Global oceanic chlorofluorocarbon inventory

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[1] Chlorofluorocarbons (CFCs) dissolve in the oceans, but the total quantity and spatial distribution in the oceans was not previously known. The first estimate of the global oceanic CFC-11 uptake using field measurements is calculated from WOCE (World Ocean Circulation Experiment) CFC-11 concentrations. Here we find the total oceanic uptake of 5.5 (±1.2) $\times$ 10^8 moles was about 1% of total emissions through 1994. Eighty-two percent of the CFC-11 inventory is in the upper 1000 meters. The CFC inventory distribution implies that the dominant physical air-sea exchange of gases on decadal time scales occurs due to a combination of high gas solubility in cold high latitude waters and effectiveness of the wind-driven circulation. The global inventory provides a benchmark for models simulating climate change. *INDEX TERMS:* 1635 Global Change: Oceans (4203); 4283 Oceanography: General: Water masses; 4599 Oceanography: Physical: General or miscellaneous.
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1. Introduction

[2] Chlorofluorocarbons (CFCs) are a group of anthropogenic compounds that have been widely used as coolants in refrigeration and air-conditioning systems, solvents, propellants in consumer products, and as foaming agents. Following their introduction in the 1930s, the concentrations of CFCs in the atmosphere increased rapidly during the next five decades. Although they mainly accumulate in the atmosphere [*Molina and Rowland*, 1974; *Cicerone et al.*, 1974], CFCs are slightly soluble in seawater, with higher solubility at cold temperatures [*Warner and Weiss*, 1985]. CFC-11 is biologically and chemically inert in oxygenated seawater.

2. Data and Methods

[3] Oceanic CFC inventories can be used to calculate rates of ocean circulation [*Smethie and Fine*, 2001; *Orsi et al.*, 1999; *Orsi et al.*, 2002; *Rhein et al.*, 2002], highlight prominent regions of air-sea exchange and estimate the anthropogenic CO_2 inventory [e.g., *Gruber*, 1998; *McNeil et al.*, 2003]. The World Ocean Circulation Experiment (WOCE) data were used to estimate the global oceanic inventory for one CFC, CFC-11, from measured concentration data. Inventories in the Atlantic, Pacific, Indian, and Arctic oceans were calculated from an irregularly spaced collection of station data. At each station, the inventory was computed by trapezoidal integration of CFC-11 depth profiles from the sea surface down to the depth of the lowest detectable CFC-11 concentration (usually <0.005 pmol/kg). The CFC-11 inventories by station were gridded to a 5° longitude by 2.5° latitude grid [*Wessel and Smith*, 1991]. Finally, all of the gridded inventory values were area-integrated and summed to estimate the total oceanic CFC-11 inventory as of 1994 (see below) of 5.5 $\times$ 10^8 moles, or 75,500 metric tons.

[4] The WOCE CFC-11 data used to calculate inventories and estimate total uptake were collected over an approximately 10-year interval, 1988–97. Therefore the data set does not provide a true snapshot of the oceanic inventory at a single point in time. However, 93% of the data used in the inventory were collected between 1991 and 1997. While the Indian Ocean was mostly occupied in 1995, most of the cruises in the Pacific occurred during 1991–94 and in the Atlantic during 1993–97. The inventory is given as of 1994, since an equal number of stations were occupied before and after that year (i.e., 1994 is the median year). Thus, as most of the CFC measurements were made within

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Table 1. The Estimated Uptake of CFC-11 Ocean Volume and Uptake per Volume

Ocean	Indian	Pacific	Atlantic	Arctic	Total
ΣCFC-11 (moles)	1.1×10^8	2.2×10^8	1.9×10^8	2.8×10^7	5.5×10^{8a}
% of total CFC-11	20	40	35	5	100
Volume (km^3)	2.9×10^8	7.1×10^8	3.2×10^8	1.7×10^7	1.3×10^9
CFC-11/volume (moles/km^3)	0.38	0.31	0.59	1.65	0.42

[a]The estimated cumulative error is 1.2×10^8 moles.
Ocean volumes (excluding adjacent seas) are from *Sverdrup et al.* [1942], and each includes its respective Southern Ocean sector.

two years of the median year (1994), and any temporal corrections introduce errors [*Warner et al.*, 1996], no attempt was made to normalize the concentration data to the same date. Furthermore, most (82%, see below) of the inventory lies in the upper 1000 meters. Since these waters are relatively young, corrections to a common date would be fairly small due to the slow rate (<5% y^{-1}) of increase in atmospheric CFC-11 concentrations over the past 25 years [*Walker et al.*, 2000]. In older waters where the correction factor might be large, the concentrations are low and thus have little impact on the global- and basin-scale inventories.

[5] The U.S. WOCE CFC investigators performed the quality control for the CFC-11 data used in the global inventory calculation. At CFC-11 concentrations >0.1 pmol/kg, all quality-controlled data used, except P01W (145–155°E), meet a WOCE relaxed standard precision of ≤3%. Some of the quality-controlled results for the South Atlantic CFC-11 data are not yet available.

[6] Errors in the calculation of inventories and total oceanic uptake of CFC-11 may be due to several factors. Analytical and integration errors for each station inventory are each about 3%. Errors in the basin-wide calculations are likely, propagated by the averaging and gridding algorithms, especially in regions of sparse data. The impact of these errors on the inventory is difficult to quantify and the errors have been estimated to be approximately 10–20%, depending on spatial coverage [*Smethie and Fine*, 2001; *Rhein et al.*, 2002]. Treating data collected over 10 years as synoptic will also introduce errors. However, since 83% of the data were collected within two years of 1994 it is likely that this error is small. Finally, most of the mid-to-high latitude WOCE cruises in both the Northern and Southern hemispheres were occupied in the summer season, when mixed layer temperatures are higher than the annual mean, and hence the CFC-11 solubilities (and CFC-11 concentrations) are lower than the annual mean. We estimate that combining predominantly summertime mid-to-high latitude data from both hemispheres leads to the mean global CFC-11 inventory being underestimated by several percent. The cumulative effects of these errors will be at most 22%, and this is indicated wherever total oceanic uptake is discussed. Finally, ocean volumes [*Sverdrup et al.*, 1942] were used to calculate inventory per-unit- volume (Table 1). Using these volumes rather than volumes based on the specific region integrated and topography that matches our grid spacing could lead to small errors in the inventory per-unit-volume.

3. Spatial Distribution of Inventory

[7] The spatial distribution of the inventory varies between the oceans. Forty percent of the CFC-11 inventory is in the Pacific, consistent with its volume being about equal to the sum of the other oceans (Table 1). Approximately one-third of the global inventory resides in the Atlantic, where the inventory per-unit-volume is almost double that in the Indian and Pacific oceans. The high inventories in the North Atlantic (Figure 1) are due to effective ventilation by the wind-driven circulation and a nearly equal contribution from the North Atlantic Deep Water (NADW). On a per-unit-volume basis the Arctic Ocean inventory is highest due to cold waters and relatively shallow depths [*Wallace et al.*, 1992]. In contrast, low CFC-11 inventories are found in upwelling regions, in regions where subsurface waters are only ventilated to shallow depths or have not recently been ventilated, and where surface waters are warm, e.g., the tropics. More than 60% of the total oceanic CFC-11 inventory is found in the Southern Hemisphere, despite Southern Hemisphere atmospheric concentrations lagging slightly behind those in the Northern Hemisphere [*Walker et*

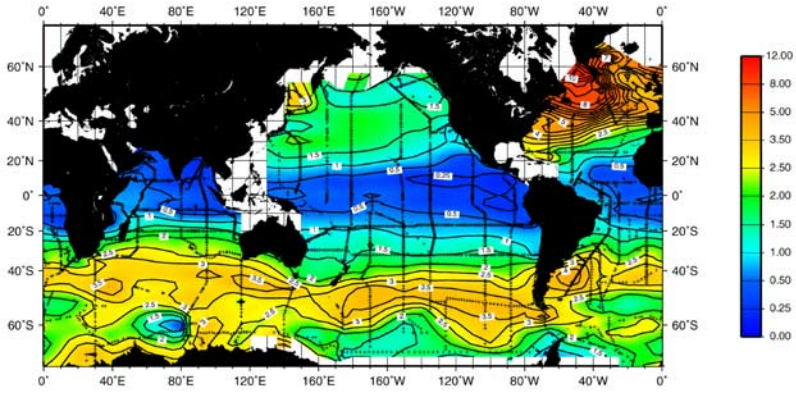

Figure 1. Map of vertically integrated CFC-11 in moles/km^2. Highest values are in red, lowest are in blue. The + symbol shows station locations.

al., 2000]. The higher inventory in the Southern Hemisphere is due to effective ventilation of a large volume of its upper ocean.

[8] Eighty-two percent of the CFC-11 oceanic inventory lies in the upper 1000 meters, with another 10% between 1000–2000 meters. Water within the upper 1000 meters includes the thermocline. It also includes the cold high latitude upper waters of the Arctic Ocean, and waters that eventually lie in the deeper layers of the ocean, NADW and Antarctic Bottom Water (AABW)/Circumpolar Deep Water (CDW), occurring in near surface layers at their formation regions.

[9] There are two prominent deep water mass sinks of CFCs, NADW and AABW/CDW, which participate in the thermohaline circulation. As discussed above, the highest CFC-11 inventories in Figure 1 are found downstream of NADW formation regions in the high latitude and western subtropical North Atlantic. High inventories also occur around the Antarctic continent. In the early 1990s, the inventories of CFC-11 in NADW [*Smethie and Fine*, 2001] and in the dense AABW/CDW [*Orsi et al.*, 1999, 2002] were each about 0.3×10^8 moles. Based on those inventories, calculated using pre-WOCE data for NADW and primarily WOCE data for AABW/CDW, and the results presented here, it is estimated here that there are 1.0×10^8 moles observed below 1000 meters. Thus, about 18% percent of the CFC-11 inventory is taken up by NADW and AABW/CDW. These results indicate that the global oceans' ability to take up anthropogenic gases is sensitive to the rate of thermohaline overturning, which has varied in the past and may change in the future. Thus, variations in both the wind-driven and the thermohaline circulation have the potential to change the oceans' future CFC, and thus CO_2, uptake capacity.

[10] The other prominent site of CFC accumulation is in the region around 50°S (Figure 1). CFC-11 inventory maxima are observed near air-sea CO_2 flux [*Takahashi et al.*, 2002] maxima in the three Southern Hemisphere basins. The South Pacific CFC inventory maximum is the southernmost of the three oceans because of the poleward displacement of the Subantarctic Front in that basin. Inventory maxima are co-located with maxima in wind stress curl and are north of the Subantarctic Front. Just north of the Subantarctic Front is where cold deep layers of Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) (southeast Pacific and southwest Atlantic) are formed [*McCartney*, 1982]. These waters spread equatorward to fill the lower thermocline and intermediate levels of the Southern Hemisphere subtropical gyres. The SAMW/AAIW bear large CFC inventories due to the high solubility of gas in cold water and their large volumes of recently ventilated water.

4. Comparison of CFC-11 Uptake and Emissions

[11] The calculated global emissions of CFC-11, based on market surveys from 1950 to 1994, and the total release of CFC-11 reported by Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) for 1931–1994 are 5.8×10^{10} moles and 5.5×10^{10} moles, respectively [*McCulloch et al.*, 2001; *AFEAS*, 2002]. The total oceanic inventory of CFC-11, 5.5 (±1.2) $\times 10^8$ moles (Table 1), accounts for a small fraction of these emissions. Using either the CFC-11 calculated emissions or release values, the global oceans have provided a sink for approximately 1% of the total quantity of CFC-11 emitted through 1994.

[12] A recent global ocean model analysis [*Craig et al.*, 1998] yielded a total integrated CFC-11 uptake as of January 1990 of 2.7×10^8 moles, approximately half of the present study's total uptake estimate as of 1994. As part of the Ocean Carbon Model Intercomparison Program, thirteen global ocean models that incorporated CFCs [*Dutay et al.*, 2002] yielded CFC-11 inventories in 1994 ranging from about 4.5×10^8 to 8.3×10^8 moles The observation-derived inventory presented here falls within this range. It would be useful to use the observed inventories to gain further insight into the ventilation processes in the models. In an ocean model constrained by carbon isotopic changes [*Quay et al.*, 2003], adding the CFC-11 inventory as an additional constraint reduced the overall uncertainty in the CO_2 uptake calculation by more than 30%.

5. Conclusions

[13] As of 1994, the global ocean had taken up 5.5 (±1.2) $\times 10^8$ moles (75,500 metric tons) of CFC-11, approximately 1% of the total amount of CFC-11 emitted into the atmosphere through 1994. About 82% was in the upper 1000 m of the ocean. The global oceanic inventory provides a visualization of prominent sites of accumulation, for example, for SAMW/AAIW and NADW and AABW/CDW. In addition, the CFC-11 inventory provides a powerful constraint on model simulations of oceanic uptake of anthropogenic gases such as CO_2.

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