Use of SF$_5$CF$_3$ for ocean tracer release experiments

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[1] SF$_6$ tracer release experiments (TREs) have provided fundamental insights in many areas of Oceanography. Recently, SF$_6$ has emerged as a powerful transient tracer, generating a need for an alternative tracer for large-scale ocean TREs. SF$_5$CF$_3$ has the potential to replace SF$_6$ in TREs, due to similarities in their properties and behavior, as well as techniques for injection, sampling, and analysis. The suitability of SF$_5$CF$_3$ for TREs was examined in Santa Monica Basin, off the coast of Southern California. In January 2005, a mixture of ca. 10 mol of both SF$_6$ and SF$_5$CF$_3$ was injected on an isopycnal surface near 800 m depth. Over the next 23 months, concentrations of the two tracers mirrored each other very closely, indicating that SF$_5$CF$_3$ is a viable replacement for SF$_6$ in ocean TREs. The mixing parameters inferred from the experiment confirmed the results from an earlier SF$_6$ TRE in the Santa Monica Basin. **Citation:** Ho, D. T., J. R. Ledwell, and W. M. Smethie Jr. (2008), Use of SF$_5$CF$_3$ for ocean tracer release experiments, *Geophys. Res. Lett.*, *35*, L04602, doi:10.1029/2007GL032799.

1. Introduction

[2] Large scale open ocean tracer release experiments conducted with sulfur hexafluoride (SF$_6$) have yielded fundamental insights into ocean mixing [e.g., *Ledwell et al.*, 1993, 2000], air-sea gas exchange [e.g., *Watson et al.*, 1991; *Wanninkhof et al.*, 1993; *Ho et al.*, 2006], and deep water formation processes [e.g., *Watson et al.*, 1999]. Furthermore, SF$_6$ has served as an important marker of iron-infused water parcels during Lagrangian iron fertilization experiments [e.g., *Coale et al.*, 1996; *Boyd et al.*, 2000; *Coale et al.*, 2004].

[3] Recently, SF$_6$ has emerged as a potential transient tracer in the ocean [e.g., *Law and Watson*, 2001; *Tanhua et al.*, 2004; *Bullister et al.*, 2006], whose atmospheric mixing ratio has been increasing rapidly over the past few decades [*Geller et al.*, 1997; *Maiss and Brenninkmeijer*, 1998]. There exists a pressing need for a new transient tracer for ocean studies because chlorofluorocarbons (CFCs), which were used to investigate subsurface water formation, circulation and mixing for waters ventilated between the late 1950s and the early 1990s have lost some of their effectiveness for the most recently ventilated waters due to their declining atmospheric mixing ratios. The increasing SF$_6$ mixing ratio restores a unique time marker for recent decades (see auxiliary material).[1]

[4] The availability of an alternative tracer for large-scale ocean tracer release experiments would eliminate interference between these two uses for SF$_6$. Trifluoromethyl sulfur pentafluoride (SF$_5$CF$_3$) has the potential to replace SF$_6$ for tracer release experiments, due to similarities in their properties and behavior, as well as techniques for injection, sampling, and analysis.

2. Properties of SF$_5$CF$_3$

[5] SF$_5$CF$_3$ is a gas with a boiling point of $-20°C$ at atmospheric pressure, and an atmospheric mixing ratio of 0.12 ppt in 1999 [*Sturges et al.*, 2000]. It appears to be predominately of anthropogenic origin, released as a byproduct during manufacturing of certain fluorochemicals [*Santoro*, 2000], and as a breakdown product of SF$_6$ [*Huang et al.*, 2005; *Carrier et al.*, 2007]. SF$_5$CF$_3$ is a strong greenhouse gas with a radiative forcing about 10% higher than SF$_6$ on a per molecule basis [*Sturges et al.*, 2000]. However, because of its shorter atmospheric lifetime relative to SF$_6$ (800 vs. 3200 y), its global warming potential is less than that of SF$_6$ [*Takahashi et al.*, 2002]. Furthermore, because of their low atmospheric mixing ratios, the impact of both SF$_5$CF$_3$ and SF$_6$ on greenhouse warming has been negligible. *Sturges et al.* [2000] estimated that annual emission of SF$_5$CF$_3$ has been 270 metric tons, and hence ocean tracer injections of a few hundred kilograms over the next decade would be an insignificant addition to the global budget.

3. Solubility of SF$_5$CF$_3$

[6] The solubility of SF$_5$CF$_3$ in freshwater was determined in preliminary laboratory experiments to be about half as great as that of SF$_6$ (Figure 1). Also, SF$_5$CF$_3$ and SF$_6$ were found to be about 1000 and 150 times more soluble at 20°C, respectively, in 1-octanol than in fresh water, suggesting that SF$_5$CF$_3$ may have a greater tendency than SF$_6$ to adhere onto organic rich particles. Systematic experiments should be conducted to refine the solubility/temperature relationship for SF$_5$CF$_3$ in both freshwater and seawater. Furthermore, if SF$_5$CF$_3$ were to be used in experiments aimed at quantifying air-sea gas exchange, its diffusion coefficient in water must be determined.

4. Experiment in the Santa Monica Basin

[7] The suitability of SF$_5$CF$_3$ for ocean tracer release experiments was examined in Santa Monica Basin (SMB), where the first pilot SF$_6$ tracer release experiment was

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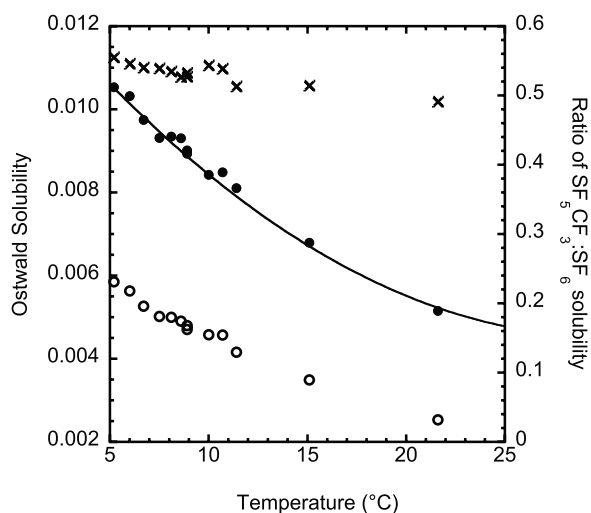[2]Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

Figure 1. Ostwald solubility coefficients in freshwater as a function of temperature for SF$_5$CF$_3$ and SF$_6$. The solid line is the solubility/temperature relationship for SF$_6$ determined by *Bullister et al.* [2002]. The open and solid circles are SF$_5$CF$_3$ and SF$_6$, respectively. The crosses are the ratio of solubility factors for SF$_5$CF$_3$:SF$_6$ as a function of temperature. Throughout the entire range of temperatures examined (5 to 21°C), SF$_5$CF$_3$ appears to be about half as soluble as SF$_6$ in water with the SF$_5$CF$_3$:SF$_6$ solubility ratio decreasing from 0.56 to 0.48 between 5 and 21°C.

conducted in the mid 1980's [*Ledwell et al.*, 1986]. SMB is located off the coast of Southern California near Los Angeles, and forms part of the California Borderland (Figure 2). It has a maximum depth of 920 m, and is joined with San Pedro Basin (SPB) to the southeast via a channel at about 900 meters. The sill depth for the system is 737 m at the southeastern end of SPB. The area of SMB at sill depth is about 1850 km^2, while that of SPB is about one third as large.

4.1. Background Samples

[8] One week prior to the tracer release experiment, water samples were taken from 24 depths at one station each in SMB and SPB to measure the background SF$_5$CF$_3$ and SF$_6$ concentrations. Samples were stored under cold water in 500-ml bottles and analyzed at LDEO with the system described by *Ho* [2001]. The background concentration of SF$_6$ at the start of the experiment was found to be approximately 0.3 fmol kg^{-1} between 500 m and 900 m, five times less than found in August 1985 [*Ledwell and Hickey*, 1995]. The source of the SF$_6$ background in the California Borderland basins is not known. No background SF$_5$CF$_3$ was found.

4.2. Tracer Injection

[9] In January 2005, a mixture of 10.6 mol of SF$_6$, 10.0 moles of SF$_5$CF$_3$, and 219 moles of CFC-12 was released on an isopycnal surface ($\sigma_\theta = 27.1776$ kg m^{-3}) near 800 m depth using a 2-m long neutrally buoyant injection sled described in detail by *Ledwell et al.* [1998]. The tracer mixture was injected in two streaks (Figure 2a) over 12 hours at a tow speed of about 0.5 m s^{-1}, while the injection sled was kept

close to the target isopycnal surface using potential density calculated from the output of the CTD sensors (rms error = 0.0021 kg m^{-3}).

[10] As in past experiments, 50-μm diameter orifices were used to atomize the mixture during the injection so that the droplets dissolve before falling more than a meter. However, because SF$_5$CF$_3$ is about half as soluble as SF$_6$ at 1 atm pressure, and has a fugacity that is approximately 7 times less than SF$_6$, the rate of dissolution of liquid SF$_5$CF$_3$ in the deep ocean will be about 14 times less than for SF$_6$. The fall distance is proportional to the fourth power of the droplet diameter [*Watson and Ledwell*, 2000], and inversely proportional to the solubility. This means that for future experiments, it will be necessary to use 25-μm orifices to inject pure SF$_5$CF$_3$ to insure that the tracer dissolves before falling more than a meter from the target density surface [*Watson and Ledwell*, 2000].

4.3. Sampling

[11] After injection, the evolution of the vertical and horizontal distributions of SF$_5$CF$_3$ and SF$_6$ were sampled and compared during 4 cruises (S1, S2, S3, and S4) over the next 23 months. The sampling campaigns were conducted one week (S1; January 2005), 5 months (S2; June 2005), 12 months (S3; January 2006), and 23 months (S4; December 2006) after the injection.

[12] One week after the injection, because the tracers had not mixed horizontally and the patch was still streaky, an array of 20 integrating samplers [*Ledwell et al.*, 1998] at a vertical spacing of 3 to 5 m was towed along the tracks shown in Figure 2a to sample the tracer. After 5 months, the tracers had mixed horizontally so discrete vertical profiles taken at individual stations using a 24-bottle rosette were sufficient to determine the vertical distribution of the tracers on S2, S3, and S4 (Figure 2b). Samples for SF$_5$CF$_3$ and SF$_6$ were collected in 100 ml glass syringes and analyzed onboard the ship during S2 and S3, and collected from the Niskin bottles in 100 ml glass bottles with ground glass stoppers during S4 and shipped back in refrigerated containers to the laboratory for analysis. On S2 and S3, 27 stations were occupied, and on S4, 8 stations, which comprise a subset of the 27 stations, were occupied.

5. Measurement of SF$_5$CF$_3$ and SF$_6$

[13] Water samples were analyzed using an automated purge and trap system [*Bullister and Weiss*, 1988; *Smethie et al.*, 2000] interfaced to a gas chromatograph equipped with an electron capture detector (GC/ECD). Water was transferred from the glass syringe or bottle through a calibrated volume into a stripper, where gases including SF$_5$CF$_3$ and SF$_6$ were stripped from the water using ultra-high purity (UHP; 99.999%) N$_2$ and transferred at 75 ml min^{-1} to a 1/8″ diameter × 25 cm long trap of Porapak-Q cooled to −78°C. The trap was then heated to 100°C and the sample injected into the GC/ECD with a carrier flow rate of 35 ml min^{-1}. SF$_5$CF$_3$ and SF$_6$ were separated from other gases at 110°C with a 1/8″ diameter × 120 cm long 80/100 mesh Porasil B pre-column, a 1/8″ diameter × 183 cm long 80/100 mesh Carbograph-1AC main column, and a 1/8″ diameter × 10 cm long 80/100 mesh Molecular Sieve 5A post column at
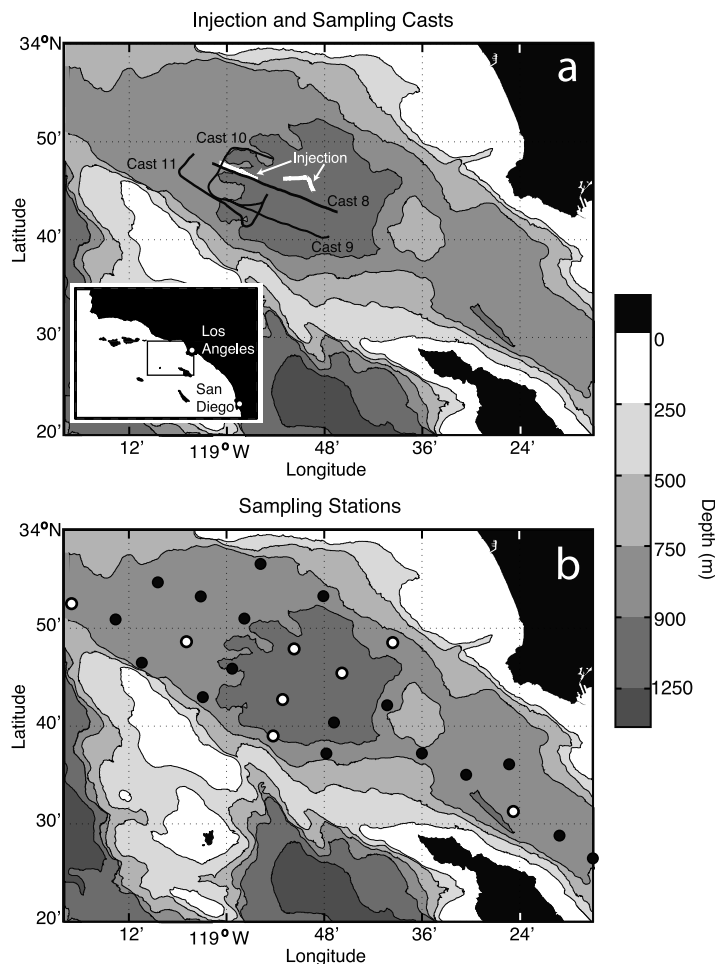
Figure 2. Maps of the Santa Monica Basin (SMB) and San Pedro Basin (SPB) showing the (a) injection (white lines) and sampling tows (black lines) during S1 and (b) sampling locations during S2 and S3 (both open and filled circles), and S4 (open circles). The interruption in the injection line in Figure 2a was due to an oversight. The inset in Figure 2a shows the location of the experiment relative to the coast of Southern California.

45°C. Retention times for SF_6 and SF_5CF_3 were 1.0 and 1.4 min, respectively (see auxiliary material).

[14] An SF_6 standard and the known ratio of SF_5CF_3 to SF_6 in the injected mixture were used to calibrate the GC/ECD; the detector response with respect to peak areas was determined to be 14 ± 3 % higher for SF_6. Given a water sample size of 20 ml, the minimum detectable levels of the method described here are 0.4 and 0.8 fmol kg^{-1} for SF_6, and SF_5CF_3, respectively.

6. Results and Discussion

6.1. Dispersal of SF_5CF_3 and SF_6

[15] A week after injection (S1), 4 tows were conducted with the integrating sampler array over 4 days (Figure 2a). Only one of these tows yielded a complete vertical profile (Figure 3 and auxiliary material). This profile of SF_5CF_3 and SF_6 shows that they were successfully injected together. The peak concentration found was ca. 3000 fmol kg^{-1}.

[16] After 5 months (S2), the tracers had sufficient time to mix both horizontally and vertically, and were found throughout SMB, as well as in SPB. Within SMB, the concentrations of both SF_5CF_3 and SF_6 were higher in the center part as well as the western side of the basin. Overall, the tracer concentrations were higher in the interior of SMB (peak concentration: 125 fmol kg^{-1}) than the boundaries on the north and south side of the basin (peak concentration: 75 fmol kg^{-1}), and tracer concentrations were also significantly higher in SMB than they were in SPB (peak concentration: 37 fmol kg^{-1}; see auxiliary material for individual profiles).

[17] After 12 months (S3), concentrations of the tracers were fairly well mixed in the interior of SMB, and the peak concentrations (35 fmol kg^{-1}) were about the same as near the boundaries (30 fmol kg^{-1}). However, the tracer concentrations in SMB remained higher than in SPB (12 fmol kg^{-1}). Finally, after 23 months (S4), the tracer concentrations were well mixed in the interior of SMB (8–12 fmol kg^{-1}), and still significantly higher than in SPB (5 fmol kg^{-1}). Concentrations along the southwest boundary of SMB were lower than in the interior, perhaps due to new water entering over the sill to Santa Cruz Basin, and flowing southeast along this boundary.

[18] Of the 10 mol of SF_5CF_3 injected, 8.8 ± 1.2 and 8.0 ± 0.7 mol were found during S2 and S3, respectively. The
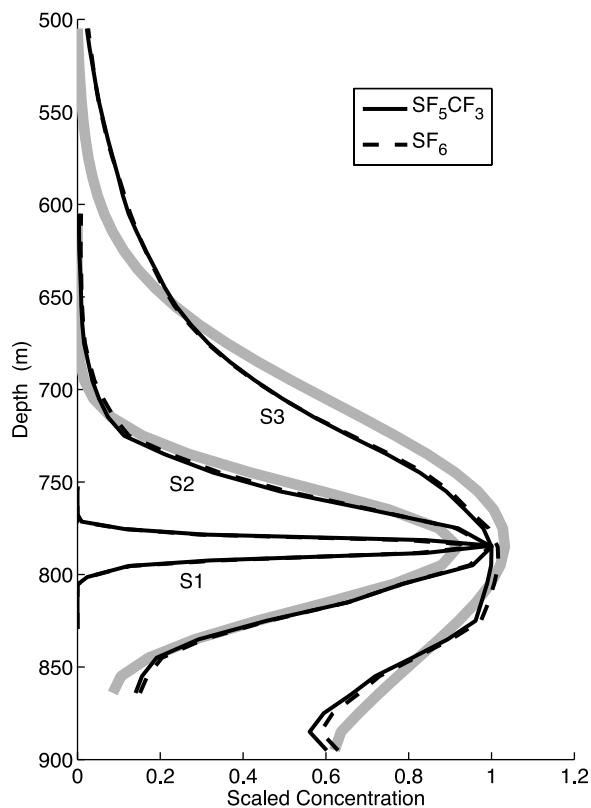
Figure 3. Mean SF$_5$CF$_3$ (solid) and SF$_6$ (dashed) profiles, and model results (grey). Each profile has been scaled by dividing by the corresponding maximum mean SF$_5$CF$_3$ concentration for the given survey. S1 was used as the initial condition for the diffusion model between S1 and S2. The final condition is given by the curve labeled S2, which is the mean profile in the interior of SMB from S2. The grey curve nearby is the model fit for a constant diffusivity of 4×10^{-5} m^2 s^{-1}. The curves labeled S3 are the means of all profiles averaged over both SMB and SPB, boundary and interior for S3. The grey curve near S3 is a model result for a whole-basin diffusivity, which varies with depth with a value of 1.1×10^{-4} m^2 s^{-1} at 785 m. (See Auxiliary Material for plots of different plausible diffusivities) The initial condition for this model is not shown, to avoid clutter, but is similar to the S2 curves. The difference is that it is a basin-wide average rather than an interior average. The inversion at the bottom of S3 is due to allowing profiles to drop out of the mean when the bottom is reached. The differences between SF$_5$CF$_3$ and SF$_6$ profiles are small and can be attributed to the slightly different amounts injected and the presence of a background of less than 1 fmol kg^{-1} of SF$_6$ in the basins.

losses were presumably due to advection and dispersion across the sills.

[19] SF$_5$CF$_3$ and SF$_6$ tracked each other nearly identically for every profile from SMB and SPB collected during S2, S3 and S4 (see auxiliary material), indicating that SF$_5$CF$_3$ and SF$_6$ behaved the same way and that SF$_5$CF$_3$ is a viable replacement for SF$_6$ in ocean tracer release experiments. The same behavior can be seen in mean profiles of SF$_5$CF$_3$ and SF$_6$, shown in Figure 3.

[20] Although SF$_5$CF$_3$ appears to have the potential for stronger adsorption onto organic rich particles based on laboratory experiments with 1-octanol, this effect could not be seen in the vertical profiles of SF$_5$CF$_3$ and SF$_6$ from the SMB, which has relatively high particle fluxes [*Thunell et al.*, 1994]. Subtle trends in the ratio of SF$_5$CF$_3$ to SF$_6$ with depth are within the analytical uncertainty or the uncertainty of the SF$_6$ background (see auxiliary material).

6.2. Mixing in the Santa Monica Basin

[21] A 1-D diffusion model similar to that used by *Ledwell and Watson* [1991] was applied to the evolution of the mean tracer profiles for the first 5 months, from S1 to S2 (Figure 3). These profiles were treated as interior ones, i.e., hypsographic and boundary effects were not included in the analysis. The best estimate of the interior diffusivity is $(4 \pm 1) \times 10^{-5}$ m^2 s^{-1}, a bit larger than the value of $(2.9 \pm 0.6) \times 10^{-5}$ m^2 s^{-1} found for the first 6 months of the earlier experiment by *Ledwell and Watson* [1991]. The difference might be due to a lower buoyancy frequency at the target density surface (1.4×10^{-3} s^{-1}) than in the prior experiment (1.9×10^{-3} s^{-1}), that was in turn perhaps due to a different recent renewal history. The diffusivity found by *Ledwell and Bratkovich* [1995] in the interior of Santa Cruz Basin was ca. 1×10^{-4} m^2 s^{-1} at a buoyancy frequency of 0.3×10^{-3} s^{-1}, indicating the same trend in the basins. In all cases, some influence of boundary mixing is likely.

[22] As in the earlier experiment, the time scale for mixing of the tracer to the boundaries and for homogenization within the basin seemed to be about 5 months. Hence, to estimate the basin-wide diapycnal diffusivity from the evolution of the tracer profile from June 2005 to January 2006 (S2 to S3), a full-basin model was used. The model included hypsographic effects, and renewal and vertical advection were estimated from the heat budget. The model is similar to one described for the later stages of a tracer experiment in Santa Cruz Basin (Legs 4 to 5 and Legs 5 to 6) by *Ledwell and Bratkovich* [1995]. As in that experiment, assumptions must be made about new water entering and leaving the model domain. For the model result shown in Figure 3, new water was allowed to enter the model domain below sill depth only in the bottom layer. Above sill depth, the model was constrained by setting the diapycnal diffusivity to a constant. The fit shown in Figure 3 is for a cold anomaly of new water relative to the bottom water of $-0.07°C$, which is consistent with the coldest temperatures observed in suspected plumes entering SMB from the sill to Santa Cruz Basin. The diffusivities of heat and tracer for the fit in Figure 3 decrease smoothly from 2.5×10^{-4} m^2 s^{-1} near the bottom to 1×10^{-4} m^2 s^{-1} at the sill and above and is equal to 1.1×10^{-4} m^2 s^{-1} at the depth of the tracer release (ca. 785 m). The depth dependence of the diffusivities is constrained by the assumptions in the model. Other sets of assumptions give various results, but all lead to the conclusion that the basin-wide diffusivity at the depth of the tracer release was 1–2×10^{-4} m^2 s^{-1}. The poor fit of the model to the data is due to oversimplifications, such as the assumption of fast isopycnal mixing implicit in a 1-D model, the assumption that the diffusivity for heat is the same as that for tracer, and allowance of new water only in the bottom layer. The range

estimated for the diffusivity includes the value of 1.3×10^{-4} m^2 s^{-1} estimated for SPB from heat and nutrient budgets by *Berelson* [1991] and the lower limit of 1.0×10^{-4} m^2 s^{-1} found from the heat budget by *Ledwell and Hickey* [1995]. This range is much larger than the interior diffusivity, implying that mixing is greatly enhanced in the boundary regions of the SMB and SPB, as found by *Ledwell and Hickey* [1995] and for Santa Cruz Basin by *Ledwell and Bratkovich* [1995].

7. Conclusions

[23] The experiment conducted over a two-year period in the Santa Monica Basin has shown that SF$_5$CF$_3$ is a viable tracer for ocean tracer release experiments. It can be injected using the current technology to inject SF$_6$, and the measurement technique is similar to that used for CFCs. Despite having a solubility that is roughly half that of SF$_6$, SF$_5$CF$_3$ appears to behave identically to SF$_6$ in the basins, in which particle fluxes are relatively high. Diapycnal diffusivities calculated from SF$_5$CF$_3$ would be the same as those from SF$_6$, well within the error bounds of any oceanic experiment. The experiment also confirmed the results of earlier mixing experiments performed in the California Borderland Basins, namely the magnitude of the diapycnal diffusivity in the interior of the basins, the time for homogenization and mixing to the walls, and the much greater whole-basin diapycnal diffusivity compared to that of the interior.

[24] SF$_5$CF$_3$ in 100-kg quantities is not currently commercially available, although Fluorochemika Poland is currently developing a technique to make 100-kg batches. To preserve the usefulness of SF$_6$ as a transient tracer, the use of SF$_6$ in subsurface ocean tracer release experiments should be halted immediately, in accordance with a recommendation adopted by the SF$_6$ tracer community at the 13th Ocean Sciences Meeting in 2006. An international consortium should be formed to acquire a stock of SF$_5$CF$_3$ and to distribute it to oceanographers conducting deep ocean tracer release experiments in order to encourage and enable the use of SF$_5$CF$_3$ in experiments that would otherwise use SF$_6$. Finally, systematic experiments should be conducted to better determine the solubility and diffusion coefficient of SF$_5$CF$_3$ in natural waters if it is to be used in gas exchange experiments.

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