Tellus (1983), *35B*, 170–176

Henry's Law constants and the air-sea exchange of various low molecular weight halocarbon gases

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(Manuscript received November 2, 1982; in final form January 27, 1983)

ABSTRACT

The McAuliffe (1971) multiple equilibration technique has been used to measure the Henry's Law constants (H) for a variety of low molecular weight halocarbon gases in distilled and sea waters at a number of temperatures. The following equations are best-fit lines from van't Hoff plots of the results: Freon-11, $\ln H = -2652/T + 10.50$ (seawater) and $\ln H = -2372/T + 9{\cdot}25$ (distilled water); Methyl Iodide, $\ln H = -3541/T + 10.34$ (distilled water); Chloroform, $\ln H = -3649/T + 10.63$ (seawater); Methyl Chloroform, $\ln H = -3905/T + 13.04$ (seawater) and $\ln H = -2915/T + 9{\cdot}15$ (distilled water); Carbon Tetrachloride, $\ln H = -3230/T + 11.27$ (seawater) and $\ln H = -2918/T + 9.77$ (distilled water); where T is the temperature in degrees absolute.

Halocarbon measurements made on an oceanographic cruise from 48° N to 65° S in the Atlantic in late 1981 indicate a small but statistically significant difference in atmospheric concentrations of Freon-11 between N and S hemispheres (198.8 and 184.7 pptv, respectively). In contrast, similar measurements for carbon tetrachloride show no significant inter-hemispheric gradient. Surface water concentrations of carbon tetrachloride are much higher at low southern latitudes compared to further north, concomitant with the lower water temperatures, and hence higher solubilities, between 30 and 60° S. However, using the Henry's Law constants reported in this paper, the surface water over the whole section appears to be close to equilibrium with respect to the concentration of carbon tetrachloride in the overlying air, a situation identical to that currently found for Freon-11 in the N. Pacific (Gammon et al., 1982).

1. Introduction

In the study of air–sea transfer of gases, their Henry's Law constants (H = concentration in air/concentration of unionized gas in seawater, at equilibrium) are of importance in two main ways. In the first place they are important in establishing whether the resistance of the liquid or gas phase controls the exchange (Liss, 1973). For most low molecular weight halocarbon gases (e.g. Freons, CCl_4, CH_3I) it is readily apparent from existing Henry's Law data that liquid phase resistance will dominate their air–sea exchange (Liss and Slater, 1974). This comes about essentially because partitioning of these gases between air and water is not sufficiently in favour of the latter, coupled with their lack of reactivity in aqueous solution. A second reason why values of H are of importance is in calculating the degree of disequilibrium (if any) of the surface seawater with respect to the overlying air, and hence the direction of any net flux. In assessing the saturation state of the sea surface, an accurate knowledge of the Henry's Law constant is required since the air and water are often quite close to equilibrium. Furthermore, it is necessary to know values of H over the temperature range covered by oceanic surface waters, i.e. at least 0–35 °C. Low molecular weight halocarbon gases discussed in this paper are: Freon-11 (F-11, CCl_3F), carbon tetrachloride (CCl_4), chloroform ($CHCl_3$),

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methyl chloroform (CH_3CCl_3) and methyl iodide (CH_3I).

Existing data on H values for the above gases at environmental concentration levels are very sparse, frequently of dubious quality, and generally not available for the whole range of surface water temperatures found in the oceans. Furthermore, in many cases H is known only for distilled water and was determined at concentration levels much higher than are typical in the marine environment. In this paper we report laboratory measurements, using the McAuliffe (1971) technique, of the Henry's Law constant for the simple halocarbon gases listed above. The measurements were made at or near environmental levels and determined over much of the temperature range exhibited by ocean surface waters. For most of the gases H values were measured in both distilled water and seawater. Also reported are field measurements of Freon-11 in the marine atmosphere and carbon tetrachloride in both surface seawater and the overlying air, made on an oceanographic cruise from 48° N to 65° S in the Atlantic Ocean.

2. Experimental

2.1. *Theory of Henry's Law constant determination*

The Henry's Law constants for F-11, CH_3I, $CHCl_3$, CH_3CCl_3 and CCl_4 in fresh and seawater were determined by McAuliffe's (1971) method of multiple phase equilibration. In this method a given volume of water in a syringe is shaken with a known volume of pure nitrogen. When equilibrium between the two phases has been achieved, the headspace is separated and analysed for the gas of interest. A fresh charge of nitrogen, of equal volume to that used initially, is added to the water remaining in the syringe, and the whole operation repeated until the gas is undetectable in the headspace.

McAuliffe showed that for successive equilibrations of equal volumes of water and nitrogen the Henry's Law constant could be related to the measured gas phase concentration by:

$$G_n = \frac{HX_0}{(H+1)^n} \qquad (1)$$

where G_n = amount in gas phase after n equilibrations, X_0 = initial sample amount, and $H = G_nV_l/V_gL_n$, with V_l = liquid volume, V_g = gas volume, and L_n = amount in liquid phase after n equilibrations. It follows from (1) that the plot of $\log G_n$ vs n is linear with H being determined from the slope $-\log(H+1)$.

When determining H for relatively insoluble gases more data points can be obtained if larger volumes of water than nitrogen are used, since a smaller proportion of the dissolved gas is removed at each equilibration. If different volumes are used then:

$$G_n = \frac{HVX_0}{(HV+1)^n} \qquad (2)$$

where $V = V_g/V_l$. In fact, (1) is a special case of (2) with $V_g = V_l$. It follows that the plot of $\log G_n$ vs n then has a gradient $-\log(HV+1)$ and intercept $\log(HVX_0)$. Fig. 1 shows representative McAuliffe plots for 4 gases (a), and for F-11 at several temperatures (b). When comparing results it is often convenient to make all the lines have a common origin, by plotting $\log(G_n/G_1)$ against n (as in Fig. 1). In this case the gradient of the lines is still $-\log(HV+1)$ but the intercept is zero.

2.2. *Collection of air and water samples*

Determination of atmospheric and surface seawater concentrations of F-11 and CCl_4 were made on the cruise of the R.R.S. *John Biscoe* from the U.K. to the Antarctic Peninsula between September 16 and November 12, 1981. Samples from 58 stations from 48° N to 65° S (shown in Fig. 2) were analysed by gas chromatography. The cruise track is close to that followed by Lovelock et al. (1973) in carrying out a similar exercise approximately 10 years ago.

Atmospheric samples were taken from the bow of the ship with the wind approaching from within a 60° sector. Occasionally when the wind speed was above force 7 atmospheric samples were taken from the bridge wing. The air samples were collected in a 100 ml glass syringe fitted with a 3-way tap and analysed immediately.

Surface water was collected from the bow wave of the ship using a polypropylene bottle of a type previously found to be satisfactory for sampling halocarbons in seawater. On recovery water from the sampling bottle was immediately transferred with minimum turbulence into a 100 ml glass syringe. Once in the syringe, all air was expelled and the water allowed to equilibrate to the

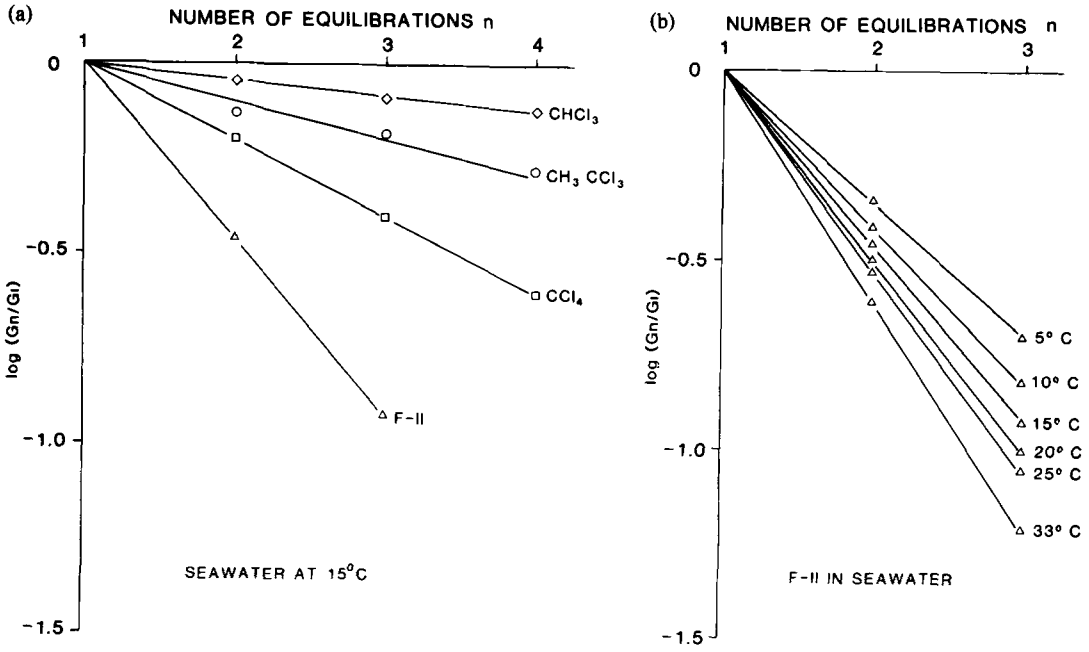

Fig. 1. McAuliffe equilibration plots for: (a) different gases in seawater at 15 °C and (b) F-11 in seawater at several temperatures.

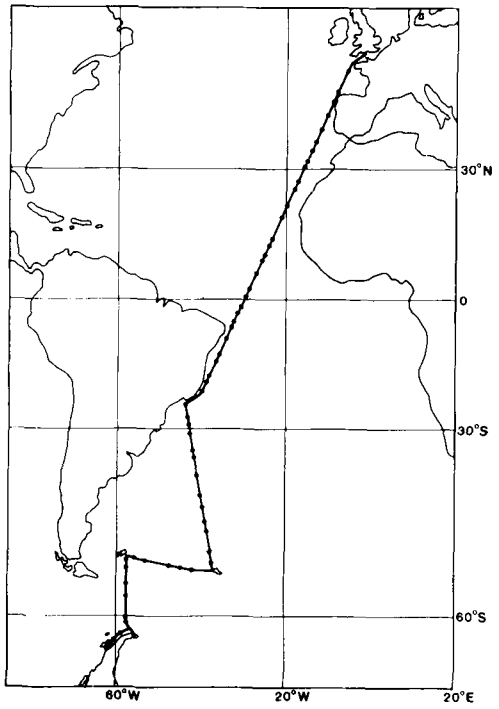

Fig. 2. Sampling positions occupied on track of R.R.S. *John Biscoe* from the U.K. to Antarctica, Sept.–Nov. 1981.

laboratory temperature. Analysis of these samples was completed on board ship within a maximum period of 2½ h.

2.3. *Analysis*

A purpose built portable gas chromatograph (Brazzos Ltd.) fitted with a long-bodied electron capture detector was used for the analysis. A six foot (¼" outside diameter) column filled with Chromosorb W coated with OV 101 served to separate the halocarbons which were injected via a 5 cm^3 sample loop. The carrier gas was 99.5% N_2 and 0.5% H_2 with a flow rate of 40–45 cm^3 min^{-1}. The carrier gas was cleaned by passing it through a column of pallidized asbestos heated to 350 °C. A soda-asbestos pre-column, connected before the sample loop, was used to remove water and carbon dioxide from the samples before injection. The output from the detector was connected to a chart recorder.

The chromatograph was calibrated twice daily by injection of a standard gas. The standard used was an air sample stored in an aluminium cylinder and itself calibrated against a primary air standard provided by R. A. Rasmussen (ALE Calibration Tank No. 119). The standards did not change

relative to one another over the duration of the cruise.

Air samples, collected in the syringe, were flushed through the sample loop before being injected into the gas chromatograph. For water samples approximately 50 cm^3 aliquots were shaken vigorously with approximately 50 cm^3 N_2 for 2 min inside the syringe. The gas phase containing the extracted gases was then flushed through the loop prior to injection. The water concentration is related to the measured gas phase concentration by

$$W = N(V_g/V_l + 1/H) \quad (3)$$

where W = water concentration, N = gas phase concentration, H = Henry's Law constant for temperature at which laboratory equilibration takes place.

Water samples used in determination of Henry's Law constants were treated in the same way, except that the ratio of water to N_2 was 70:30 by volume, and the equilibration temperature was more tightly controlled (± 0.2 °C) by the use of a thermostatically controlled water bath. Determinations of H were all performed in the laboratory in Norwich.

3. Results

Henry's Law constants were determined over a temperature range of 5 °C–33 °C in distilled and seawater ($S \sim 35‰$) for F-11, CH_3CCl_3 and CCl_4. A more limited data set was obtained for CH_3I and $CHCl_3$. The temperature dependence of the measured Henry's Law constant are shown as van't Hoff plots in Fig. 3. Each point represents the mean of the two results with the bars showing the range. Equations for the least squares fit through these data points are given in Fig. 3. Standard errors of the estimate of H are on average 3.2% and never exceed 5.5%.

The atmospheric concentrations of F-11 and CCl_4 measured on the Atlantic cruise between 48° N and 65° S are plotted in Fig. 4a and b, respectively. The corresponding surface water values for CCl_4 are shown with surface water temperature in Fig. 4c. The surface water concentrations of F-11 are not presented due to contamination problems experienced on board ship.

By using the Henry's Law constant data for CCl_4 in Fig. 3 it is possible to determine the relative saturation of CCl_4 in surface seawater with respect to the atmosphere and this is shown in Fig. 4d.

4. Discussion

4.1. *Henry's Law constants*

As expected, for all the gases examined, the solubility decreases with increase in temperature, and from fresh to seawater. Furthermore, they all seem to behave in a near-ideal way, as shown by the reasonably straight lines obtained for the van't Hoff plots in Fig. 3.

There are few other results with which to compare the Henry's Law constant data. Values for F-11 and CH_3I at very much higher partial pressures (0.1–1.0 atm) in distilled water (Park et al., 1982; Glew and Moelwyn-Hughes, 1953, respectively) agree with our results to better than 10%. A similar level of agreement is obtained when values of H for CCl_4, $CHCl_3$ and CH_3CCl_3, derived from solubility data (Horvath, 1982) and corresponding saturated vapour pressures (Weast, 1972), are compared to our experimental results. These comparisons imply that Henry's Law is obeyed to probably better than this accuracy for concentrations spanning 9–10 orders of magnitude. Zeininger (1975) gives H values for Freon-11 (and Freon-12) in fresh and seawater. His freshwater results are in reasonable agreement with ours, but for salt water there are discrepancies of up to a factor of two. For example, at 20 °C Zeininger has $H_{F\text{-}11} = 7.1$ for seawater, whereas our value is 4.2.

Use of Zeininger's data has led Hammer et al. (1978) and Singh et al. (1979) to conclude from their measurements of Freon-11 in open ocean surface seawaters that the water was substantially supersaturated. This conclusion appears unreasonable since F-11 emissions are largely to the air, and atmospheric concentrations had been on an upward trend for several years prior to the time the measurements were made. Recomputation of the Hammer et al. (1978) and Singh et al (1979) results using the solubility data presented here shows the water to have been close to or somewhat undersaturated; which seems more reasonable.

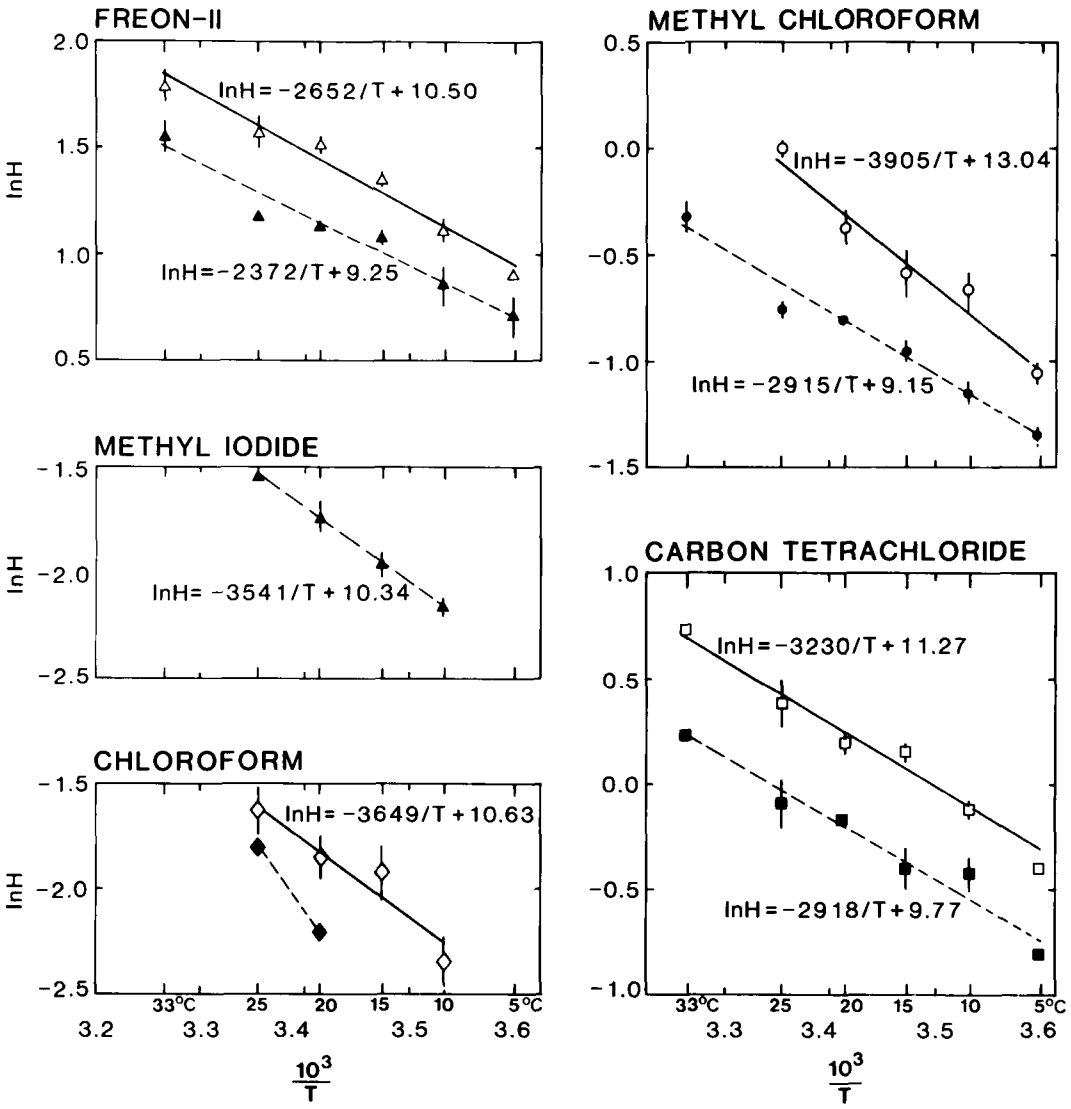

Fig. 3. van 't Hoff plots (i.e. ln H vs T^{-1} where T is the absolute temperature) for various halocarbon gases in distilled water (closed symbols, dotted lines) and seawater (open symbols, full lines). Equations for the best-fit lines through the data points are also given.

4.2. *Field results*

The mean Freon-11 concentration in the air over the Atlantic (48° N to 65° S) is 188.9 pptv from the data shown in Fig. 4a (but omitting the outlyer of 134 pptv at 63° S), which agrees very well with the value of 190 pptv reported recently by Gammon et al. (1982). The mean N and S hemisphere concentrations from our data are 198.8 (σ = 7.0) and 184.7 (σ = 6.8) respectively; this difference is statistically significant at the 0.1% level. In calculating the hemispheric averages the three points immediately north of the Equator have been included in the southern hemisphere average, since the likely position of the ITCZ indicates that air from below the Equator was probably being sampled. Air concentrations of CCl_4 (Fig. 4b) are more scattered than those from Freon-11 but show

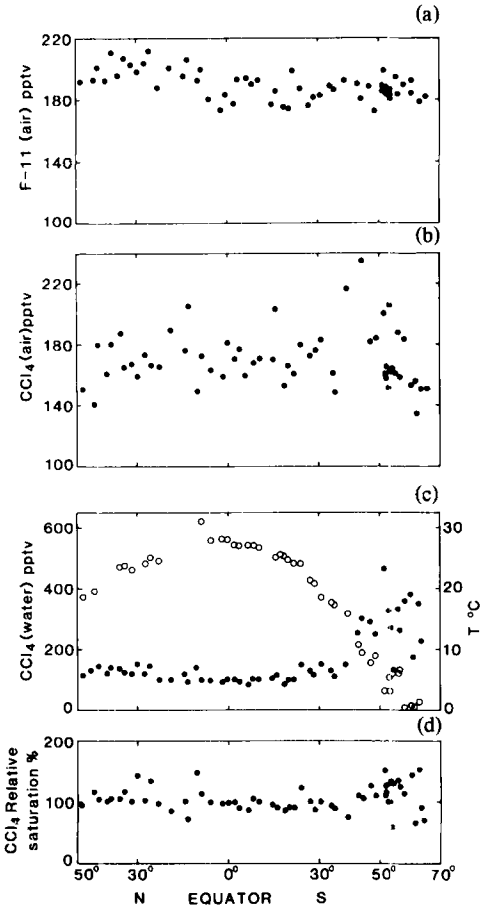

Fig. 4. Results of measurements made on samples collected at the stations shown in Fig. 2 plotted as a function of latitude. (a) Concentration of F-11 in air. (b) Concentration of CCl_4 in air. (C) Concentration of CCl_4 in surface seawater (●) and water temperature (○). (d) Relative saturation of surface seawater with respect to the overlaying air.

no statistically significant N–S gradient. The mean concentration for all the CCl_4 data in Fig. 4b is 171.1 pptv, with the N and S hemisphere averages being 169.6 (σ = 16.1) and 171.8 (σ = 20.2), respectively.

It is interesting to compare these results with the data obtained by Lovelock et al. (1973) on a similar cruise track 10 years ago. Then, not only were the concentrations of F-11 and CCl_4 considerably lower than found today, but also a marked concentration gradient, particularly pronounced with F-11, occurred between the higher concentrations of the northern hemisphere and the lower levels of the south. Some of the interhemispheric F-11 difference found by Lovelock et al. may be due to inclusion of air from N. America (Cunnold et al., 1978) or Europe in their North Atlantic samples. However, it is clear that the N–S concentration difference has decreased over the last decade. For example, Hyson et al. (1980) cite values for the interhemispheric difference of 10–11% in the mid- to late 1970s which compare with our figure of 7.4% for the end of 1981 and Lovelock et al.'s (maximum) value of about 30% more than 10 years ago. These interhemispheric differences have been defined, following Hyson et al. (1980), as $2(\bar{C}_{NH} - \bar{C}_{SH})/(\bar{C}_{NH} + \bar{C}_{SH}) \times 100\%$, where C_{NH} and C_{SH} are average concentrations in the northern and southern hemispheres, respectively. Calculated this way the difference is normalized to absolute atmospheric concentrations which for F-11 have increased several-fold over the 10-year period. For these N–S differences to have evened out over recent years it is necessary for the input into the southern hemisphere, due to direct emissions and interhemispheric mixing, to have been larger than the input into the north. For F-11 at least, this probably occurred in the latter part of the 1970s when its usage (largely in the N hemisphere) changed from the exponential growth of 10 years back to the recent levelling off and decline in release to the atmosphere (Diprose, 1980).

Fig. 4c shows much higher concentrations of CCl_4 in the surface water at low southern latitudes, corresponding to the rapid decrease in water temperature from 30–60° S and indicating the importance of such waters for uptake of gases produced naturally and by man. In fact, when the degree of saturation of the water with respect to the measured air concentrations is calculated using the H values from Fig. 3, an almost horizontal line is obtained (Fig. 4d) corresponding closely to 100% saturation; the actual mean value is 104% (σ = 25%), but the apparent 4% supersaturation is not significant in view of the large spread of the individual air and water values. The data of Gammon et al. (1982) show a similar situation for Freon-11 in the Pacific, with the air and water close to 100% saturation. Thus surface seawater now appears to be very close to saturation with respect to atmospheric concentrations for both Freon-11 and CCl_4, which contrasts with the situation a

decade ago when significant undersaturation of the water was observed (Lovelock et al. 1973). This difference may be a result of the past lack of reliable H values for seawater as a function of temperature, or may be real and for F-11 produced by the changing pattern of release mentioned earlier.

5. Acknowledgements

We thank the Director and staff of the British Antarctic Survey, Natural Environment Research Council, for enabling us to sample from the R.R.S *John Biscoe*; and especially Captain C. Elliott, his officers and crew for their help while at sea. Professor R. A. Rasmussen kindly provided the halocarbon calibration cylinder, Dr. P. J. Fraser suggested several improvements to the text, and Professor J. E. Lovelock gave much useful advice. We are indebted to three anonymous referees for their helpful comments on the manuscript. During the period of this work P.W.B. and R.H.S. were in receipt of research studentships from the U.K. Natural Environment Research Council. This study is part of the Sea–Air Exchange (SEAREX) Program of the U.S. National Science Foundation.

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