

and the environment

G. McConnell, D. M. Ferguson, and C. R. Pearson

In recent years there has been concern about the potential toxic hazards of chlorinated organic compounds used as insecticides. It has come to be assumed that similar hazards are presented by chlorinated hydrocarbons generally, many of which are manufactured and used in large quantities. The evidence reviewed in this article indicates that while a number of C_1 and C_2 chlorinated aliphatic compounds are widely distributed, they do not accumulate to the same extent as the chlorinated insecticides nor do they have their extreme persistence in the environment.

In recent years concern has been shown over the environmental effects, on both wildlife and man himself, of the organo-chlorine insecticides (of which DDT is a familiar example) and the polychlorinated biphenyls (PCB). This concern has extended to all 'chlorinated hydrocarbons': consequently they have been included in the class of chemicals banned by the Oslo and Paris Conventions to regulate the discharge of waste into the sea. We have made a study of the potential environmental impact of those chlorinated aliphatic hydrocarbons that are manufactured on a large scale. Several surveys relevant to such a study have been published recently, either as review articles or in government or intergovernmental reports; a useful discussion has been presented by G. T. Goodman [1]. The following factors must all be considered. (a) What quantities are produced; how, where, and in what form the materials are released to the environment; (b) how they are distributed, and in what concentrations they occur in the atmosphere, in fresh and marine waters, and in soil sediments; (c) at what levels they exhibit toxic effects to man or wildlife; (d) whether they accumulate in living organisms, and, in particular, become concentrated up food chains; (e) how stable they are in the environment, and whether any of the products of degradation are themselves likely to have ill-effects.

Emission and distribution pathways

World production capacities for all the major chlorinated hydrocarbons are shown in Table 1. Of the compounds in column (a) the fluorochloromethanes are extensively used as aerosol propellants; and are therefore almost completely lost to the atmosphere after use. The others are employed principally as solvents in industrial or

domestic applications. Although industrial solvents are to a large extent recovered, the production of these solvents represents the need to replace the handling losses incurred in their use. The quantities in column (a) therefore represent the annual losses to the environment. This loss will arise from a multiplicity of sources, correlated with local factors such as population density and industrial activity.

The products in column (b) serve primarily as chemical intermediates. The amount of them that enters the environment is a very small fraction of the total production, and is limited to relatively few chemical manufacturing sites. At these sites smaller amounts of by-products will also be produced; these range from other chlorinated C_2 hydrocarbons to chlorinated hydrocarbons of higher molecular weight and tarry residues. These residues have in the past been dumped partly on land, but particularly at sea; A. Jernelov and co-workers [2] have described the effects of 'EDC tar' dumped in the North Sea. The residues are now either incinerated under controlled conditions, or returned where possible as raw material to modified production plants, in particular for manufacture of carbon tetrachloride.

The products listed in Table 1 are characterized by high volatility and low solubility in water; some of their physical properties are shown in Table 2. They enter the environment primarily by evaporation to the atmosphere. Some chlorinated hydrocarbons will, however, be found in aqueous effluents from factories handling them, and even in household sewage, and so will pass into municipal drainage systems and rivers. During the determination of the partition coefficients shown in the last column of Table 2, it was found that there is a rapid transfer of the chlorinated compound both from air to water, and from water to air. Irrespective of whether the initial loss of chlorinated hydrocarbon is to the atmosphere or the hydrosphere, the transfer processes will lead to a wide distribution of these compounds, with aerial transport playing a major part. Such processes explain the occurrence of some chlorinated hydrocarbon in rainfall and upland waters.

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Table 1
Estimated world production capacities (1973)
of major chlorinated hydrocarbons, in 10^3 tons/year

(a)		(b)	
Trichloroethylene	1010	Vinyl chloride	10 500
Perchloroethylene	1050	1,2-Dichloroethane	19 500
1,1,1-Trichloroethane	480	Carbon tetrachloride	1000
Methylene chloride	400	Chloroform	245
Trichlorofluoromethane	485	Methyl chloride	350
Dichlorodifluoromethane	570		

G. McConnell, M.A., B.Sc.

Was born in England in 1919. Educated at the Collegiate School, Liverpool, and the University of Oxford, where he graduated in chemistry in 1941. In 1942 he joined the Research Department of the then General Chemicals Division of ICI (since merged into Mond Division). He has been involved in a range of industrial research problems, mainly in the field of organic chemicals and since 1971 has had a major interest in the environmental impact of the halo-organic compounds.

D. M. Ferguson, B.Sc. Ph.D.

Was born in Scotland in 1940. He graduated (in physiology) from Aberdeen University in 1963 and obtained his Doctorate from Edinburgh University in 1969. In 1966, he joined ICI's Industrial Hygiene Research Laboratories (now Central Toxicology Laboratory) where he has been concerned with the toxicological evaluation of a wide range of industrial and agricultural chemicals.

C. R. Pearson, M.A.

Was born in England in 1929. Read Natural Sciences at the University of Cambridge, specializing in biochemistry. He joined ICI in 1952, at the Brixham Laboratory in Devon. He has been involved in a wide range of studies associated with both assessment and prevention of water pollution.

Occurrence in the environment

Techniques for the isolation, identification, and measurement of DDT and PCB have been extensively studied and described. Almost all depend on solvent extraction, careful clean-up by column chromatography, and measurement by gas-liquid chromatography (GLC) using an electron capture detector. Where possible, identification is confirmed by a linked mass-spectrometer (MS). Although the same basic methods can be applied to the other industrially important chlorinated hydrocarbons, their high volatility introduces considerable difficulties at the sampling, extraction, and GLC separation stages. In addition, the response of the electron capture detector varies widely according to the number of chlorine atoms in the molecule, and this results in very considerable differences in the sensitivity and accuracy of determinations of different compounds. But these difficulties have been overcome.

Initial observations of the occurrence of chlorinated hydrocarbons in the atmosphere have been made by J. P. Riley [3], J. E. Lovelock [4], P. E. Wilkiss [5], and P. G. Simmonds [6]. Our own observations in the atmosphere of north-western England, as well as a much fuller range of measurements in water, sediments, and marine organisms are given elsewhere [7]. All the authors agree that fluorochloromethane, tri- and perchloroethylene, chloroform, and carbon tetrachloride are found universally in the atmosphere at concentrations normally in the range between 1 and 10 ng/l; we ourselves also found 1,1,1-trichloroethane at a similar concentration.

The distribution of fluorochloromethanes and of trichloroethylene, perchloroethylene, and trichloroethane, which are major solvents, is consistent with their usage. The concentrations of chloroform and carbon tetrachloride, which are chemical intermediates with limited losses, is somewhat surprising, and led Lovelock to suggest that they may arise naturally by reaction between chlorine and methane in the atmosphere.

Analyses of rain-water, rivers, municipal water supplies, and the sea [7] again show that tri- and perchloroethylene, trichloroethane, chloroform, and carbon

tetrachloride are widely distributed at the $\mu\text{g/kg}$ level or lower. In addition some samples of sea water from Liverpool Bay, which receives large volumes of industrial and domestic effluents, contain traces (less than 1 $\mu\text{g/kg}$) of tetrachloroethane, pentachloroethane, penta- and hexachlorobutadiene (HCBd), hexachlorobenzene, and γ -benzene hexachloride.

Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters, but there was no correlation between the chloro-organic content of the sediment and that of the mid-depth water from the same point on the sampling grid. It appears that coarse gravels have little adsorptive capacity for these compounds, whereas sediments rich in organic detritus have a much higher adsorptive capacity. Averaged over all samples, the concentrations of chlorinated C_1/C_2 compounds in the sediments were similar to those in the water; hexachlorobutadiene with its higher molecular weight does, however, show concentration factors up to a hundredfold.

Occurrence in animal tissue

Details of the distribution of chlorinated hydrocarbons in the tissues of marine plants and animals are being published [7]. The compounds found in sea water are also found in marine animals. Concentrations vary from 1 $\mu\text{g/kg}$ or less in invertebrates, to 10 $\mu\text{g/kg}$ in the flesh of fish, to a maximum of 50 $\mu\text{g/kg}$ in the eggs of sea birds and the blubber of seals. Special attention was paid to the fatty tissues of sea birds and mammals, as these represent the highest trophic levels in which DDT and PCB are found to accumulate. As man occupies a similar position at the head of a series of food chains, analyses of a wide range of foods, of both animal and vegetable origin, have been made; the results are shown in Table 3. Finally, it has been possible to carry out some analyses of post-mortem human tissue; results are presented in Table 4. During the early stages of these investigations it was not possible to distinguish analytically between carbon tetrachloride and trichloroethane, but improved technique allowed this later.

A summary of the results from this and the previous section is presented in Table 5. From these results we draw two main conclusions: (a) The concentrations of DDT and PCB in fatty tissues are at least three orders of magnitude greater than those of the industrial solvents. (b) Chloroform and carbon tetrachloride are very widely distributed, and at unexpectedly high concentrations.

Possible hazard to human health

The ubiquitous distribution of the chlorinated hydrocarbons means that a population may breathe air, drink water, and consume food containing trace quantities of these materials. In many instances, the cooking of a foodstuff will reduce these levels still further. There is, moreover, evidence for the presence of these compounds in human tissue, again at extremely low concentrations (Table 4).

Table 2
Physical properties of some aliphatic chlorinated hydrocarbons

	B.P. (°C)	Vapour pressure (mm Hg/20°C)	Solubility in water at 20°C (parts/10 ⁶ w/w)	Partition coefficient water/air at 20°C (w/v per w/v)
Methyl chloride	-24.2	3756	7250*	3.3
Methylene chloride	40.1	362.4	13 200 (25°C)	8.1
Chloroform	61.3	150.5	8200	8.6
Carbon tetrachloride	76.8	90.0	785	1.1
Ethylene dichloride	83.6	63.9	8800	26.4
1,1,1-Trichloroethane	74.1	96.0	480	0.71
Vinyl chloride	-13.9	2320	60 (10°C)*	0.02 (10°C)
Vinylidene chloride	31.9	496.5	400	0.16
Trichloroethylene	87.0	57.9	1100	2.74
Perchloroethylene	121.2	14.0	150	1.22
Fluorotrichloromethane	23.8	667.4	1100	0.03
Difluordichloromethane	-23.8	4306	280 (25°)*	0.06
Hexachlorobutadiene	215	0.15	~2	0.97

* Under 760 mm pressure of organochlorine compound

Table 5, which summarizes all the analytical data, demonstrates that there is no evidence for significant accumulation in human tissue of any of the materials under discussion. Rather, they indicate a general background, at the parts in 10^9 level, which pervades the whole ecosystem—atmosphere, hydrosphere, and biosphere. These results are in sharp contrast to those reported for DDT or PCB, where accumulation in tissues of several orders of magnitude has been observed [8].

It is interesting to compare in Table 6 the threshold limit values (TLV) set by the American Conference of Governmental and Industrial Hygienists with the maximum atmospheric concentrations measured in our survey [7].

The threshold limit values define permissible atmospheric concentrations applicable only to an 8-hour working day and a 5-day week. In the United Kingdom, maximum allowable ground level concentrations to which the public might continuously be exposed are set in the range of $1/25$ th– $1/40$ th of the TLV. It can be seen that the environmental concentrations are less by some orders of magnitude.

If we examine the possibility of poisoning by swallow-

ing, we find from tests on rats and mice [10–18] that all five aliphatic compounds of Table 6 have low toxicities with LD₅₀ values varying between 2 and 12 g/kg. The LD₅₀ value is the dose that will kill 50 per cent of a group of experimental animals.) The corresponding LD₅₀ value for DDT with rats was 0.15–0.4 g/kg. Clearly the presence of a few parts per 10^9 of these substances in food or water will not give rise to acute poisoning.

The acceptable daily intakes (ADI) of substances in foodstuffs are set by bodies such as the FAO Working Party of Experts and the WHO Expert Group on Pesticide Residues. They are generally calculated by applying safety factors (of 100–2000) to the maximum no-effect levels observed in long-term feeding studies on animals, taking into account the absorption, metabolism, and excretion of the substance.

Absorption, metabolism, and excretion

Published reports indicate that most of the chemicals are moderately to well absorbed from the gastrointestinal tract after oral administration [20, 21, 22]. Typically, a very large fraction of the administered dose is excreted unchanged in the expired air. It has been established

Table 3
Chlorinated hydrocarbons in foodstuffs
(Concentrations in $\mu\text{g}/\text{kg}$)

Foodstuff	Chloroform	Carbon tetrachloride	Trichloroethane	Trichloroethylene	Perchloroethylene	Others
Dairy produce						
Fresh milk	5	0.2		0.3	0.3	HCBD 0.08 HCB 1
Cheshire cheese	33	5		3	2	ND
English butter	22	14		10	13	HCBD 2
Hens eggs	1.4	0.5		0.6	ND	ND
Meat						
English beef (steak)	4	7	3	16	0.9	ND
English beef (fat)	3	8	6	12	1.0	ND
Pig's liver	1	9	4	22	5	TCE 0.5 PCE 0.4
Oils and fats						
Margarine	3	6		6	7	PCE 0.8
Olive oil (Spanish)	10	18	10	9	7	ND
Cod liver oil	6	16	5	19	2	TCE 2
Vegetable cooking oil	2	0.7		7	0.01	HCBD 0.2 HCB 0.7
Castor oil	NA	NA	6	ND	3	NA
Beverages						
Canned fruit drink	2	0.5		5	2	PCE 0.8
Light ale	0.4	0.2		0.7	ND	HCBD 0.2
Canned orange juice	9	5		ND	ND	ND
Instant coffee	2	5		4	3	ND
Tea (packet)	18	4	7	60	3	ND
Wine (Yugoslav)	NA	0.3		0.02	ND	NA
Fruit and vegetables						
Potatoes (S. Wales)	18	8	4	ND	ND	NL
Potatoes (N. W. England)	4	3	1	3	0.7	TCE 0.7
Apples	5	5	3	6	2	ND
Pears	2	4	2	4	2	ND
Tomatoes*	2	4.5		1.7	1.2	HCBD 0.8 HCB > 0.1
Black grapes (Imported) †	ND	19.7		2.9	ND	TCE 1.0
Fresh bread	2	5	2	7	1	HCBD 3.7

* Tomato plants were grown on a reclaimed lagoon at Runcorn Works of ICI.

† HCBD is still used in some countries as an insecticide for vineyards.

‡ TCE, PCE = Tetra-, penta-chloroethane; HCBD = Hexachlorobutadiene; HCB = Hexachlorobenzene
NA = No Analysis; ND = Not Detected

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Table 4

Occurrence of chlorinated hydrocarbons in human tissue.
Concentrations in µg/kg (wet tissue)

Age of subject	Sex	Tissue	Chloroform	Carbon tetra- chloride + trichloro- ethane	Trichloro- ethylene	Perchloro- ethylene	HCBD	Others
76	F	Body fat	19	24	32	6	—	—
		Kidney	2	1	<1	<0.5	—	—
		Liver	5	1	5	<0.5	—	—
		Brain	4	<1	1	<0.5	—	—
76	F	Body fat	5	4	2	1	—	—
		Kidney	5	3	3	6	—	—
		Liver	1	4	2	2	—	—
		Brain	2	2	<1	<5	—	—
82	F	Body fat	67	1.6	1.4	0.4	0.8	—
		Liver	8.7	3.5	3.2	1.2	12.1	—
48	M	Body fat	67	2.1	6.4	0.8	1.8	—
		Liver	9.5	3.5	3.5	0.7	5.7	—
65	M	Body fat	64	11.0	3.4	21	1.8	—
		Liver	8.8	3.5	5.2	3.4	11.8	TCE <0.5
75	M	Body fat	65	13.6	14.1	29.2	0.8	—
		Liver	10.0	5.1	5.8	4.3	13.7	γ-BHC 24
66	M	Body fat	68	1.6	4.6	0.5	1.2	γ-BHC 7.5
74	F	Body fat	52	5.2	4.9	4	4	γ-BHC 22

that metabolism results in the formation of trichloroacetic acid (from trichloroethylene and perchloroethylene), trichloroethanol (from trichloroethylene), chloroform (from carbon tetrachloride), and CO₂ (from carbon tetrachloride and chloroform) [20-23].

Some of the compounds have non-industrial uses and it is possible to compare permitted use concentrations with the maximum concentrations found in the survey described above. The relevant data are summarized in Table 7.

This table demonstrates that, with one exception, there are enormous differences between permitted-use concentrations of the chemicals, admittedly in some instances for discontinuous use, and the maximum levels found in food. The exception is carbon tetrachloride, where the suggested guidelines for grain residues are similar to the amount of this material in food; the grain

Table 5

Occurrence of chlorinated hydrocarbons in the environment.
Typical concentrations (w/w) of the five major compounds
(chloroform, carbon tetrachloride, trichloroethylene,
perchloroethylene, trichloroethane)

	Minimum	Maximum
Air	10 ⁻⁹	10 ⁻⁸
Rain water	10 ⁻¹¹	10 ⁻⁹
Surface water	10 ⁻¹¹	10 ⁻⁹
Potable water	10 ⁻¹¹	10 ⁻⁹
Sea water	10 ⁻¹⁰	10 ⁻⁹
Marine sediments	10 ⁻¹⁰	10 ⁻⁹
Marine invertebrates	10 ⁻⁹	10 ⁻⁸
Fish	10 ⁻⁹	10 ⁻⁸
Waterbirds	10 ⁻⁹	>10 ⁻⁷
Marine mammals	10 ⁻⁹	>10 ⁻⁸
Fatty foods	10 ⁻⁹	10 ⁻⁸
Non-fatty foods	10 ⁻⁹	10 ⁻⁹
Human organs	10 ⁻⁹	10 ⁻⁹
Human body fat	10 ⁻⁹	10 ⁻⁸

residues, however, do refer to regular daily intake. To put the remaining figures in perspective, some 500 kg of cheese would have to be consumed to give an intake of chloroform equivalent to one dose of the linctus described.

Effects on wildlife

So far only a few results are available for the levels of the C₁/C₂ chlorinated hydrocarbons in land animals (other than marine and avian species) or plants. The indications are, however, that the levels in such species are not significantly different from the general background concentrations shown in Table 5. Hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD), of which we have found traces in fish and foodstuff samples, are used on a small scale as pesticides. J. G. Vos [24] showed that toxic effects occur only in birds fed high dose rates of HCB, namely 20 mg/l over 3 months. At the end of the trials, the average HCB concentration found in the liver was 35 mg/l.

Our own study of effects on marine organisms has been described [7]. Acute toxicity levels for marine fish, barnacle nauplii, and a unicellular alga are reproduced

Table 6

Threshold limit value compared with maximum observed concentrations (mg/l)

	TLV	Max. observed concentration
Trichloroethylene	0.50	0.00015
Perchloroethylene	0.67	0.00009
Trichloroethane	1.80	0.00009*
Carbon tetrachloride	0.06	0.00009*
Chloroform	0.12	0.00004

* Not differentiated by analysis, therefore, the concentration shown is the maximum value, assuming the GLC peak represents wholly trichloroethane or carbon tetrachloride.

Table 7
Comparison of observed concentrations in food
and permitted use concentrations

Chemical	Uses	Permitted concentrations/dose	Max. concn. measured ($\mu\text{g/kg}$)
Trichloroethylene	Anaesthetic Extraction solvent	10-25 mg/kg decaffeinated coffee*	60 (packet coffee)
Perchloroethylene	Anthelmintic (veterinary and human medicine)	1.6-8.0 g/60 kg † (therapeutic dose)	13 (butter)
1,1,1-Trichloroethane	?	?	20 (black grapes)
Carbon tetrachloride	Grain fumigant	50 $\mu\text{g/kg}$ (cooked cereal products):	20 (black grapes)
Chloroform	Anaesthetic Flavouring agent	15-30 mg/dose † (cough linctus)	33 (cheese)

* US Food and Drug Administration (1973) Food Chemical News Guide

† Martindale 'The Extra Pharmacopoeia' 26th Ed. (1972)

‡ FAO/WHO Expert Committees, WHO Pesticide Residues Series I, 1971 (1972)

in Table 8; comparison with Table 5 shows that they are at least three orders of magnitude higher than those found in sea water. There is no evidence that the bioaccumulation up food chains, which is such a feature of DDT and PCB, occurs to any significant extent with the commercial solvents. There is some indication that in fish, by-product 'heavies' such as HCBd show some bioaccumulation intermediate between the two former classes, but this does not increase in birds and mammals feeding on fish.

Degradation in the environment

Biochemical degradation. As the major chlorinated hydrocarbons are so widely distributed in the environment, they are exposed to a wide range of potential degradation routes. Although there is evidence that they can be metabolized by mammalian tissues, we do not know how many other phyla have this ability. It is generally accepted, however, that micro-organisms, whether aerobic or anaerobic, do not have it. Microbiological degradation, which is so important for the destruction of many organic compounds, therefore probably does not have any significant direct part to play in this case.

In mammals, the metabolic pathways of all the compounds discussed so far lead to chlorinated acetic acids, either directly or via chloroethanols. Chlorinated acetic acids have all been shown to be susceptible to further degradation by micro-organisms in sea water [7].

It has been suggested that low concentrations of chlorinated solvents could, however, inhibit microbial degradation processes generally, especially in anaerobic environments. Particular concern has been expressed over the effects on sewage treatment. Our observations show that concentrations in raw sewage are normally less than 0.1 mg/l; some of this is adsorbed on to primary sludge, while most is lost to the atmosphere during biological oxidation, either by activated sludge or trickling filters.

Our initial experiments show that inhibition of aerobic oxidation does not occur at concentrations below 10 mg/l; this concentration will not normally be found in any sewage works. An extensive investigation of the effects on anaerobic digestion in sewage works, particularly by chloroform, is given in [25].

Physico-chemical degradation. There is evidence for the chemical breakdown of chlorinated hydrocarbons in water, but in general these reactions are very slow; we estimate the chemical half-life of perchloroethylene in water to be about six years. Exceptions to this arise for compounds which are easily dehydrochlorinated; the reaction rate in such cases depends on the pH. An important example of this is the dehydrochlorination of the solvent 1,1,1-trichloroethane, which would have a chemical half-life in sea water (pH 8, 10°C) of about 9 months. The decomposition product is vinylidene chloride, with (at environmental temperatures) only a minor amount of acetic acid arising by hydrolysis. Rapid degradation in aqueous systems does, however, occur in the presence of metallic iron. At the present time the resulting degradation products have not been identified, but this faster rate in the presence of metals could be important.

The current implication of our work is that it is by tropospheric photo-oxidation that the environmental aliphatic organo-chlorine compounds are principally destroyed. This will apply also to those compounds present in the hydrosphere,

Table 8
Acute toxicity of chlorinated hydrocarbons to marine organisms
(Concentrations expressed as mg/l)

	96 h LC 50 to Dab (flat-fish)	48 h LC 50 to Barnacle nauplii	EC 50 to Unicellular algae
Trichloroethylene	16	20	8
Perchloroethylene	5	3.5	10.5
Trichloroethane	33	7.6	5
Chloroform	28	—	—
Carbon tetrachloride	~50	—	—
Hexachlorobutadiene	0.45	0.87	—
Ethylene dichloride	115	188	340
Propylene dichloride	61	53	50

since transfer reactions between hydrosphere and atmosphere occur rapidly [26]. Oxidation can easily be demonstrated by introducing a few mg/l of the organochlorine compound into a sealed quartz flask and exposing the latter out of doors. Monitoring the organic residue shows that the mean half-lives of the chlorine-substituted ethylenes lie in the range 6–12 weeks, and of the chlorine-substituted methanes and ethanes in the range 10–33 weeks. These experiments are naturally influenced by diurnal and climatic variations of temperature and incident solar radiation, and the half-lives are reproducible only to within ± 50 per cent. Nonetheless, they serve to show that the simpler aliphatic organochlorines do not have the high persistence associated with the chlorinated insecticides and PCB, nor on the other hand are they sufficiently reactive to give rise to photo-chemical smog, a view confirmed by the work of M. F. Brunelle *et al.* [27].

Similar experiments have been carried out exposing the flask to radiation from a xenon arc, suitably filtered to remove radiation below 290 nm, taken as the lower limit of tropospheric solar radiation. Under these conditions of constant radiation flux and temperature it has been found in a number of cases that the order of the reaction with respect to the halo-organic compounds is fractional, tending to zero at the higher (100 mg/l) initial concentrations and to unity at the lower concentrations (0.1 mg/l). At the much lower concentrations (ng/l) found in the troposphere we can—at least to a first approximation—assume a first-order reaction with respect to the halo-organic compounds.

The kinetic pattern observed does not appear to arise from heterogeneous reactions, since packing the reaction vessel with quartz wool has a negligible effect on half-life. It can, however, be explained in terms of initial attack on the halo-organic compounds by some transient species present in the troposphere, possibly by active photolysis products of such species as nitrogen peroxide, ozone, or chlorine, known to be present in the troposphere at concentrations very similar to those of the halo-organic compounds. Deliberate addition of these inorganic species in the xenon arc experiments can

accelerate the decay rate, even when the inorganic material is present in much less than stoichiometric equivalence. The implication is that, because of the excess of halo-organic compounds over trace inorganic species present in the outdoor flask experiments, the latter do not represent a true microcosm of the troposphere. In that case, the half-life ranges quoted above are probably over-estimated.

We have also identified the degradation products arising from xenon arc exposure. For the most part these are simple inorganic species (CO , CO_2 , H_2O , HCl) already present in the atmosphere; in some cases (CCl_4 , CH_2Cl_2) molecular chlorine can also be formed. Only tri- and perchloroethylene yield relatively stable chloro-organic intermediates, the di- and trichloroacetyl chlorides, with minor amounts of phosgene. The latter rapidly hydrolyses to CO_2 and HCl , but the chloroacetyl chlorides will enter the hydrosphere as the di- and trichloroacetate anions, which have very long chemical half-lives at environmental temperatures. However, we have already noted the microbial breakdown in sea water of both these anions, complete oxidation occurring during a 20-day incubation period. It thus appears that not only are the simple chloroaliphatic compounds not particularly persistent, but their degradation products are simple species commonly found in the environment.

Conclusion

From evidence so far available we conclude that several chloroderivatives of methane, ethane, and ethylene are very widely distributed in the environment at a level of concentration of the order of 1 part in 10^9 . The particular compounds are chloroform, carbon tetrachloride, trichloroethylene, perchloroethylene, and trichloroethane. The assumption that the last three occur as a result of chemical manufacturing processes is tenable, but the occurrence of the first two may also be due to unidentified geochemical processes. All these compounds are fairly rapidly degraded in the environment to carbon dioxide, water, and chloride ion, and there is no evidence for their significant bio-accumulation, via the food chains, to higher trophic levels.

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