Chlorofluorocarbons in the Atmosphere

THE chlorofluorocarbon CCl_3F (trichlorofluoromethane) occurs in the atmosphere[1], and seems especially attractive for use as a tracer of air and water mass movements[2,3]. Its use as a propellant-solvent for aerosol dispensers results in its entry to the atmosphere where, due to its stability, it can accumulate. There has been an exponential increase in the use of this compound in recent years. Its residence time in the atmosphere has been estimated to be greater than ten years[3].

The trichlorofluoromethane is formed in roughly equal amounts with dichlorodifluoromethane (CCl_2F_2) during their production from carbon tetrachloride. In the United States the production rates are 0.12 and 0.18 Mton yr^{-1} for CCl_3F and CCl_2F_2 respectively. The world production rate probably is three times these values. The dichloro-compound is much less sensitive to gas chromatographic assay than its trichloro-counterpart and as yet its occurrence has not been reported in the atmosphere. Because it is somewhat more stable in its packages as an aerosol[4-6] and presumably more stable in the atmosphere, one would expect it in higher concentrations than CCl_3F. Further, its relative stability would enhance its use as a tracer. The aim of the investigation we describe here was to seek out the levels of these two chlorofluorocarbons in the atmosphere of Southern California.

Analyses were carried out with a gas chromatograph fitted with an electron capture detector and a column using 'Porapak' T. Air was sampled in brass tubing, either end of which had a "quick connect". Before sampling, the tubes were purged with helium and evacuated.

The air samples were combined with helium to a pressure of about 3.5 atm and subsequently introduced into the gas chromatograph with helium as a carrier gas. Using an electron capture detector, the sensitivity for dichlorodifluoromethane is about 1/45 of that for the trichlorofluoromethane[7].

Samples were taken from the downtown area of San Diego, the Scripps Institution of Oceanography Pier and the Anza-Borrego desert region, about 100 km north-east of San Diego. The trichlorofluoromethane values are in agreement with those of Lovelock[1,3] (Table 1) and up to an order of magnitude less than those of the dichlorodifluoromethane.

Table 1 Atmospheric Chlorofluorocarbon Concentrations

		Trichloro-fluoromethane	Dichloro-fluoromethane *
La Jolla pier	Maximum	22.0×10^{-10}	8.0×10^{-9}
	Minimum	0.12	0.3
	Average	3.7 ± 5.6	5.8 ± 4.6
San Diego	Maximum	18.0	7.0
	Minimum	0.1	0.58
	Average	2.9 ± 2.4	3.2 ± 1.4
Desert		0.97	0.70
Marine airs between the United Kingdom and the Antarctic[3]		0.5	—
Ireland[1]		0.1 to 2.0	—

* ml per ml of air.

Our expectation that the dichlorofluoromethane would be more abundant than the trichlorofluoromethane is borne out in samples taken from the industrialized area of San Diego and from the adjacent desert regions. The substantially smaller abundance of trichlorofluoromethane is probably related to the relative instability of its C–Cl bonds. The homolytic cleavage of this bond in the presence of such substances as hydrocarbons and alcohols in the atmosphere and in the containers in which it is used can result in its hydrolysis to formic acid by the path[4-6]

$$CCl_3F \rightarrow CHCl_2F \rightarrow HCOOH$$

Table 2 Chlorofluorocarbon Concentrations in Laboratory Gases

Gas *	Trichloro-fluoromethane †	Dichloro-fluoromethane †
N_2 (Hi-dry)	6.2×10^{-11}	1.4×10^{-9}
He (99.998%)	2.1×10^{-11}	1.0×10^{-9}
Compressed air	4.0×10^{-10}	3.5×10^{-9}

* All gases were obtained from Liquid Carbonic Company, San Diego, California.
† ml per ml of gas.

Compressed gases, now used in laboratory work, contain a burden of the chlorofluoromethanes (Table 2). The chlorofluorocarbons probably have origins in the airs from which the gases were made, as well as in leakages from refrigeration equipment used in their production. The relatively low value of the trichlorofluoromethane emphasizes its lower stability compared to its dichloro counterpart.

Using an estimated world production of the dichlorodifluoromethane of 0.54 Mton yr^{-1} and an atmospheric concentration of 0.70×10^{-9} ml per ml of air, we obtain a residence time of around 30 yr, which is substantially higher than that of CCl_3F (about 10 yr, ref. 3). This longer residence time in the atmosphere can be of decided advantage in studying air-sea interactions, especially because we have little knowledge about the environmental sinks for either of these chlorofluorocarbons.

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Pb in Particulates from the Lower Atmosphere of the Eastern Atlantic

MAN-INDUCED changes affecting the trace metal composition of seawater through river runoff have their initial effects in coastal regions close to the source of pollution. It is now recognized, however[1,2], that atmospheric transport can introduce pollutants directly to the open ocean. There are still few data on the trace metal compositions of atmospheric particulates from oceanic areas and those that are available[3-5] are from latitudinally restricted locations. Recently, we have carried out a sampling programme[6-8] in which particulates have been collected from seawater and from the lower atmosphere (~15 m above the sea surface) over large tracts of the world ocean. The collection details have been described elsewhere[6] and here we present data on the concentration of Pb in atmospheric particulates collected along the length of the Atlantic Ocean from a variety of air masses. The results are listed in Table 1, and the ship's track is shown in Fig. 1.