

Atmospheric Fluorine Compounds as Indicators of Air Movements

GASEOUS fluorine compounds are supposed not to occur naturally in the atmosphere. Volatile fluorine compounds would not be expected to result from chemical equilibria between fluorine compounds on the surface of the Earth, and it is improbable that biological systems contribute significant quantities of organic fluorine compounds.

It is, however, estimated that about 10^6 tons of fluorine compounds are released each year into the atmosphere, and these include halomethanes from aerosol dispensers, fire extinguishers, refrigerant fluids and anaesthetics, and sulphur hexafluoride from electrical equipment. By contrast with these stable compounds, reactive compounds such as hydrogen fluoride, which are also industrial products, are rapidly scavenged from the atmosphere by physical and chemical processes.

The presence of stable sulphur and carbon fluorides in the atmosphere is not in any sense a hazard, and their existence has only been detected by the very sensitive technique of gas phase electron absorption. The fluorides are, however, of special interest because they enter the atmosphere only from industrial and domestic sources, whereas other gaseous industrial emissions are also natural products; their distribution in the atmosphere can therefore be a useful indicator of air movements and wind directions.

Table 1 Observations at Adrigole, Co. Cork, Ireland ($51^{\circ} 40' N$, $09^{\circ} 45' W$)

Wind heading	Concentration by volume		Turbidity
	CCl_3F	SF_6	
45° – 135°	1.0×10^{-11}	2.9×10^{-14}	0.03
	(4)	(3)	(7)
225° – 315°	1.9×10^{-10}	1.2×10^{-13}	0.19
	(3)	(3)	(2)

The number of observations is shown in parentheses.

We report in this communication preliminary measurements of the atmospheric concentrations of sulphur hexafluoride and trichlorofluoromethane in south-west Ireland during July and August 1970. Analyses were made using a gas chromatograph with an electron capture detector. Experimental conditions were arranged so that ionization in the detector was complete¹ and under these circumstances errors are only likely to be caused by loss of sample during collection and chromatography; for example, by irreversible adsorption. Calibration of the system showed that such losses probably did not exceed 30%. Our results are shown in Table 1; the atmospheric turbidity was measured with a 'Volz' sun photometer using the technique described by Flowers, McCormick and Kurfis². Air arriving at the monitoring site from a north-westerly direction does not pass over any source of either CCl_3F or SF_6 and so the concentrations measured under these conditions can be regarded as representative of the northern hemisphere background. If the industrial outputs of these compounds are assumed constant at about 2×10^5 and 10^2 tons per year respectively, the atmospheric lifetimes would seem to be 1 yr and 4.6 years.

Although other halocarbons such as CF_2Cl_2 and perfluorocyclobutane are almost certainly present in the atmosphere, they were not observed in our preliminary experiments because of their relatively low rate of reaction with thermal electrons in the electron capture detector. An unknown electron absorbing compound was, however, always found to be present in the air at a concentration of about 3×10^{-11} by volume and, although its retention time in the chromatograph column suggested a boiling point of about $75^{\circ} C$, it has not been possible to identify it.

The high concentrations of CCl_3F and SF_6 associated with easterly winds from continental Europe and the appreciably

increased turbidity lend support to the proposal that these compounds can be used as indicators of air masses which have recently been polluted by industrial effluents.

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¹ Lovelock, J. E., in *Gas Chromatography 1968* (edit. by Harbourn, C. L. A.) (Elsevier, Amsterdam, 1969).

² Flowers, E. C., McCormick, R. A., and Kurfis, K. R., *J. App. Meteorol.*, **8**, 955 (1969).

Reply to Cherry, Barnes and Fullman

MY answer to the question raised by Cherry, Barnes and Fullman¹ about the structure I proposed for anomalous water² can only be "why not?" I agree that my structures are similar to the structures of ice 1h and 1c, but they are not just a scaled down version of them. I demonstrated how the structures could be built up from six-molecular rings and therefore one can see that it might be the way water molecules hold themselves together to form ice. I also indicated that the anomalous water could only be formed in the presence of foreign cations and was analogous to the structure of water in concentrated aqueous salt solutions. I do not see why the structures cannot be liquid under the condition described.

An obvious question to ask is how far out from the capillary wall these structures (or anomalous water) can be maintained without foreign cation impurities among the rings. The answer may be the chief reason for the difficulty in obtaining pure anomalous water and the questioning of its existence. I believed, when proposing the mechanism, that the oxygen ion in the water molecule was depolarized and became more ionic when it was surrounded symmetrically by four hydrogen ions (or cations) and the molecule as a whole was further polarized. The stretching of the O–H bond is therefore the transformation of covalent bonding to ionic bonding. It seems that the lone pair has a tendency to attach to a bare cation, as in the formation of complexes, and the experiments with anomalous water indicate that water molecules may take some cations with them when evaporating from salt solutions: this is disturbing if true.

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¹ Cherry, I., Barnes, P., and Fullman, J., *Nature*, **228**, 590 (1970).

² Chua, K. S., *Nature*, **227**, 834 (1970).

Fluid Orthodoxy?

A RECENT article¹ by the molecular physics correspondent of *Nature* began: "If there is an orthodoxy in the theory of liquids . . . it has little place for notions which depart very far from the familiar, well founded and regrettably somewhat sterile formalism of Gibbsian statistical mechanics". We suggest that the problem with the statistical mechanics of Gibbs and Boltzmann is more closely related to frugidity than sterility; the response is difficult to evoke, but once evoked is usually fruitful. It is surely unfair to brand as sterile a septuagenarian formalism which gives birth to a complete description of solids², liquids^{3,4} and gases⁵ and of the phase equilibria between them⁶. No doubt the impression of sterility arose from the long gestation period which was necessary