Final Report

Development of Perfluorotracers (PFT's) for marine use

Department of the Environment contract 1983/1986

by

Andrew J. Watson

Marine Biological Association of the United Kingdom
The Laboratory, Citadel Hill,
Plymouth PL1 2PB

July 1986

CONTENTS

PAGE

INTRODUCTION

1.1 The schedule of research. (extracted from Programme Identification form).

1.1.1 "To develop techniques and hardware to enable certain perfluorinated compounds to be used as economic and practical tracers of water movements over distances up to hundreds of kilometres".

Specifically, the contractor will:

a. set up equipment to measure perfluorotracers (PFT's) and investigate their background levels (if any) in sea-water.

b. Develop methods of injecting selected PFT's into water.

c. Build a self-contained sampling instrument to measure a suitable PFT with a minimum detectable level of at least 10^{-15} g/g, and a sampling rate of order one minute. The instrument to be compact and capable of running several hundred samples between major "services".

d. Conduct field trials to evaluate the performance of selected PFT's as practical tracers.

1.2 Background

Certain perfluorocarbons and fluorosulphurs may be sensed in the environment at concentrations as low as 10^{-15} v/v, by electron capture detention (Lovelock and Ferber, 1982). Many of these compounds are extraordinarily stable, inert, and non-toxic. Thus they make excellent tracers, by the controlled release of which transport and mixing processes may be studied. For some time now they have been exploited in this manner to monitor atmospheric motions by NOAA in the United States (FERBER et al., 1981). Some of these experiments have been on a global scale - sufficient tracer being released to enable its detection thousands of kilometers away. Numerous experiments on a smaller scale (10-100km) have also been performed.

These tracers are detected in the gas phase. However, tracer which is dissolved in water may be easily transferred to a gas stream by 'stripping' the water with the gas. Thus the same techniques used for the atmosphere could be modified for use in marine and estuarine systems. The object of our research was to conduct the necessary preliminary studies, including the development of a sampling instrument, to enable perfluoro-tracers to be used as marine tracers.

Up to now, fluorescent dyes have been the normal choice when it has been required to trace marine transport (PRITCHARD andCARPENTER, 1960; EWART and BENDINER,1974, 1979; TALBOT and TALBOT, 1974). These dyes have been followed after dilution into areas up to tens of kilometres in scale. However, larger scale experiments are barely practical for several reasons. The detection limit for rhodamine in seawater is of order 10^{-12} g ml^{-1} at the best. While this is an excellent sensitivity by most standards of chemical analysis, it nevertheless implies that to 'mark' a volume of water 100 km x 100 km x 100 m deep would require in excess of a ton of dye. The raw material for such a release would therefore be expensive. In addition there may be environmental problems associated with the release of large quantities of dye, for it can be both unsightly and toxic when concentrated. Dyes also tend to be absorbed onto particulates and are probably not conservative if the experiment extends over a long time period. Perfluorotracers are potentially superior to fluorescent dyes on all the above counts. However, their different properties and methods of detection make them in some respects less convenient to work with than dyes. For example, since they are only sparingly soluble, their release into water is more difficult, they cannot be simply tipped over the side of a ship. They tend to escape to the atmosphere from the surface and will not be conservative in surface waters. In addition, the method of analysis is slower than fluorometry and cannot (as yet) be performed in situ. Section 6 summarizes the advantages and disadvantages of fluorescent dyes and perfluorochemicals as water.

In this research we have developed technology to make marine perfluorotracer experiments practical and useful. We have concentrated on two substances; Sulphur hexafluoride (SF_6), which is a gas at room temperature, and perfluorodecalin (PFD), a liquid. Neither of these substances has any toxic effects, even in the pure form. Injection and analysis techniques are different for each on account of their widely different solubility and volatility. In the body of the report we describe the analysis and injection techniques. Greater attention is paid to PFD analysis and injection than to SF_6. This, is because we found that large-scale injection of PFD was easier than that for SF_6, so that our self-contained instrument was built to sample for this compound. Our later field experiments showed that, as far as conservative behaviour is concerned, SF_6 is the preferred tracer through both compounds can be effectively used to follow water movements.

2. Analysis techniques

2.1 Sulphur hexafluoride analysis

Sulphur hexafluoride was determind by electron capture gas chromatography, with concentration of the sample by equilibration with a purge gas and subsequent trapping of volatiles from the gas. The tracer was trapped by means of a 10cm x ¼" o.d. pre-column of Porapak QS, cooled to -90°C. The trap was mounted in the sample loop of a Hewlett Packard 5880a GC. The purge gas was first cleaned of SF_6 by passing it over an activated Pd catalyst at 400°C. After trapping, the pre-column was valved off and heated to 100°C before being switched into the carrier gas.

Separation was carried out on a molecular sieve 5A column. For seawater analyses, 50 cm^3 of the purge gas was shaken very vigorously with 1.05 litre samples of water for two minutes; this appeared to strip about 90% of the SF_6 from the water. The measurement technique was relatively slow (20 minutes per analysis). Fig. 1a,b show chromatograms of background marine air and water from 500m in the N.E. Atlantic, obtained with this apparatus. Fig. 1c,d show the system blank and the response to calibration gas. The minimum detectable concentration of SF_6 in the 1.05 litre samples was about 3×10^{-17} moles per litre.

This system was used to investigate the background of SF_6 in seawater and the marine atmosphere (see section 3.1). However, the relatively slow analysis made it unsuitable for use in tracer experiments. The long analysis time was due to the necessity of waiting for "heavy" peaks to elute from the column, and could be avoided by incorporating a backflush of the analytical column. A fairly crude system incorporating backflush was used by us in our first field experiment, in September 1983. This set-up used activated charcoal as the trapping substrate rather than Porapak QS, and was found to operate at low efficiency. J.R. Ledwell, of Lamont-Doherty Geological Observatory in New York, constructed a rapid - analysis system with backflush which was used in our definitive field experiments (conducted jointly with LDGO) in September 1985.

2.2 Perfluorodecalin Analysis.

2.2.1 Self-contained Sampling Instrument.

The method of determining PFD was basically the same as for SF_6, i.e. purge-and-trap followed by electron capture gas chromatography. However, the analysis was reduced to a fully automated procedure which processed samples continuously. A dedicated instrument was constructed to carry out the analysis. Fig. 2 shows a schematic of the method. The tracer was first stripped from the water into the gas phase. Because of the very low solubility of PFD this process is comparatively rapid and stripping can be a continuous process. Seawater was pumped at a rate of 190ml min $^{-1}$ into the top of a sparger having a barrel 20cm long and internal diameter of 2.2cm. The water was exhausted at the base of the sparger. Separate peristaltic pumps were used for the input and output flows, the input pump being of a type where the speed is adjustable by means of a control voltage (Watson-Marlow type 501u). The water level in the sparger was sensed by a pair of platinum contacts sealed into a side-arm, the speed of the input pump being automatically adjusted to keep the level constant. This arrangement had the advantage that the water level in the sparger could be maintained regardless of pressure fluctuations.

Nitrogen was bubbled at a rate of about 60ml min^{-1} through the sparger, than via a spray-trap packed with glass wool and a tubular drier filled with potassium carbonate, into one of two molecular sieve traps connected in the sample loop positions of an eight-port valve (see Fig.2). At timed intervals, usually three minutes, the valve was operated to switch the charged trap into the carrier supply of the gas ghromatograph and move the second trap into the sparge gas supply. The charged trap was then heated to about 200°C in the space of ten seconds, causing it to desorb the trapped volatiles in a pulse.

A Shimadzu mini-2 gas chromatograph was employed for the analysis. This instrument is sufficiently compact that it could be built into the instrument package without sacrificing portability. The carrier gas train consisted of a 2m x 6mm o.d. aluminium column packed with Porasil D. The first 10cm of the column was filled with a catalyst of palladized asbestos. The catalyst section of the column was passed through an aluminium block which could be raised above the main oven temperature by an auxiliary heater. The column temperature was 115°C.

The purpose of the palladium catalyst was removal of unwanted compounds which might otherwise interfere with the analysis.

The perfluorocarbons are unusually stable compounds which will pass over such a catalyst unchanged, under conditions sufficient to hydrogenate most of the compounds to which the ECD is sensitive. The hydrogenation products capture electrons weakly or not at all, so this treatment greatly attenuates the corresponding peaks in the chromatogram (LOVELOCK and WATSON, 1978). Prior to use the catalyst was activated by passing a mixture of 1% hydrogen in nitrogen through the system for several hours, and this mixture was normally used as the carrier gas during analysis. The molecular sieve traps were constructed from 1.6mm o.d. stainless steel tubing packed with 0.015 g of MS 5A. The retention volume for PFD on this absorbent was found to be approximately 30 1 g^{-1} at room temperature so that even these small traps were able to absorb the tracer from 450ml of gas.

In the completed, self-contained instrument package, the Shimadzu gas chromatograph was mounted above a 'control box' which contained the associated electronics. These included the circuitry required to time the switching of the valve and the rapid heating of the traps, control and readout of the palladium catalyst temperature and the trap temperatures, and control of the variable speed pump. The control box also generated a signal at the beginning of each analysis which was used to start an external integrator, (type Hp 3392a), which provided the final data readout. The system as a whole was designed and built in part by means of a subcontract to Brazzos Limited.

2.2.2 Calibration

For calibration purposes, standard dilutions of PFD in both air and water were made. Our primary standard was a preparation of 100 pptv in air, made as follows: 0.193 g of PFD was dissolved in 100 ml of acetone and the solution kept in a sealed flask until required. Fifty μl of this solution was evaporated in front of the circulating fan of a very large (5 x 10^7cm^3) dilution chamber owned by J.E. Lovelock of Brazzos Ltd. After running the circulation fan for another two minutes to ensure uniform dispersion, a stainless steel cylinder was flushed and filled with air from the chamber. The accuracy of standards prepared by this method is estimated to be 5%. Known amounts of PFD in seawater were prepared by first making a solution of 3.2 x 10^{-8} g ml^{-1} PFD in acetone in two serial dilutions. This mixture was refrigerated and stored in a tightly stoppered flask with very small headspace until required. Microlitre quantities of this solution were then added to 100ml syringes filled with seawater and subsamples added to the pump input. Both gaseous and liquid standards were used for routine calibrations at sea. However, the final diluton of acetone into seawater was freshly made immediately before each aqueous calibration.

Fig. 3 shows output from the instrument obtained at sea when the incoming water, taken from the ship's non-toxic supply, was free of PFD. No 'system blank' is observable at the retention time of the tracer under these conditions. 5 cm^3 of primary air standard was injected into the purge gas, immediately after the sparger, at time A. The corresponding peak appears after the next switching of the valve. 10cm^3 of water containing 3.2 x 10^{-9} g 1^{-1} PFD was mixed with the inflow to the sparger at time B. The analysis following the next switching contains most of the sample but a small fraction is also observed in the next-but-one. From such pairs of 'air' and 'water' calibrations the efficiency with which the tracer was stripped from water to the gas phase by the sparger could be calculated. Typically the sparging efficiency was 35% and the minimum detectable concentration of was about 4 x 10^{-15} moles 1^{-1}. Though the sparging efficiency may be expected to change with flow rate and temperature, in practicethe response of the machine changed little over periods of prolonged use: the precision, measured over a period of 12 hours, was 8% to water standards like that in fig. 3.

2.2.3 Response time.

In tracer experiments, a fast response time for the analytical instrumentating is advantageous because it allows more detailed resolution of the tracer distribution. In this respect our technique is considerably inferior to fluorescent dye measurements which can have response times of less than a second (EWART and BENDINER, 1974). The minimim response time of the apparatus described here is the time set between samples, i.e. 3 minutes in our tests. In addition there is the possibility that tracer will reversibly absorb onto components in the gas stream, tending to further increase the response time. The impulse response of the instrument was therefore tested by injecting a dose of dissolved PFD sufficient to give a large signal and observing the decay of the peak over the following cycles of analysis.

In a typical experiment, 79.3% of the total signal appeared in the first cycle, 19.3% in the second, 1.2% in the third and 0.2% in the fourth. After repeated injection of high levels of PFD a persistent blank frequently appeared, associated with residual tracer absorbed onto the K_2CO_3 drier and the silicone rubber tubing in the input pump.

3. PRE-EXISTING BACKGROUND OF TRACERS IN THE SEA.

3.1 SF_6

Sulphur hexafluoride has a background concentration which is already easily measurable in surface and upper thermocline waters, due to its penetration from the atomosphere where its background is presently about 1.5 parts per trillion by volume (pptv) and rising. Fig. 4 shows a depth profile as measured at a station in the eastern North Atlantic. The profile is compared with simultaneous determinations of freon-11 ($CFCl_3$. Both F-11 and SF_6 are present in the atmosphere because of releases from industry over the past thirty years. The release rate of freon-11 is very well documented, and, comparative measurements such as those of Fig. 4 enable the reconstruction of the release history of sulphur hexafluoride (WATSON and LIDDICOAT, 1985). The maximum concentration for SF_6 is about 3×10^{-16} moles/litre and occurs at the surface. This background sets a lower limit on concentrations which must be generated in any marine tracer experiment: to be successful, a deliberate release must produce sufficiently large concentrations for the background level to be small by comparison. Fortunately the background is still low enough for this to be easily achievable; the surface background corresponds to only 0.05 g. SF_6 per cubic kilometre of seawater.

3.2 Perfluorodecalin

No pre-existing background level of perfluorodecalin could be detected. This is consistent with our understanding of PFD as a very insoluble substance, (solubility less than 10^{-7} g/g). Since the atmospheric background of PFD is about 0.1pptv, or $2 \times 10^{-15} g\ cm^{-3}$, the amount in dissolved form in equilibrium with the atmosphere would be less than 2×10^{-22} g cm^{-3}, which is well below detection level.

4. INJECTION METHODS

4.1 SF_6.

Three injection methods have so far been used for sulphur hexafluoride:

a. Seawater is sprayed into a small flask filled with SF_6 gas. This method produced water saturated with SF_6 at the slow rate of about 2 litres per minute. It was used on our first field trial.

b. Water in a 200 litre tank on the deck of the ship is saturated by bubbling SF_6 through it. The tank is then pumped out into the sea. This method is somewhat faster and was used in our final field trial.

c. A "bubble stone" is lowered into the water and SF_6 is bubbled directly into the sea. This method has been used by WANNINKOF et al (1985) for lake experiments. It is much faster than the other methods, but has the disadvantage that the release is less controlled and the exact quantity dissolved is harder to assess. Using the second method, we achieved an injection rate of about 10 grams per hour. However, WANNINKOF et al achieved a rate of approx. 250 grams per hour by the "direct" method, so it is clearly superior if the imprecision of the initial injection can be tolerated.

4.2 Perfluorodecalin

Perfluorodecalin, a very insoluble liquid, was injected by first forming a micro-emulsion of PFD in distilled water. The "recipe" for micro-emulsion, as used in our final field trial, was as follows:-

17.5% w/v	Perfluorodecalin
18% w/v	Perfluoro-tributylamine,(PFTBA). (3M Corp)
2% w/v	'Pluronic F-68' (Blagdon Campbell, Croydon Surrey)
0.5% w/v	Yolk phospholipids (Alpha therapeutics Ltd, Los Angeles)
balance	distilled water

The Pluronic F-68 and yolk phospholipids act as surfactants, while the PFTBA is a 'helper' perfluorocarbon, miscible with PFD but more easily emulsified than 'neat' perfluorodecalin.

To make emulsion, the surfactants were first dissolved in the water. The two perfluorocarbons were mixed and added to the water forming a separate layer. The mixture was then placed in a 'Waring' blender and homogenized at low speed for one minute to produce a crude emulsion. The crude emulsion was then passed repeatedly through a Manton-Gaulein homogenier, with a ram pressure of 3000 p.s.i. After each pass, the liquid was cooled to 20°C to offset the heating of approx. 5°C which the homogenizing process engendered. The optical density of the liquid was measured after each pass, the process being repeated until the optical density no longer decreased. The emulsion was then frozen slowly, in which state it was stored until required for use. Subsequent analysis (for which we are indebted to Dr. C. Heldebrandt of Alpha-therapeutics inc., Los Angeles) showed that the emulsion consisted entirely of droplets less than 0.5 micron diameter.

Having reduced the PFD to an emulsified form, the injection into the sea was much easier than for SF_6. The material wassimply lowered to the required depth and pumped out at the desired rate. Estimates of the time required for the emulsion droplets to dissolve once released are uncertain, because the solubility of PFD is unknown. However, the time should be less than one hour provided the solubility is greater than 10^{-8}g/g.

5. FIELD EXPERIMENTS

5.1 Jersey-Minquiers SF_6 release, September 1983.

Fifteen grams of sulphur hexafluoride were injected using method (a) described in section 4.1 The tracer was detected using a crude, manually operated SF_6 system which gave rather erratic and unsatisfactory results. However, the tracer patch was positively identified, near the limit of detection, three days after release and 15km from the release site. The rather equivocal results obtained in this first trial were due in part to our inability to release a larger quantity of tracer. This prompted us to devote most of our subsequent efforts to developing PFD as a tracer.

5.2 Lyme bay PFD release, February 1985

This experiment was designed to test the emulsion release technique and the PFD sampling instrument. In Lyme bay during the winter, the water column (about 40 metres deep) is vertically well mixed by the tide, and it was accepted that some loss of the tracer by venting to the atmosphere from the surface would occur. To mark the deployment a "Hermes" drifting buoy with a 9m diameter drogue was released. The deployment ship then steamed around the buoy in circles of about 200m radius at a speed of 2.5 knots while emulsion was pumped into the water at a rate of 12ml per minute. The outlet was kept at a depth of approximately 5m. In total, 1 litre of emulsion containing 200g of PFD was released.

The deployment was made on 14 February 1985 during a lull after a period of easterly gales. Immediately after the release, strong easterly winds resumed and persisted for three days, accompanied by sea conditions too severe to allow the survey ship to leave Plymouth. During this time the buoy, as tracked by satellite, drifted 80km to the west, leaving Lyme bay and heading towards Plymouth (see Fig. 5a). When conditions moderated on 17 February the tracking ship made a rendezvous with the buoy. No tracer could be detected in the immediate vicinity and it was clear that the buoy had been driven wellahead of the tracer patch by the storm.

A search for the tracer was initiated, beginning at the point of release and working to the west. The tracer was contacted on 20 February and a portion of the distribution mapped.

(see Fig.5b). Having overrun our schedule we were unfortunately unable to obtain a more complete mapping or to search further to the westward where it is likely that more of the tracer was to be found.

In plotting the distribution in Fig.5b it was necessary to correct the ship's track for the effect of the tide. A tidal velocity of the form

$$U = 60 \cos (\omega(t - t_0)) \text{ cm s}^{-1}$$

in a direction of 042^0 was assumed. Here, ω is the angular velocity of the M_2 tide, t is the time of observation and t_o the time of maximum stream. The magnitude and direction were taken from a navigational chart of the area and are only approximations to the real tide. Since the survey took four hours to steam, during which time the tide moved the water several kilometres, some tidal correction is necessary to bring the observed distribution into a frame of reference which is stationary with respect to the water.

As an experiment to quantitatively evaluate PFD as a marine tracer this release was not ideal, with the bad weather and resulting high venting rate introducing uncertainties which are compounded by the incomplete coverage of the tracer patch. We estimate that only 1.5% of the PFD originally deployed was present in the surveyed volume of water. The low 'recovery' must be due to a combination of three factors: incomplete dissolution of the tracer, loss to the atmosphere, and incomplete mapping of the distribution.

An estimate of the amount vented to the atmosphere can be made using a sea-air transfer velocity of 0.15m hr^{-1}, based on radon deficit measurements in the open ocean. Applying this figure to a well-mixed water column 40m in depth, we find that about 40% of the dissolved tracer would have been lost to the atmosphere during the 6 day period between release and detection. The true figure may be considerably higher bearing in mind the severe storm which prevailed during this period and tidally active nature of the waters. Wind tunnel measurements (LISS, 1983) suggest that at high wind speeds the transfer velocity may be three or four times faster. If the transfer velocity was 0.5m hr^{-1} for the three days of the storm and 0.15 m hr^{-1} for the remaining three days,then 70% of the dissolved tracer would have been vented. However, even if we use this high venting rate, the surveyed water would still have contained only one twentieth of the total mass of tracer which we would expect to be present in measurable form. We believe therefore that we missed most of the tracer distribution and mapped only a minor portion of a fragmented pattern of tracer.

In addition we suspect that the PFD had either not fully dissolved from the emulsion, or had dissolved but subsequently partially bound to particulate surfaces. These suspicions were confirmed in our final experimant (see 5.3).

5.3 Santa Monica Basin SF_6/PFD release experiment September 1985

This experiment was jointly mounted by ourselves and by J.R. Ledwell and W.S. Broecker of Lamont-Doherty Geological Observatory, New York. It was designed as a full and exhaustive test of the comparative properties of the tracers, which in addition would yield important data on the physics of diapycnal mixing in the ocean. By performing the release in a small (80 x 30 km) ocean basin, and by releasing in subsurface water, we elimated the two sources of error which made it difficult to evaluate the tracers in previous experiments, namely loss of the tracer by breakup of the patch and by venting to the atmosphere. The experiment is described in the Annex to this report. Below we give a brief description of the experiment, concentrating on the evaluation of the tracers.

SF_6 was injected by method (b) in Section 4.1. PFD was injected by emulsification, (section 4.2). Both tracers were pumped out at about 750 metres depth, onto an accurately targeted isopycnal surface. The injection was accurate to about ± 5m depth, and was targeted using a conductivity - temperature - depth (CTD) probe mounted on the injection apparatus. SF_6 and PFD were laid in streaks near the centre of the Santa Monica basin, which is a seafloor depression about 80km long by 30km wide off the Southern California coast. 15 streaks of SF_6-saturated water were interspersed with four streaks of PFD emulsion. In all, 200g of SF_6 and 2kg of PFD were released.

Sampling was performed using an array of twelve 5 - litre Niskin bottles equipped with integrating samplers. These samplers were designed to draw 50ml of water into glass syringes in 90 minutes while the array was towed a distance of one or two kilometers. The bottles were spaced at intervals of five to twelve meters with a CTD near the centre of the array. The CTD was held on the injection surface in the same way as the tracer injection package. The samplers themselves did not remain on unique isopycnal surfaces due to considerable temporal and spatial variations in the fine structure of the temperature profile.

Sampling was performed on three cruises, 2-14 days, 46-55 days and 155-165 days after injection. By the time of the second sampling cruise the tracers were sufficiently evenly spread in the horizontal to enable estimates of the amount of tracer in dissolved form in the water to be made by integrating over the patch. For SF_6 this procedure gave a result in agreement with the amount originally injected, i.e. 200g± 10%, confirming that this tracer is ideally conservative. For PFD the integration showed that only about 30% of the amount originally injected was present in measurable form. This confirmed our earlier suspicion that PFD is not a fully conservative tracer, though it should be noted that neither did it appear to be <u>progressively</u> lost, since the final cruise at about 160 days gave a similar "recovered fraction". We believe therefore that PFD suffers some loss mechanism, probably in the early stages after an emulsion release, but have been unable to determine the exact nature of this process.

PFD also showed some tendency to stick to the surfaces of the sampling gear, leading to additional error in the measurements particularly in the initial stages of the experiment when concentrations were very high. Once recognised however, this problem was an annoying rather than a fatal draw back. After use, boiling the samplers for a few minutes and then allowing them to dry by evaporation was sufficient to remove any traces of PFD remaining on the surfaces.

Despite the above caveats on the use of PFD, both substances proved very effective marine tracers during this experiment. Either tracer could have been used alone to derive the information on vertical mixing. The physical oceanographic results obtained during this exercise are unique and extremely valuable.

6. SUMMARY: EVALUATION OF PERFLUOROTRACERS

We have developed the necessary skills required to use perfluorodecalin (PFD) and sulphur hexafluoride (SP$_6$) as marine tracers. An automated analyser for PFD has been constructed. Below we summarize the relevant information on the use of SF$_6$ and PFD as marine tracers. For comparison, equivalent information on the well-established fluorescent dye technique is also included.

a) Toxicity:

SF$_6$, PFD - No toxic effects reported to date.

Fluorescent dyes - Some carcinogenic activity suspected.

b) Environmental impact:

SF$_6$, PFD - Colourless, odourless and used at low concentrations. No deleterious evnironmental effects reported

Fluorescent dye - At concentrations$>$10 p.p.b. these visibly colour water.

c. Detection limit:

SF$_6$ - 10^{-16} moles litre $^{-1}$

PFD - 2 x 10 $^{-15}$ moles litre $^{-1}$

Fluorescent dye - 2 x 10 $^{-12}$ moles litre $^{-1}$

d. Volatility:

SF$_6$, PFD - volatile compounds which tend to escape from surface waters into atmosphere.

Fluorescent dye - Non-volatile

e. Conservative behaviour:

SF$_6$ - excellent conservative properties in subsurface water.

PFD - Some loss, possibly due to absorption on particles.

Fluorescent dye - Some loss due to absorption on particles and photo-degredation.

f. Injection method:

SF$_6$ - pre-dissolution in water (slow) or bubbling gas directly into sea.

PFD - preparation of micro emulsion.

Fluorescent dye - Direct dissolution in water.

g. Detection method:

SF$_6$,PFD - Automated purge and trap apparatus followed by electron - capture gas chomatography. (Ship-borne).

Fluorescent dye - Fluorometer (ship borne or in situ)

h. Time constant for detection:

SF_6, PFD	- 3 minutes
Fluorescent dye	- 1 second

i. Appropriate Scale for tracer experiments:

SF_6	- up to whole ocean.
PFD	- up to 1000 km
Fluorescent dye	- up to 50 km

References

Ewart, T.E. and Bendiner, W.P. (1974). Techniques for estuarine and open ocean dye dispersal measurement. Rapports et proces-verbaux des reunions du Conseil International pour l'exploitation de la mer. u167, 201-12.

Ewart, T.E. and Bendiner, W.P. (1981). An observation of the horizontal and vertical diffusion of a passive tracer in the deep ocean. Journal of Geophysical Research, 86, 1094-1082

Ferber, G.S., Telegades, K. Heffter, J.L., Dickson, C.R., Dietz, R.N., and Krey, P.W. (1981). Demonstration of the use of a long range atmosphere tracer system using perfluorocarbons. NOAA Technical Memorandum ERL ARL - 101.

Liss, P.S. (1983). Gas transfer: experiments and geochemical applications, in Air - Sea exchange of gases and particles; P.S. Liss and W.G. Slinn eds, D. Riedel, Dordrecht, Holland, pp. 241-298.

Lovelock, J.E. and Watson, A.J. (1978). The electron capture detector, Theory and practice II. Journal of chromatography, 158, pp. 123-38

Lovelock, J.E. and Ferber, G.J. (1982). Exotic tracers for Atmospheric studies. Atmospheric Environment, 16, 1467-71

Pritchard, D.W. and Carpenter, J.H. (1960). Measurements of turbulent diffusion in Estuarine and Inshore Waters. Bulletin of the International Association for Scientific Hydrology, 20, 37-50

Talbot, J.W. and Talbot, G.A. (1974). Diffusion in shallow seas and in English coastal and estuarine waters. Rapports et proces-verbaux des reunions du Conseil International pour l'exploitation de la mer, 167, 93-110

Wanninkof, R., Ledwell, J.R. and Broecker, W.S. (1985). Gas exchange - wind speed relation measured with sulfur hexafluoride on a lake. *Science*, *227*, 1224-1226.

Watson, A.J. and Liddicoat, M.I. (1985). Recent history of atmospheric trace gas concentrations deduced from measurements in the deep sea: application to sulphur hexafluoride and carbon tetrachloride. *Atmospheric Environment*, *19*, 1477-1484

Publications acknowledging this research grant:

Watson, A.J., and Liddicoat, M.I., (1985). Recent history of atmospheric trace gas concentrations deduced from measurements in the deep sea: application to sulphur hexafluoride and carbon tetrochloride.

Atmospheric Environment, 19. 1477-1484.

Watson, A.J., Liddicoat, M.I. and Ledwell, J.R. (1986) "Perfluorodecalin and sulphur hexafluoride as purposeful marine tracers and deployment and analysis techniques. Deep sea Research, in press.

Ledwell, J.R., Watson, A.J., and Broecker, W.S., A deliberate tracer experiment in Santa Monica Basin. (Nature, in press).

Figure Legends

Fig. 1. High sensitivity SF_6 analyses; (a) 10 cm^3 background marine air containing 1.6 pptv SF_6 (June 1984). (b) 1.05 litre water containing 2.4×10^{-16} moles per litre SF_6 collected from 500m in the N.E. Atlantic, 48°07'N, 10"01'W June 1984. (c)System blank obtained using 1.05 litre degassed seawater. (d) 0.5ml calibration gas containing 80 pptv SF_6

Fig. 2. Schematic of instrument for the analysis of perfluorodecalin in sea water.

Fig. 3. Repeat chromatograms obtained using the PFD instrument. Vertical marks above the chromatogram show the retention time of PFD, approx 1 min 50 seconds after the start of each analysis. After each valve switching at time 0 min, Freon-II and a small unidentified peak appear. (Note that the size of the F-II peak varies considerably according to the ambient temperature of the molecular sieve traps since this substance is not quantitatively retained).

(a) response of the instrument to 5 cm^3 of 100 ppt standard injected at time A.

(b) the response to 3.2×10^{-11}g of PFD injected in dissolved form at time B.

Fig. 4. Background SF_6 and $CFCl_3$ depth profiles measured in the North Atlantic, in June 1984.

Fig. 5a. Location of the trial release. the track of the Hermes drifting buoy is shown. The vertical divisions mark the buoy position at midnight on 14th, 15th.... 19th of February 1985.

Fig. 5b. Enlarged chart showing the distribution of PFD measured on 20th February. The distribution has been corrected for tidal drift during the measurement period as described in the text.

FIG.1

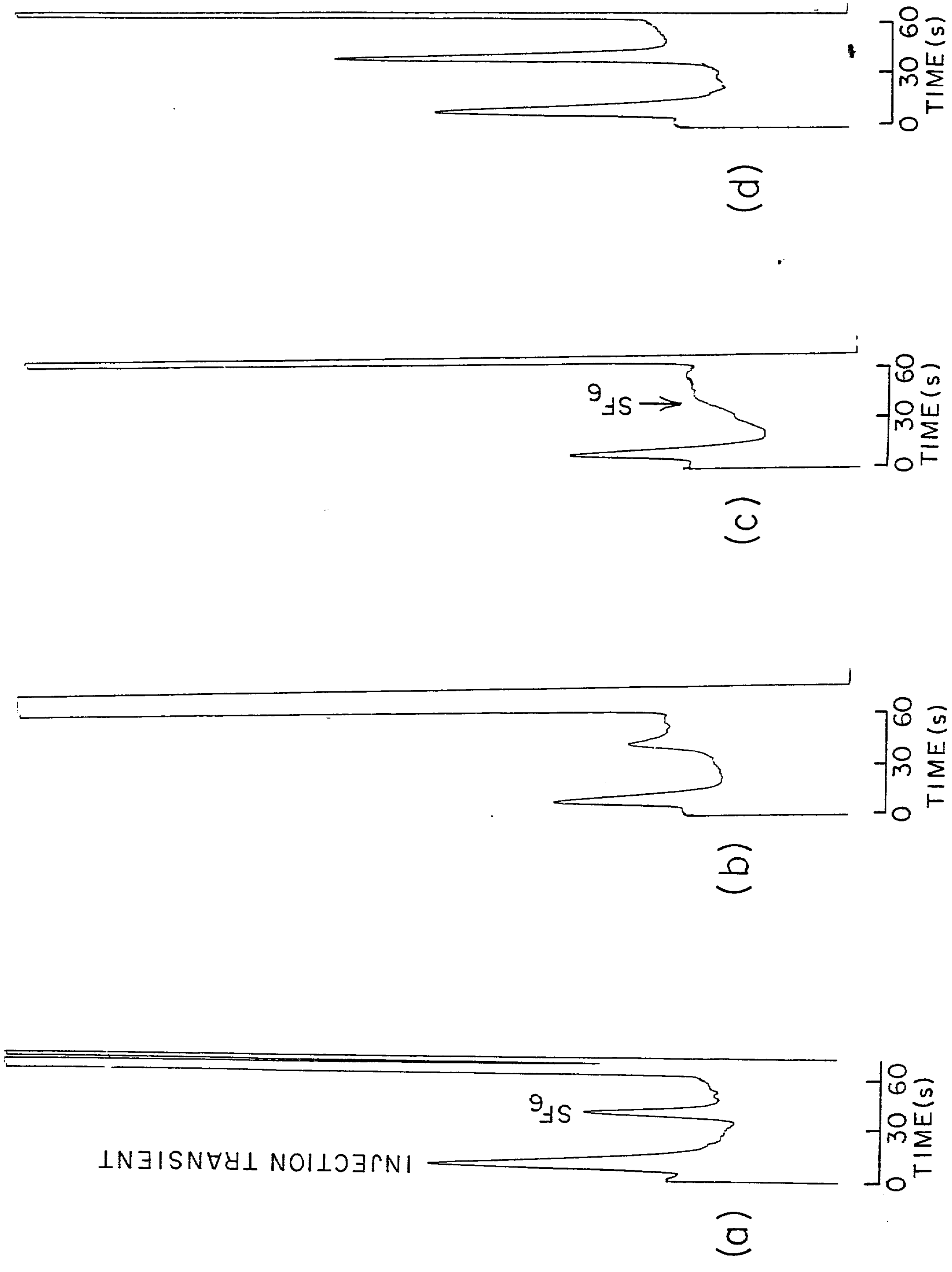

(a)
INJECTION TRANSIENT
SF6
0 30 60
TIME(s)
(b)
0 30 60
TIME(s)
(c)
SF6
0 30 60
TIME(s)
(d)
0 30 60
TIME(s)

FIG. 2

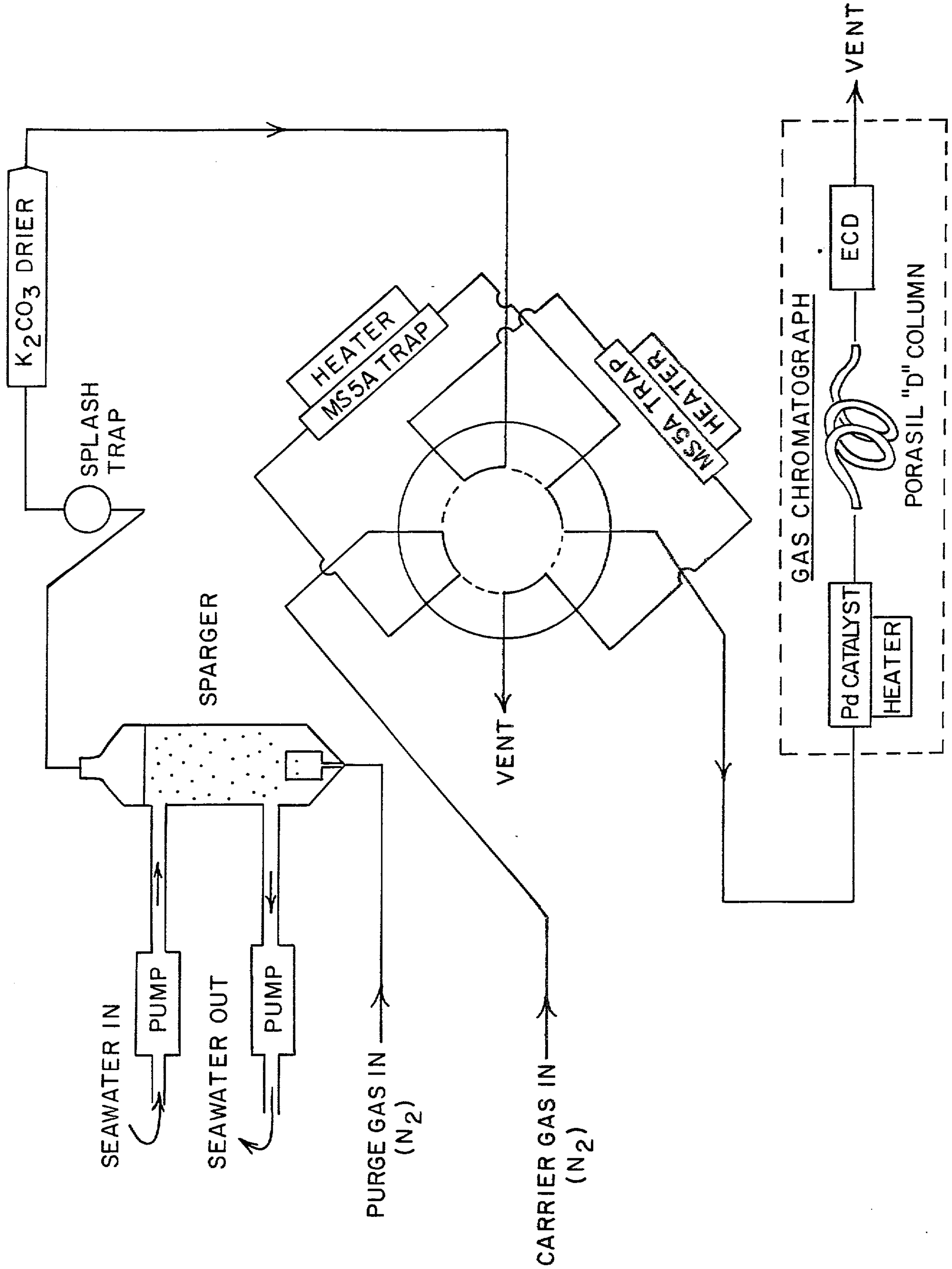

K$_2$CO$_3$ DRIER
SPLASH TRAP
SPARGER
PUMP
PUMP
SEAWATER IN
SEAWATER OUT
PURGE GAS IN (N$_2$)
CARRIER GAS IN (N$_2$)
HEATER
MS5A TRAP
MS5A TRAP
HEATER
VENT
VENT
GAS CHROMATOGRAPH
ECD
PORASIL "D" COLUMN
Pd CATALYST
HEATER

FIG. 3

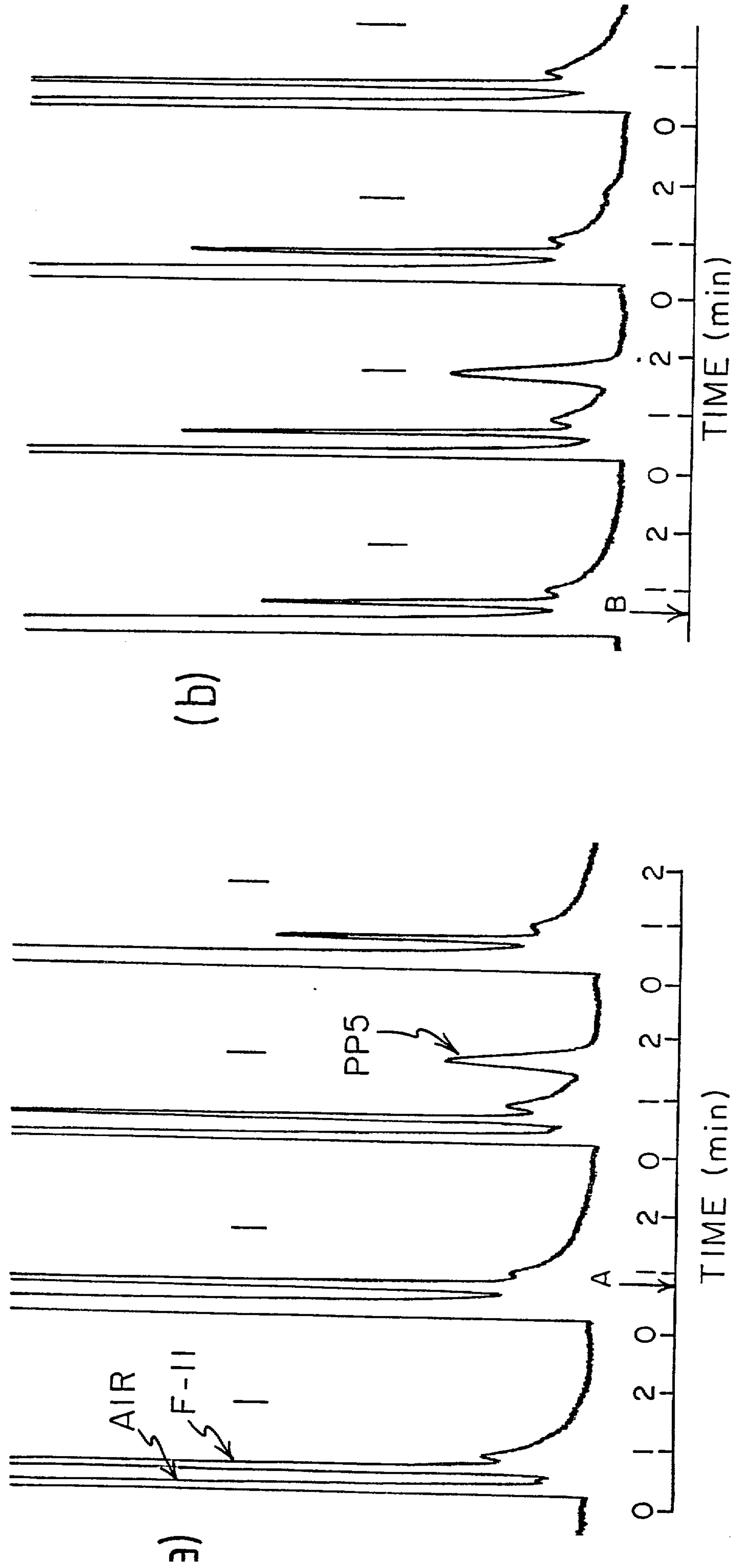

(b)
B
TIME (min)
0
1
2
0
1
2
0
1
2
0
1
a)
AIR
F-11
PP5
A
TIME (min)
0
1
2
0
1
2
0
1
2
0
1
2

FIG. 4

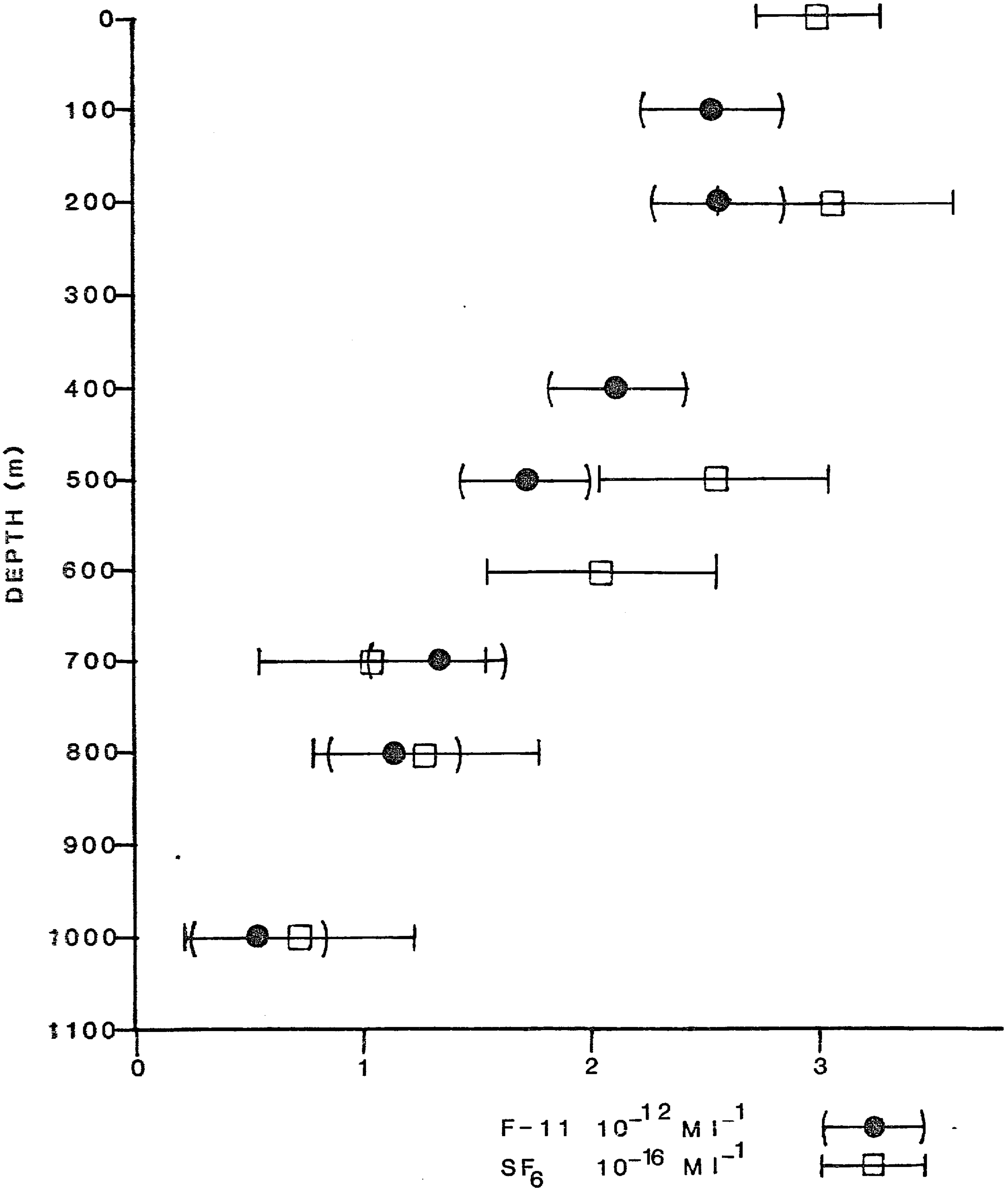

DEPTH (m)
0
100
200
300
400
500
600
700
800
900
1000
1100
0
1
2
3
F-11 10^{-12} M l^{-1}
SF$_6$ 10^{-16} M l^{-1}

FIG. 5a

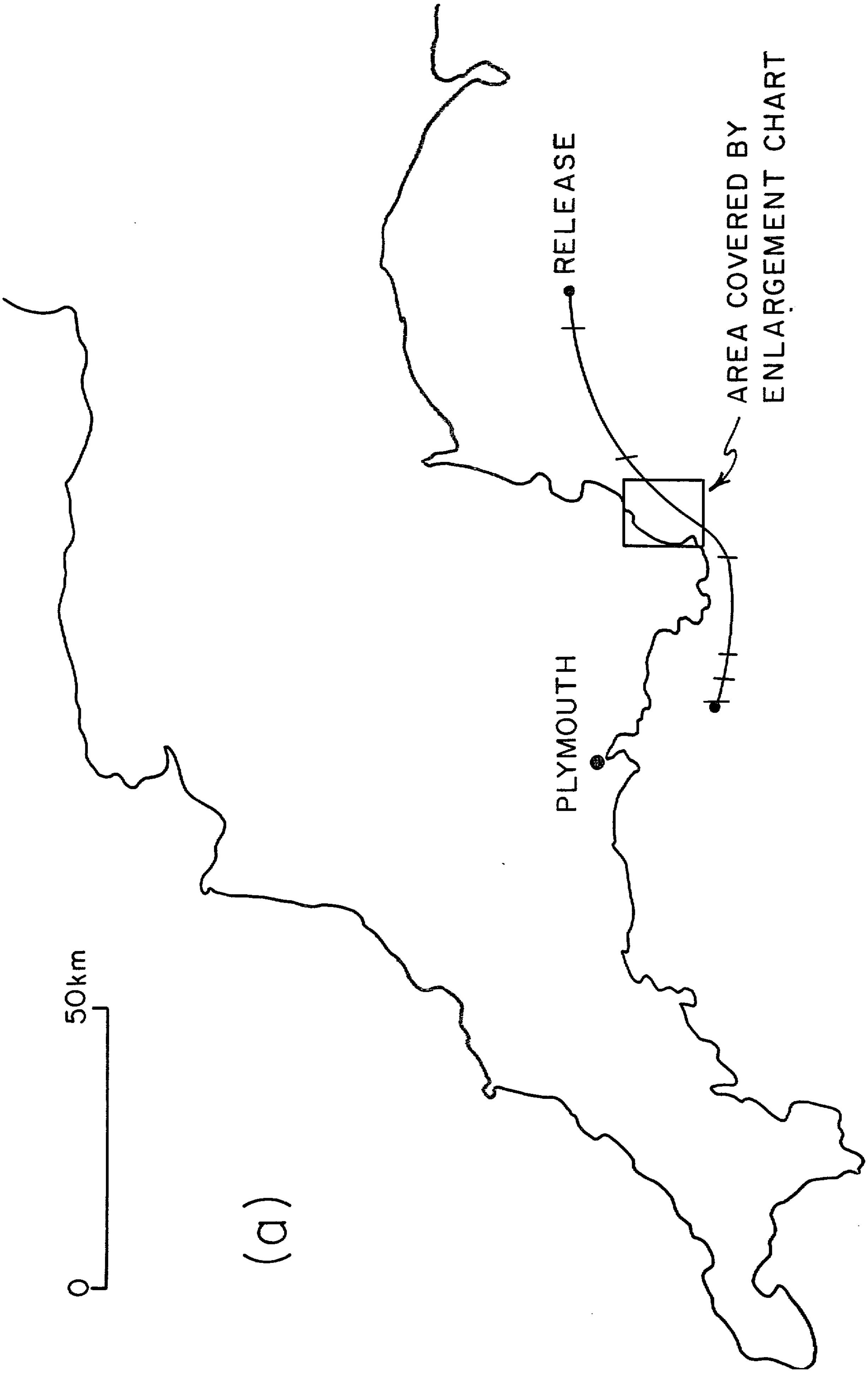
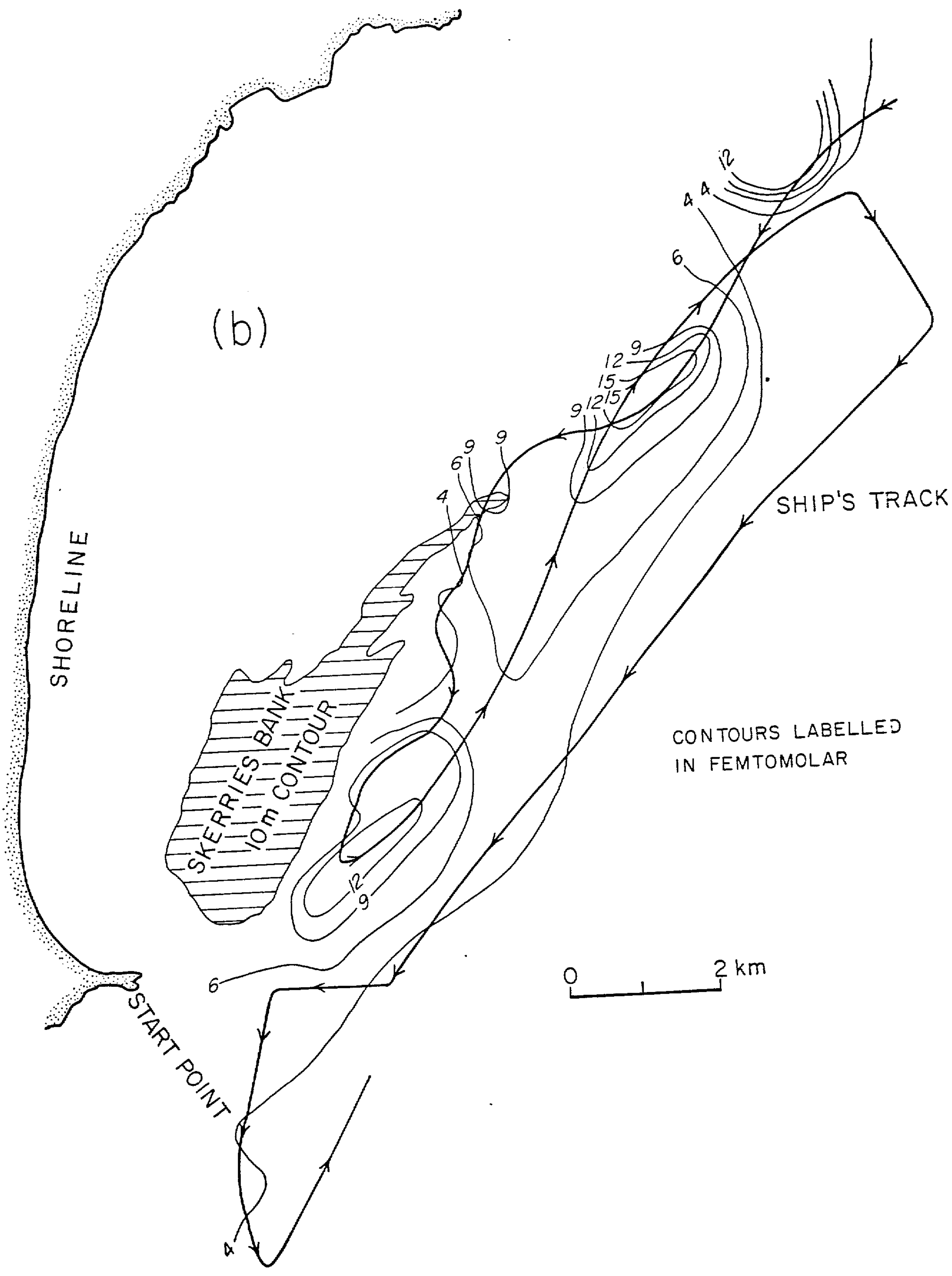

RELEASE
AREA COVERED BY ENLARGEMENT CHART
PLYMOUTH
0
50km
(a)

FIG 5b


(b)
SHORELINE
START POINT
SKERRIES BANK
10m CONTOUR
SHIP'S TRACK
CONTOURS LABELLED IN FEMTOMOLAR
0
2 km
4
4
4
4
6
6
6
6
9
9
9
9
9
9
12
12
12
12
15
15

ANNEX

A deliberate tracer experiment in Santa Monica Basin

by

James R. Ledwell*, Andrew J. Watson , and
Wallace S. Broecker*

*Lamont-Doherty Geological Observatory of Columbia University
Palisades, New York 10964, USA

Marine Biological Association of the United Kingdom, The Laboratory,
Citadel Hill, Plymouth PL1 2PB, United Kingdom

A prototype deliberate tracer experiment is underway in Santa Monica Basin, 50 km west of Los Angeles. Sulfur hexafluoride (SF_6) and perfluorodecalin (PFD) were injected on the 5.15°C surface to study mixing in the basin, especially across density strata (diapycnal mixing). After 50 days tracer had mixed to nearly every part of the basin on the 5.15°C surface, although very little had penetrated to the basin boundaries. From the increase in vertical spread of the tracer distributions between two surveys roughly 43 days apart, apparent eddy diffusivities can be calculated. The SF_6 and PFD results indicate eddy diffusivities of respectively 0.36 and 0.26 cm^2/s at a mean density gradient of $4.4x10^{-9}$ g/cm^4.

Both SF_6 and PFD are extremely safe compounds to handle and are almost certainly harmless in the environment. They are remarkably inert, both chemically and biologically, under normal conditions and we therefore expect them to be conservative in the oceanic system. Yet fewer than 10^8 molecules can be detected using gas chromatography with an electron capture detector.

An enclosed basin was chosen as the site of the experiment to insure that the tracer could be found easily. Table 1 summarizes the characteristics of Santa Monica Basin and Figure 1 shows the bathymetry. San Pedro Basin lies to the southeast, beyond a narrow, low saddle, and the two basins together form a single basin with the deepest sill at the southeastern end of San Pedro at 737 m.

The tracers were injected from R/V New Horizon in a series of streaks, each about 2 km long, located in the circle shown in Fig. 1. SF_6, a very insoluble gas, was injected by saturating cooled water in 200

L drums, lowering the drums to the 5.15°C surface, and pumping the water out through a heat exchanger at a rate of 2.2 L/min. As the water was pumped out of a plastic bag lining the drum, new water of the appropriate salinity entered on the other side of the bag to be brought on deck for another cycle of saturation and injection. Fifteen drums of water containing about 0.1 moles of SF_6 each were injected in this way between 29 August and 4 September 1985.

The PFD, a very insoluble liquid, could be injected in higher concentrations, as it had been emulsified into submicron droplets prior to the cruise. A very fine emulsion is required to insure that the droplets dissolve before they sink beneath the desired density stratum. Four streaks of emulsion, with a total of 4.3 moles of PFD, were interspersed with the fifteen SF_6 streaks. The use of two tracers provides a useful duplication of the dispersion measurements and allows evaluation of different tracer compounds and injection methods.

The injection system was kept within 0.01°C of the 5.15°C surface by operating the winch in response to the output of a conductivity-temperature-depth probe (CTD) accompanying the injection system. The pump turned off automatically on the relatively rare occasions when the package was outside this temperature range. Temperature is an adequate surrogate for potential density for our purposes since variations in potential density on the 5.15°C surface due to salinity and pressure variations are less than ±1 ppm.

Sampling was performed from R/V <u>Robert Gordon Sproul</u> from 29 August to 16 September and from 18 October to 25 October 1985 with an array of twelve 5-liter Niskin bottles equipped with integrating samplers. These samplers were designed to draw 50 ml of water into glass syringes in 90 minutes while the array is towed a distance of one or two kilometers. The bottles were spaced at intervals of five to twelve meters with a CTD near the center of the array. The CTD was held on the 5.15°C surface in the same way as the tracer injection package. The samplers themselves do not remain on unique temperature surfaces due to considerable temporal and spatial variations in the fine structure of the temperature profile.

During the injection phase, Sproul was positioned to drift across individual tracer streaks within a few hours of injection. The second moment of the vertical distribution of tracer about the centers of mass of the eight plumes sampled averaged 41 m^2. The centers of mass of 4 of these plumes were more than 5 m below the 5.15°C surface; the deepest being 18 m below. The cause of the large displacement is not known but subsequent surveys did not reveal peaks so far from the 5.15°C surface, indicating that the displacement was temporary.

After the injection was complete Sproul continued to sample the tracer patch for thirteen days with the integrating samplers. During this phase, which we shall call Leg 2, stations were chosen to attempt to determine the drift of the patch as well as the vertical distribution. Figure 1 shows the region in which the tracers were found. It can be inferred from this survey that during the two weeks after injection some of the tracer drifted to the east-southeast with a speed of at least 1.9 cm/s. Although it appears that the tracer was headed toward San Pedro Basin, the October survey found no tracer there. More likely the tracer moved with a gyre confined mostly to Santa Monica Basin.

The average of the 13 SF_6 profiles obtained during Leg 2 is shown as the dashed curve in Figure 2b. It is not likely that we missed large parts of the tracer patch since the product of the integral of this curve and the area enclosed by the dashed curve in Fig. 1 equals the amount of SF_6 injected. Because of the smaller number of injection streaks, the PFD was less horizontally dispersed and more difficult to find. The dashed curve in Fig. 2b shows the average of the five PFD profiles.

During the October cruise, Leg 3, SF_6 was found on every sampling track, and PFD on nearly every track, in Santa Monica Basin. These tracks are indicated in Fig. 1 along with the vertically integrated amount of SF_6. As nearly as can be estimated from these sparsely spaced stations the amount of SF_6 found in the basin again balanced the amount injected. However PFD concentrations were lower than expected from mass balance by about a factor of three for reasons as yet undetermined

The appearance of relatively small amounts of tracer near the boundaries (Fig. 1) is perhaps due to the constraint that motions toward the walls diminish there. Although the diapycnal dispersion of the tracer was much greater near the boundaries, confirming the expectation of enhanced mixing there, the concentrations were too low to have yet affected the diapycnal distribution of tracer in the interior[1].

The solid lines in Figure 2 show the average of the nine interior SF_6 profiles (Fig. 2a) and seven PFD profiles (Fig. 2b). The SF_6 curve has been multiplied by 2.4 and the PFD curve by 10.0 to normalize the areas to those of the Leg 2 profiles. These factors give estimates of the amount of lateral dilution occurring between surveys. Table 2 documents the growth in the second moments of the two distributions between Leg 2 and Leg 3. The centers of mass of the distributions remained within 3 m of the 5.15°C surface.

The results for SF_6 should be representative of the whole tracer patch since we apparently sampled most of the patch, and since there is not a great deal of variation in shape among the individual profiles from each leg. Furthermore, the large areas and long times involved insure that we have measured the effect of a number of mixing events in the interior of the basin. The smaller growth in the second moment for PFD may be because the PFD patch, being smaller than the SF_6 patch, was affected by a less representative set of mixing events.

If one crudely interprets the vertical dispersion as due to Fickian diffusion acting on a Gaussian profile, with constant diffusivity, one obtains values of 0.36 cm^2/s and 0.26 cm^2/s from the growth of the second moments of the SF_6 and PFD distributions respectively. These diffusivity estimates may be compared with 0.48 cm^2/s which we estimate from the review by Gargett[2] for the open ocean at the same stratification, and with 0.96 cm^2/s which would be estimated from the equation of Sarmiento et al.[3] based on ^{222}Rn and ^{228}Ra data from the very deep ocean.

Very few experiments using deliberately injected tracers to measure diapycnal mixing in the deep ocean have been attempted in the past, and these have been limited to a few days duration.[4,5] The present experiment shows that it will soon be feasible to perform ocean scale tracer eperiments lasting many years.

Of course, only a finite number of experiments can be performed in the ocean with a given tracer before they begin to interfere with one another. We realize, and we urge others to realize, that tracers should be used carefully and sparingly in the ocean.

Table 1. Characteristics of Santa Monica Basin

Area at sill depth[6]	1800 km^2
Volume below sill[6]	208 km^3
Bottom depth[6]	938 m
Mean depth of 5.15°C surface	782 m
Sill depth[6] (at SE end of San Pedro Basin)	737 m
Mean characteristics at 5.15°C:	
Temperature gradient:	0.0018 °C/m
Salinity gradient:	-0.24 ppm/m
Potential density gradient:	-0.44 ppm/m
Bouyancy period:	50 minutes

Table 2. Second moments of average vertical profiles.

	Time from Injection (s)	SF_6 second moment (m^2)	PFD second moment (m^2)
Leg 2	7.0×10^5	77	46
Leg 3	4.4×10^6	348	239

We thank E. Barthes, W. Berrelson, R. Cember, J. Chen, K. Coles, S. Doney, J. Gardner, M. Hamilton, G. Hargreaves, B. Huber, J. Lao, K. Lawson, D. O'Neil, J. Schmitt, L. Sullivan, S. Sutherland, S. Trumbore, R. Wanninkhof, and R. Wilson for their assistance during the cruises. We also thank the personnel at Scripps Institution of Oceanography's Physical and Chemical Oceanographic Data Facility and Nimitz Marine Facilities and Captains P. Munch of New Horizon and T. Beattie of Sproul and their crews for tremendous cooperation. This work was supported by National Science Foundation grant OCE 84-01648 and National Aeronautics and Space Administration grant NAG-667.

REFERENCES

1. A third survey, completed in February, 1986, supports this, and other inferences in this report. The data from that survey must be presented in a future publication in more detail than possible here, however.

2. Gargett, A.E. *J. Mar. Res. 42*, 359-393 (1984)

3. Sarmiento, J.L. *et al.*, *Earth Planet. Sci. Lett.*, *32*, 357-370 (1976).

4. Shuert, E.A. *J. Geophys. Res. 75*, 675-682 (1970).

5. Ewart, T.E. & Bendiner, W.P. *J. Geophys. Res. 86*, 10974-10983 (1981).

6. Emery, K.O. *The Sea off Southern California* (Wiley, New York, 1960).

Figure Legends

Figure 1. Santa Monica Basin. The injection streaks were laid within the dotted circle, which is centered at 33°49'N, 119°00'W. The dashed ellipse shows where SF_6 was found during Leg 2. The short lines show the sampling streaks during Leg 3 and the accompanying numbers give the vertically integrated amount of SF_6 in nanomoles/m^2.

Figure 2. Vertical spreading of the tracer distributions. (a) shows average profiles of SF_6, while (b) shows the same for PFD. The background of 1.6 femtomoles/L has been subtracted from the SF_6 concentrations. In each diagram, the dashed curve shows the average of all profiles from Leg 2, about 8 days after injection. The solid curve shows the average of interior profiles from Leg 3 about 51 days after injection. The Leg 3 reults have been multiplied by factors of 2.4 and 10.0 for SF_6 and PFD respectively, to make the areas under the curves equal to those of the Leg 2 profiles.

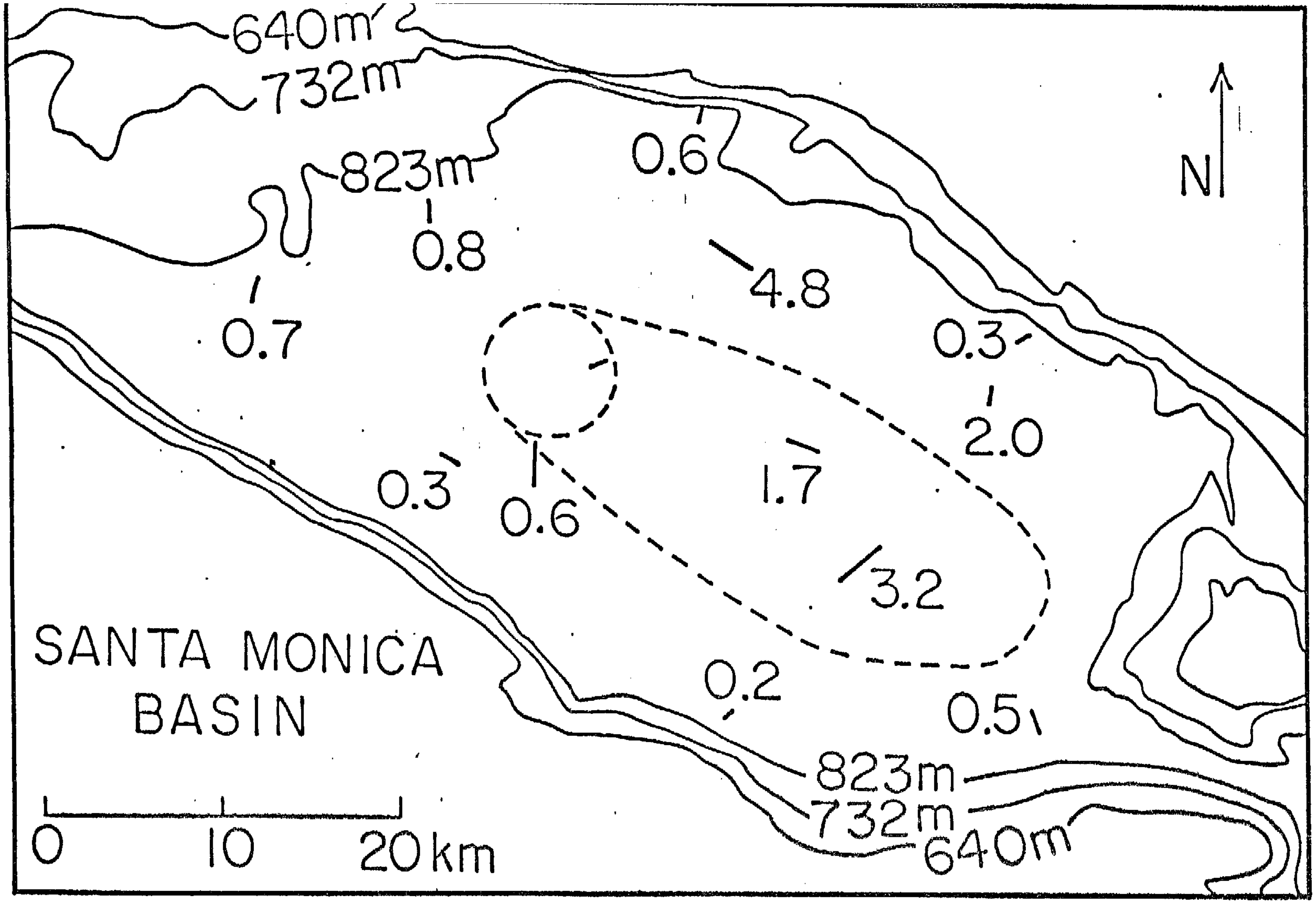

640m
732m
823m
N
0.6
0.8
4.8
0.7
0.3
2.0
1.7
0.3
0.6
3.2
SANTA MONICA
BASIN
0.2
0.5
823m
732m
640m
0
10
20 km

Figure 1

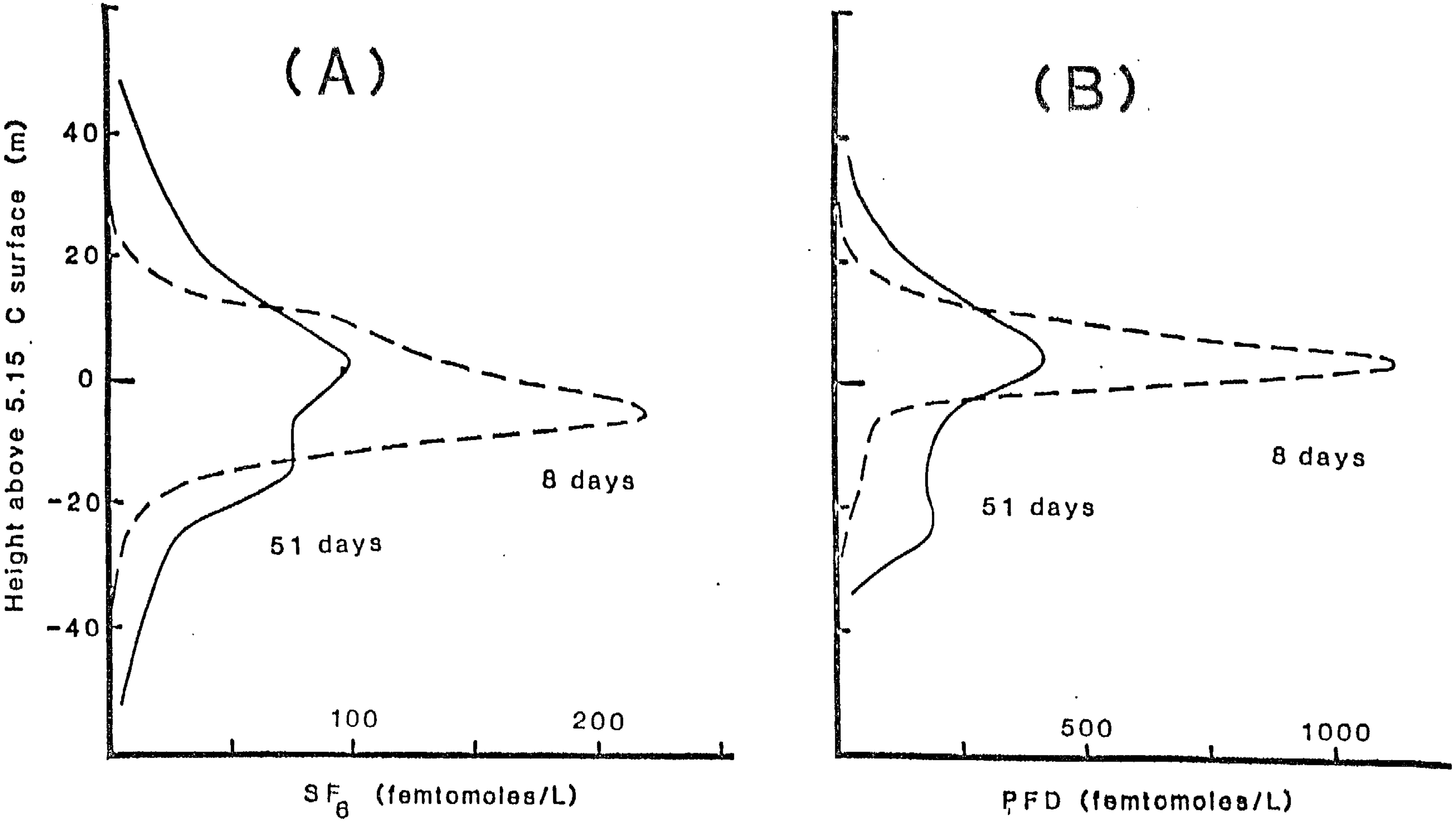

(A)
(B)
Height above 5.15 C surface (m)
40
20
0
-20
-40
8 days
51 days
100
200
SF_6 (femtomoles/L)
500
1000
PFD (femtomoles/L)

Figure 2.