tracer, and these results also support the use of the square-root law.

Figure 3 shows a compilation of results from dual-tracer experiments at sea. The dual-tracer results confirm the strong dependence of gas exchange on wind speed. They generally lie between the Liss–Merlivat and Wanninkhof parameterizations. In the light of recent results, concerning the effect of ubiquitous natural organic films, we can hypothesize
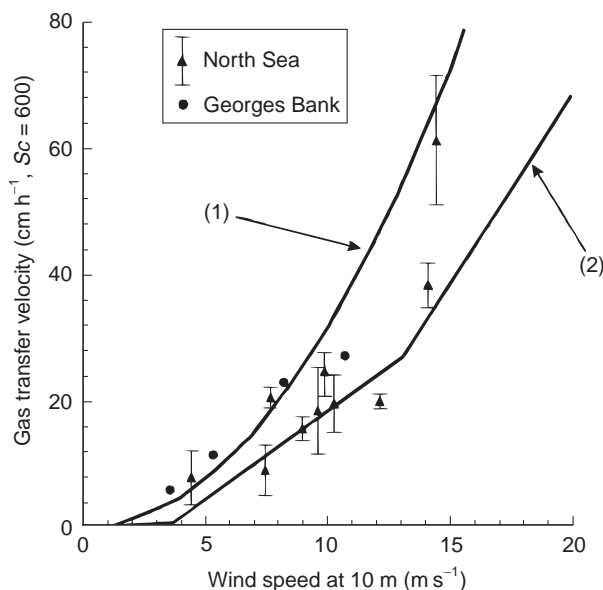
Figure 3 Compilation of dual tracer gas exchange measurements. The North Sea results include some previously published data for which revised wind speeds have been estimated using the procedures detailed by P. D. Nightingale. Data from (1) Wanninkhof (1992) and (2) Liss and Merlivat (1986).

that the trends in these data are due to the decreasing effect of organics as one moves away from coastally influenced sites out into the open ocean. The Wanninkhof parameterization, being tuned to global ^{14}C exchange rate, is most affected by the open ocean and the Liss–Merlivat formulation, originally calibrated from the result of lake experiments, the most affected by organics. The two data sets lie in between these. Georges Bank might be expected to be less coastally influenced than the North Sea, and the trend in the results is consistent with that expectation.

Small-scale Surface Patch Experiments for Biogeochemical Studies

A practical problem in carrying out open-sea dual-tracer gas exchange experiments was the difficulty of keeping track of the released tracer patch. To overcome this, in the late 1980s instrumentation was built which took advantage of the uniquely fast gas chromatographic analysis for SF_6. Gas chromatography is normally a slow, batch process, but for SF_6 using a molecular sieve column, the actual separation takes only 30 seconds and the entire analysis can be completed in three minutes. Thus it was possible to build an instrument which continually measured the concentration of SF_6 in a supply of water, and use this to 'chase' the tracer

patch from a ship. This opened the possibility of using the tracer to guide experiments to investigate the biology or chemistry of an accurately marked patch of surface water, over a period of days to weeks. Such 'lagrangian' experiments have frequently been performed in the past using drogued drifting buoys to mark movement of water. However, an early observation from the trial tracer experiments made in the English Channel was that such buoys do not normally stay co-located with a patch of water marked by a tracer release. Surface buoys are subject to windage and tend to slip downwind of the marked water.

In-situ Iron Enrichment Experiments

The first use of the tracer technique to guide biogeochemical studies was in the IRONEX experiments in the equatorial Pacific. At about the time the tracer-release technique had been developed for gas-exchange experiments, the idea was suggested of testing the 'Iron hypothesis' of phytoplankton limitation by releasing a large amount of iron in the surface waters of, for example, the equatorial Pacific. A difficulty was that if the experiment was too small, then the iron-enriched patch would be easily lost, whereas if it were large enough to be easily found (probably ~ 100 km in scale) then it would be logistically difficult and expensive. The use of the tracer release to guide a 10-km scale experiment was an obvious next step, and the design for such a study was published in 1991.

The first two unenclosed iron-enrichment studies were carried out in 1993 and 1995 in the Equatorial Pacific. In both, nanomolar concentrations of iron were induced in the surface layer by release of iron sulfate, the patches being labeled by SF_6 addition. The SF_6 (<1 mol in total) was added in a constant ratio to the initial addition of iron, the tracer component was then used as a guide to keep track of the affected patch of ocean. Sampling could be reliably categorized as 'in' or 'out' the patch, even after all the measurable iron had disappeared from solution. In the second study, the main experiment included reseeding the patch with iron, but not tracer, twice after the initial release. Important secondary aims of the tracer component of the experiments have been the study of mixing rates both horizontally in the mixed layer, and vertically across the thermocline.

Figure 4 shows a summary of the results for the effect of the iron releases on surface water fugacity of carbon dioxide (fCO_2) from Ironex I and II. fCO_2 is plotted against SF_6 measured in the water on paired samples, for various times following the initiation of the experiment. Such a plot shows whether the fCO_2 (or any other variable of interest)
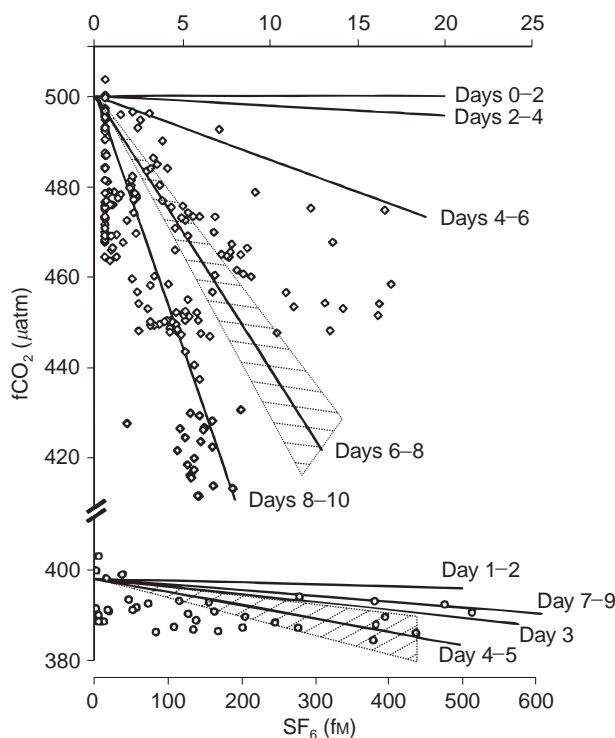
Figure 4 Linear regressions of sea surface values of fugacity of CO_2 (fCO_2) with SF_6 concentration, for specified periods after the start of the Ironex I (lower) and Ironex II (upper). Representative data points are shown, for the 'day 4–5' period during Ironex I ($\bigcirc$), and the 'day 6–8' period during the Ironex II ($\diamondsuit$). The hashed region around the two regression lines which correspond to these data shows the confidence limit ($3\text{-}\sigma$) on the slope of the line. (Data from Cooper *et al.*, 1996; Law *et al.*, 1998; Watson *et al.*, 1994.)

develops a relationship with the tracer concentration over time. It is a useful summary of the effects observed even if the evolution of the patch shape is complex and not readily mapped in space. Data at low and background SF_6 show the 'control' condition, outside the patch, while data at high SF_6 show the evolution of the center of the marked water.

Figure 4 shows the contrasting results of the experiments. Ironex II produced an intense bloom of diatoms which fixed substantial carbon, resulting in a drawdown of carbon dioxide in the surface water which at its peak amounted to 70–80 µatm below the starting 'outside patch' condition. The drawdown continued to build up beyond the first week of the experiment, and a substantial signal was left in the water even after the bloom began to fade. By contrast, during Ironex I (shown on the same fCO_2 scale) the effect on the carbon concentration of the surface water was small, only 10–20% of that seen on the Ironex II, and it was already fading by the end of the first week. As measured by carbon uptake, the response of the two experiments in the

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.

Further Reading

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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