Dichloromethane in North Atlantic waters

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[1] Dichloromethane is an atmospheric trace gas that has a tropospheric lifetime on the order of 5 months and has major anthropogenic sources. Evidence has been presented for an oceanic source. This paper reports measurements of dichloromethane in waters of the North Atlantic and Labrador Sea that are interpreted as showing that the compound has a primarily atmospheric source and appears to persist for years to decades in the intermediate and deep ocean. These characteristics have the potential to yield apparent supersaturation of the gas in surface ocean waters which may be incorrectly interpreted as an oceanic source. *INDEX TERMS:* 4820 Oceanography: Biological and Chemical: Gases; 4850 Oceanography: Biological and Chemical: Organic marine chemistry; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* dichloromethane, ocean, atmosphere

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1. Introduction

[2] The ocean is known to be a source of a many low molecular weight organohalogen compounds which have been studied for their relevance to the transport of chlorine, bromine, and iodine to the atmosphere. In the case of chlorinated and brominated compounds that are relatively long-lived in the atmosphere, the ultimate release of the halogen atoms contributes to stratospheric ozone destruction, while for more photoreactive iodine compounds the relevance is more limited to the lower atmosphere [*Vogt et al.*, 1999; *McFiggans et al.*, 2000] though vigorous atmospheric convection can cause them to have some influence on the upper atmosphere [*Solomon et al.*, 1994]. Compounds that have received a good deal of study include the methyl halides (CH_3Cl, CH_3Br, and CH_3I), the dihalogenated compounds, CH_2Br_2 and CH_2I_2, [*Moore et al.*, 1996], and the trihalogenated compound, bromoform ($CHBr_3$) [*Quack and Wallace*, 2003]. All of these, as well as various mixed halogen compounds (e.g., CH_2ClI, $CHBr_2Cl$) have been shown to be produced within the ocean, typically as a result of plant growth as is well established for CH_2Br_2 and $CHBr_3$ [e.g., *Moore et al.*, 1996]. These compounds are not known to have significant production from other sources, so their study within the ocean is somewhat simplified. Methyl chloride and bromide have been shown to have both marine and terrestrial [*Rhew et al.*, 2000] natural sources as well as, in the case of the bromide, a significant anthropogenic source to the atmosphere. In such cases the allocation of the total atmospheric source to the component sources has been a challenge, and efforts to better quantify the contributions are continuing [e.g., *Harper et al.*, 2003]. Dichloromethane (CH_2Cl_2) is a compound that is industrially produced and is, in some applications, released to the atmosphere [*McCulloch et al.*, 1999]. In its case, there are reasons to suppose that it could also have marine sources, either by simple analogy with the biological production of CH_2Br_2 and CH_2I_2 or through expected chloride substitution reactions with the same compounds. Furthermore, CH_2ClI is known to be produced in seawater certainly by a photochemical reaction of CH_2I_2, [*Class and Ballschmiter*, 1987], but perhaps also directly by marine algae. It too would be expected to undergo a substitution reaction in an aqueous chloride medium to yield CH_2Cl_2. This paper presents measurements of dichloromethane that were made simultaneously with studies of the ocean distribution and fluxes of the three methyl halides.

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2. Methods

[3] Data reported here were obtained during a North Atlantic transect at 43°N on *Poseidon* in August 1999, and a cruise in the northwest Atlantic and Labrador Sea on CCGV *Hudson* in May–June 2001 (Figure 1). Water samples were collected in Niskin bottles and drawn into 100-mL glass syringes that were stored under water until being analyzed, typically within 6 hours. The samples were forced from the syringe, through a glass fiber filter into a calibrated pipette from which they passed into a water-jacketed purge vessel maintained at 40°C. During a 12-min purge with high-purity helium, the CH_2Cl_2 was carried through a condenser to reduce the water vapor content followed by a drying tube packed with magnesium perchlorate. Trapping was achieved in a coiled steel tube (OD 1/32″) held at −150°C over liquid nitrogen. This trap was electrically heated and the trapped gases transferred in a stream of He to a pair of chromatographic columns (DB624, 30 m and 70 m length) and thence to a Fisons MD800 quadrupole mass selective detector in which masses 49 and 84 were monitored. Calibration was

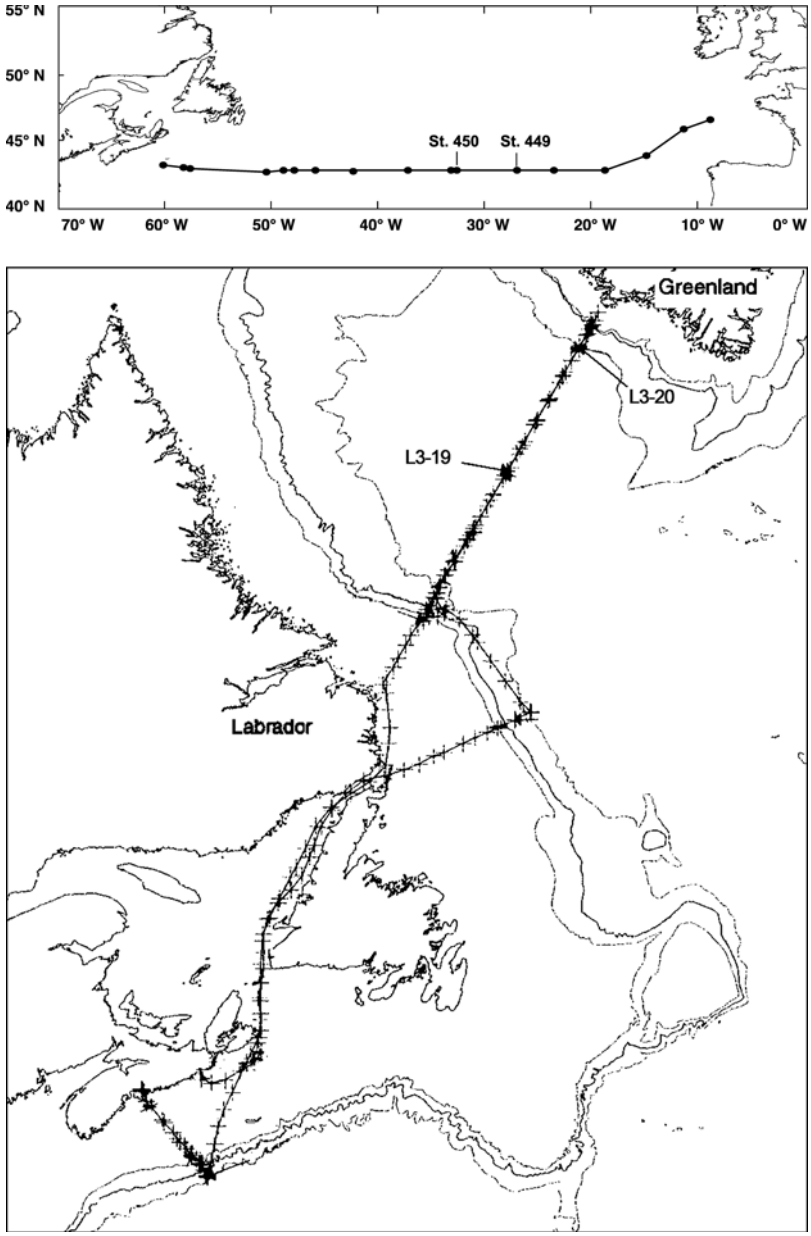

Figure 1. Cruise tracks of (a) *Poseidon* (1999) and (b) *Hudson* (2001).

achieved by injection of known volumes (typically 50–150 microliters) of a gravimetrically prepared standard via a septum port. The equipment used for these studies was optimized for analysis of dissolved methyl halides so that in the case of the more soluble CH_2Cl_2, a correction had to be applied for its incomplete purging (85%) from the water sample. CFC11 and methyl halides were measured and calibrated in the same way, but no correction was needed for purge efficiency. Replicate analysis of 25 water samples collected at the same time and at the same depth give a coefficient of variation 3.8% for CH_2Cl_2 and 1.5% for CFC11.

3. Results and Discussion

[4] Depth profiles (Figure 2a) of CH_2Cl_2 from in the North Atlantic in 1999 show that concentrations increase with depth over the upper few hundred meters, and they are substantially higher at depths of 1500–200 m than at the surface. This pattern is quite different from the trends seen for the methyl halides, exemplars of gases with in situ sources and sinks, that have their maximum concentrations in the euphotic zone, frequently with a subsurface maximum located just beneath the mixed layer. In the Labrador Sea the CH_2Cl_2 profiles (Figure 2b) are characterized by a slow decline in concentrations from 0 to 2000 m with a marked minimum at around 3000 m and a steep increase to 3450 m with indications of a small decline toward the deepest samples at 3510 m.

[5] What is strikingly apparent is the qualitative similarity between the CH_2Cl_2 profiles and those of CFC 11 (Figure 3), which was measured at the same time. While CH_2Cl_2 has a short atmospheric lifetime, estimated at 5 months [*McCulloch and Midgley*, 1996], CFC11 is long-lived

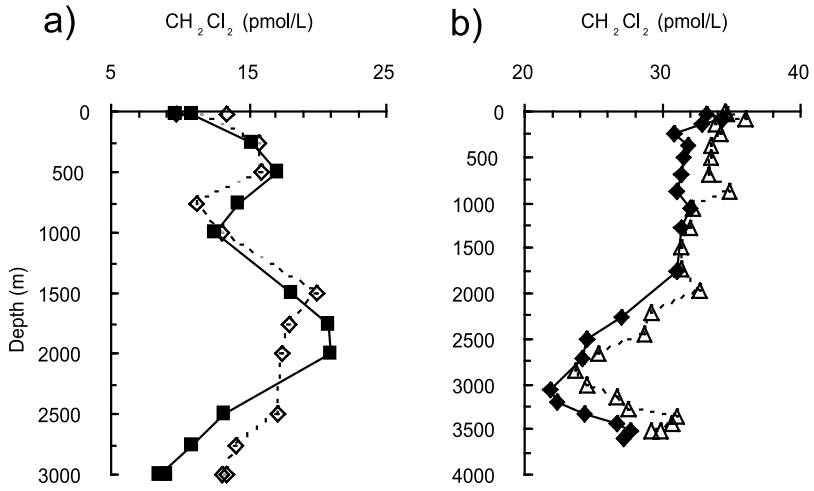

Figure 2. Depth profiles of CH_2Cl_2 from (a) the North Atlantic in 1999 from the *Poseidon* transect (squares, Station 449; open diamonds, Station 450) and (b) the *Hudson* cruise (solid diamonds, Station L3–19; open triangles, Station L3–20).

(lifetime $\sim$ 45 years [*Montzka et al.*, 1999]) and has an oceanic distribution that is the consequence of its well-documented growth in the atmosphere during the twentieth century until around 1993 [*Montzka et al.*, 1999], together with its apparent inertness in the ocean. Its oceanic depth distribution is controlled by local downward mixing from the surface coupled with deeper injection via waters that have been cooled and exchanged gases at the surface in winter. The similarity in the profiles suggests that CH_2Cl_2 shares with CFC 11 both an atmospheric source and inertness within the ocean, while having quite different atmospheric properties. While CFC11 has the greater atmospheric mixing ratio in the Northern Hemisphere by an order of magnitude (265 ppt versus $\sim$30 ppt annual average for CH_2Cl_2 at high latitudes in the Northern Hemisphere in 2000), CH_2Cl_2 has the higher dissolved concentrations by a factor of around 6 in surface waters of the Labrador Sea in June 2001). This is due to the solubility ratio of CH_2Cl_2/CFC11 being around 40 (arbitrarily at 5°C, but with this factor changing little with temperature) [*Moore*, 2000; *Warner and Weiss*, 1985]. It is informative to compare the gas profiles by plotting the ratio $[CH_2Cl_2]/[CFC11]$ against depth (Figure 4). This shows that in the North Atlantic the concentration ratio increases with depth from surface values of around 4–5 to around 10 at 3000 m. In the Labrador Sea the ratio is higher at the surface ($\sim$6.5) and shows initially an increase with depth, reaching 10 at around 2500 m followed by a decline to near the surface value at 3500 m.

[6] The distribution of CFC11 and 12 in the Labrador Sea [*Azetsu-Scott et al.*, 2003] is known to reflect the effects of periodic local ventilation in winter and the influence of Northeast Atlantic Deep Water (NEADW) and Denmark Strait Overflow Water (DSOW). NEADW originating in the Nordic seas is the oldest water with an estimated ventilation age of 12 years [*Azetsu-Scott et al.*, 2003]. It lies above the younger DSOW, the densest water of the North Atlantic, which has a ventilation age of about 6 years. The DSOW is responsible for the elevated CFC concentrations in the

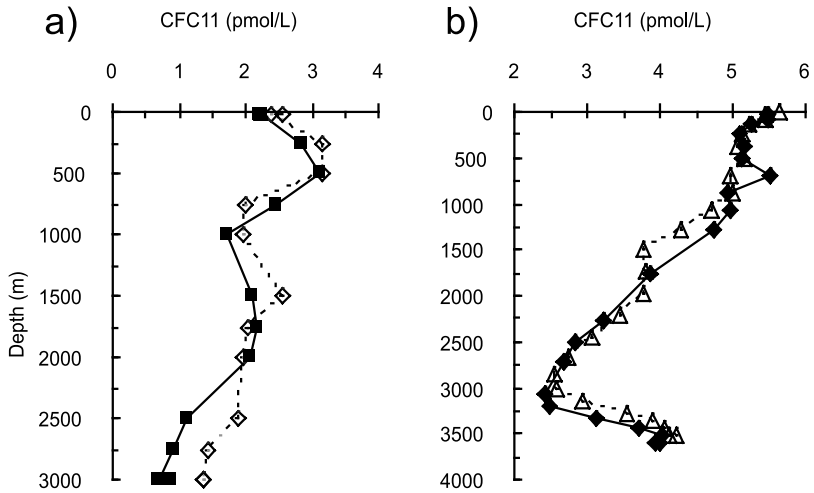

Figure 3. Depth profiles of CFC11 from (a) the North Atlantic in 1999 from the *Poseidon* transect and (b) the *Hudson* cruise. Symbols as in Figure 2.

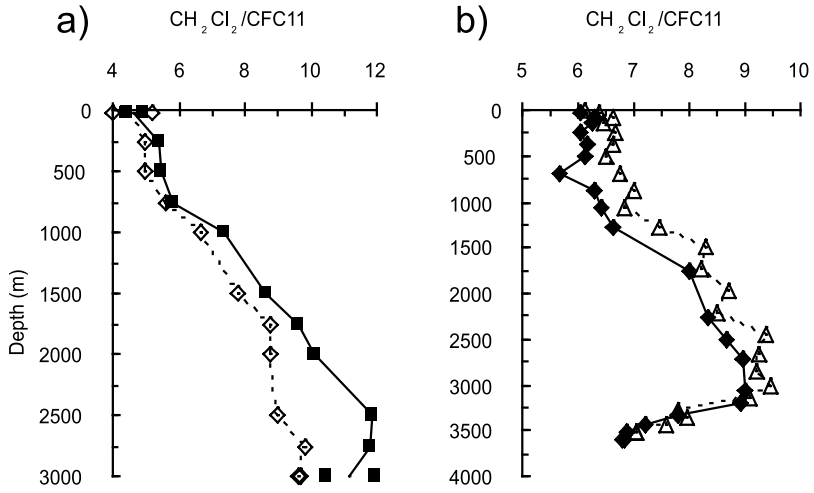

Figure 4. Depth profiles of CH_2Cl_2/CFC11 from (a) the North Atlantic in 1999 from the *Poseidon* transect and (b) the *Hudson* cruise. Symbols as in Figure 2.

deepest waters of the Labrador Sea transect, and also for elevated iodine-129 that has been used to estimate a transit time of 2–3 years from the Greenland Sea to the Labrador Sea for DSOW (J. N. Smith, paper in preparation, 2004). The difference between the two "age" estimates is due to the former referring to a weighted mean of the DSOW and Iceland-Scotland Overflow Water (ISOW) and the latter being attributable solely to DSOW, which takes a more direct path to the Labrador Sea. The increased concentration of CH_2Cl_2 below 3000 m and the CH_2Cl_2/CFC11 ratio that is similar to surface waters are consistent with both compounds having their origin in surface waters in the Greenland Sea ventilated during winter. Such an interpretation of the deep CH_2Cl_2 signal demands that it has a high degree of stability in seawater, at least at low temperatures.

[7] A full interpretation of the CH_2Cl_2/CFC11 profiles in the North Atlantic and Labrador Sea would require knowledge of the mixing ratios in the atmosphere: Unfortunately, only fragmentary data are available at present. A set of measured ratios of CH_2Cl_2/CFC11 in air samples [*Hall et al.*, 2002] from Barrow, Alaska (71°N), and Niwot Ridge, Colorado (40°N), has been made available by S. Montzka for the purpose of comparing with the water column ratios presented here. These time series clearly illustrate the seasonal variation of dichloromethane mixing ratios and also the influence of latitude: concentrations at 71°N being higher than at 40°N. To better compare the atmospheric ratio CH_2Cl_2/CFC11 with water column measurements in the Labrador Sea, it is desirable to estimate the atmospheric ratio for that latitude (58°N). This is simplified by the observation that the extracted seasonal cycle [*Khalil and Rasmussen*, 1990] of CH_2Cl_2/CFC11 at 71°N has the same amplitude as at 40°N, so it is reasonable to assume it is also the same at 58°N. The ratio CH_2Cl_2/CFC11 at 58°N has been interpolated from the higher and lower latitude time series for June 2001, which is the time of the water measurements in the Labrador Sea, and also for December–March of the preceding winter: The values are 0.091 and 0.133, respectively. Using the solubility ratio for the two compounds in seawater, equilibrium concentration ratios of 6.0 for winter and 4.2 for June have been calculated. For June, the observed surface water T of 5°C was used, and for winter, 1°C, but the ratios have a low temperature dependence, increasing by only 0.8%/°C at 1°C. The measured value of CH_2Cl_2/CFC11 in the upper 250 m of the Labrador Sea was 6.3 (range 6.0–6.7), at the upper limit of what would be predicted from a limited atmospheric data set. A part of the discrepancy can be accounted for by the lag time for the water to respond to changing gas concentrations in the atmosphere, and by the barrier to equilibration imposed in summer by the thin layer of low-salinity water resulting from melted ice.

[8] A parallel comparison can be made for the August 1999 Poseidon measurements at 43°N. In this case it is appropriate to use the Niwot Ridge CH_2Cl_2/CFC11 concentration ratio on account of the similar latitude. This ratio (0.09 in July and August) gives an equilibrium seawater concentration ratio at 20°C of 4.3 which is to be compared with the measured surface ratio of 4.6 (range 4.0–5.2). Thus both the timing of the Atlantic measurements (August) and their lower latitude are consistent with the observed lower surface ratio of CH_2Cl_2/CFC11in comparison with the Labrador Sea.

3.1. Temporal Variation in Atmospheric CH_2Cl_2

[9] Any interpretation of the increase in the ratio of CH_2Cl_2/CFC11 with depth requires knowledge of the atmospheric mixing ratios in recent decades. In the case of CFC11 the atmospheric mixing ratio has been extremely well quantified, a process made easier by its long tropospheric lifetime and consequent rather uniform hemispheric and seasonal distribution. It reached maximum concentrations of 275 ppt in 1993/1994 and has since declined at an average rate of about 0.4%/yr. The dearth of atmospheric measurements of dichloromethane makes it very difficult to establish how its concentration has changed in the atmosphere over recent decades. This problem is exacerbated by the fact that its short lifetime and its OH-dependent loss rate lead to substantial seasonal fluctuations in its mixing ratio, and also to latitudinal variations. Historical production rates are relatively poorly documented and so do little to resolve this question. A short time series of atmospheric measure-

ments points to only a small decline occurring over a few years after 1995 (S. Montzka, personal communication, 2004). A set of measurements of samples from Mace Head, Ireland, shows a decline in the wintertime maximum of about 1 ppt per year, and virtually no change in the summertime levels (P. Simmonds, personal communication, 2004). *McCulloch and Midgley* [1996] report estimated global emissions from 1988–1992, which suggest a rate of decline varying from about 1% p.a. in 1988–1989 to 9% in 1990–1991 and 4% in 1991–1992. There is potential for firn air analyses to provide a useful time series of dichloromethane in the atmosphere. At present, although such measurements have been made, they have not been modeled (W. Sturges, personal communication, 2004). The raw data show that dichloromethane had maximal values in Devon Island firn air at a time when CFC12 measured ~390 ppt and declines in the core as CFC12 climbs to ~500 ppt. From the known atmospheric record of CFC12 [*Walker et al.*, 2000] the maximum atmospheric mixing ratio of CH_2Cl_2 appears to have occurred sometime in the 1980s, but a more precise dating of the maximum and quantification of the subsequent decline must await modeling of the firn gases. It is important to note that it is unknown whether CH_2Cl_2 is conservative in firn air. A temporal decline in the atmospheric ratio CH_2Cl_2/CFC11 should be matched typically by an increase in the ratio with depth in the ocean when water ventilation ages increase with depth. This is qualitatively consistent with the North Atlantic and Labrador Sea profiles. Chemical degradation of dichloromethane in seawater would tend to decrease the ratio in older waters, again supporting the notion of it showing conservative behavior in seawater.

3.2. Potential of CH_2Cl_2 as a Water Mass Tracer

[10] Anthropogenic gases that have found application as ocean tracers are typically relatively stable in the atmosphere as well as in the ocean. A consequence of this is a tendency toward a uniform spatial distribution in the atmosphere, though with a small interhemispheric gradient resulting from predominantly Northern Hemisphere sources. Dichloromethane, in contrast, with a short atmospheric lifetime and predominantly anthropogenic sources would show a large asymmetry in its concentration between the hemispheres, together with a latitudinal concentration gradient in the Northern Hemisphere on account of its shorter lifetime at lower latitudes. Thus *Koppmann et al.* [1993] reported a level of CH_2Cl_2 over the central North Atlantic (36 ppt) twice that measured over the South Atlantic (18 ppt). Its concentration in subsurface ocean waters will differ according to the hemisphere in which the water is ventilated. At present, the history of its atmospheric concentrations is unknown, but there is the potential for this to be inferred from ice core or firn measurements. This would increase the potential for using CH_2Cl_2 as a water mass tracer.

3.3. The Ocean as an Apparent Source of CH_2Cl_2

[11] A range of dissolved gases may show supersaturation in ocean surface waters in summer on account of solar warming and diminished solubility. This effect is amplified for CH_2Cl_2 by the summertime decrease in its concentration in the atmosphere. Consequently, it is not appropriate to interpret short-term supersaturation of a gas in the ocean surface as indicative of its production within the ocean. On the basis of measurements of oceanic supersaturation of CH_2Cl_2 from *Khalil and Rasmussen* [1998] and *Singh et al.* [1983], *Khalil et al.* [1999] estimated a flux of 160Gg Cl/yr as CH_2Cl_2 from the ocean to the atmosphere. This value led *Keene et al.* [1999] to conclude that ocean emissions could account for about 25% of the total emissions to the atmosphere. It is significant that the budget for this compound had an excess of sources over sinks (200 Gg Cl/yr) that was close to the estimated ocean emission. Oceanic saturation levels measured throughout the year would be needed to establish whether the ocean is indeed a net source or is simply emitting in summer CH_2Cl_2 that was taken up in winter. This work points strongly to a transfer of CH_2Cl_2 to the deep ocean during winter where it is either accumulating, like CFC11 and CFC 12, or is balanced by hydrolytic loss. Depending on the depth to which the CH_2Cl_2 transported, it may subsequently be mixed or upwelled to the surface and re-emitted to the atmosphere. Evidence for such a process has been reported for trichloro- and tetrachloro-ethylene [*Moore*, 2000]. The quantity of CH_2Cl_2 transported into the deep ocean by waters formed in the Labrador Sea is only about 0.1% of industrial emissions to the atmosphere (based on an average formation rate of Classical Labrador Seawater of 7.4 Sv [*Smethie and Fine*, 2001] and a CH_2Cl_2 concentration of 30 pM). However, the combination of short atmospheric lifetime, high aqueous solubility, and stability in seawater leads to the surprising result that in the areas where measurements have been made, the unit area inventory of dichloromethane is greater below the ocean surface than above it, in spite of the atmosphere being the apparent source: a ratio of about 4.5 is calculated for a 3.5-km water column in the Labrador Sea. The Labrador Sea may be extreme in this respect in view of its relatively rapid ventilation through deep convection.

[12] The finding that the oceanic distribution of dichloromethane is primarily driven by wintertime atmospheric uptake makes it difficult to identify any in situ production which, as discussed above, is likely to exist at least at low levels. Its possible influence is most likely to be found in the Southern Hemisphere, where the atmospheric contribution is smaller.

4. Summary

[13] Measurements of dichloromethane in the North Atlantic and Labrador Sea show that its distribution closely matches that of CFC 11, which is known to have an entirely atmospheric source. Although CH_2Cl_2 has a short lifetime in the atmosphere, it appears to persist for years to decades in the intermediate and deep ocean. Reports of an ocean source of dichloromethane, inferred from measured supersaturation, may reflect material that had an atmospheric source with net uptake during winter and release in summer. This study is not able to identify a true, in situ, marine source of CH_2Cl_2 on account of the relatively large apparent atmospherically derived background, though very plausible source reactions can be postulated.

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