

Evaporation Rates and Reactivities of Methylene Chloride, Chloroform, 1,1,1-Trichloroethane, Trichloroethylene, Tetrachloroethylene, and Other Chlorinated Compounds in Dilute Aqueous Solutions

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■ To estimate the persistence of low-molecular-weight chlorinated hydrocarbons in natural water bodies, we carried out laboratory studies on the evaporation and reaction rates of the title compounds at the 1-ppm level in water under ambient conditions. All five compounds had evaporated to the extent of 50% in less than 30 min and to 90% in less than 90 min when stirred (200 rpm) in water at ~25°C in an open container. Addition of various contaminants (clay, limestone, sand, salt, peat moss, and kerosine) to the water had relatively little effect on the chlorinated compounds' evaporation or disappearance rates. The hydrolytic-oxidative reaction half-lives for the title compounds in sealed ampules were ~6–18 months. These data indicate that 1-ppm concentrations of low-molecular-weight chlorinated hydrocarbons would not persist in agitated natural water bodies due to evaporation.

The fate of chlorinated methanes, ethanes, and ethylenes which may be discharged to the environment has been discussed briefly in the literature (1–6). An important question in this regard is whether these compounds persist in natural water bodies. Reports have appeared from several laboratories (1, 2, 7–9) that low concentrations of these chlorinated compounds have been detected in river and ocean water. Three natural modes by which these materials could dissipate from natural water bodies are evaporation, adsorption on soils, and chemical reaction (hydrolysis, oxidation). Other modes also may exist such as microbial degradation, but we studied only the former three modes under simulated environmental conditions for the four important chlorinated compounds in use today as solvents, methylene chloride (CH_2Cl_2), 1,1,1-trichloroethane (CH_3CCl_3), trichloroethylene ($\text{CHCl}=\text{CCl}_2$), and tetrachloroethylene ($\text{CCl}_2=\text{CCl}_2$), and also for chloroform (CHCl_3). In addition, evaporation rates from water were determined for 22 other chlorinated methanes, ethanes, ethylenes, propanes, and propylenes.

As far as we are aware no data have been published on the rate at which these four major chlorinated materials evaporate from dilute aqueous solutions. However we observed earlier in work on analytical methods that, qualitatively, the concentrations of 1-ppm aqueous solutions of these compounds decreased significantly within several hours. Since all of these compounds are rather stable chemically, it appeared that the decrease in their concentrations was due to evaporation, even though the initial concentra-

tions were well below the solubility limits. A report (10) on calculations of evaporation rates of related compounds from aqueous solution also predicted rapid losses by this route. We are unaware of any adsorption studies of these chlorinated compounds on soils.

Nearly all of the data reported on the reactivity of these chlorinated compounds with water were obtained at temperatures well above ambient temperatures. CH_2Cl_2 hydrolyzed slowly at elevated temperatures to hydrogen chloride, formaldehyde, formic acid, methyl chloride, methanol, and carbon monoxide (11–15). CH_3CCl_3 , with an extrapolated half-life of 6.9 months at 25°C (16), gave mainly acetic and hydrochloric acids along with a minor amount of vinylidene chloride (16–21). $\text{CHCl}=\text{CCl}_2$ was reported to resist hydrolysis at 100°C (16, 18, 20, 22–24); oxygen accelerated the decomposition rate (20, 22, 23). The products from dilute solution hydrolysis or oxidation have not been reported. $\text{CCl}_2=\text{CCl}_2$ was very unreactive hydrolytically at 150°C in the absence of oxygen (16, 18, 20, 23); the decomposition was accelerated by oxygen (23). Trichloroacetic and hydrochloric acids have been reported as products (25).

Experimental

Evaporation Studies. The hollow fiber-mass spectroscopic method of analysis has been described previously (26). Solutions which contained 1.0 ppm (weight basis) each of the five chlorinated compounds were prepared as follows: CHCl_3 (0.67 ml), CH_3CCl_3 (0.75 ml), $\text{CHCl}=\text{CCl}_2$ (0.68 ml), $\text{CCl}_2=\text{CCl}_2$ (0.62 ml), and CH_2Cl_2 (0.75 ml) were made up to 100.0 ml with methanol. A 0.10-ml aliquot of this solution was made up to 1000.0 ml with purified water. Five liters of deionized water were purified by stirring with 50 grams of Witco 718 charcoal. Attempts to prepare these solutions without the methanol were not reproducible. Qualitatively, the evaporation rates of the chlorinated compounds were nearly the same in the presence or absence of methanol.

The silicone rubber hollow fiber probe and a 200-rpm stainless steel shallow pitch propeller stirrer were positioned inside a 250-ml Pyrex beaker. The solution of the chlorinated compounds in water (200 ml, solution depth ~65 mm before stirring the solution) was poured into the beaker, and, after starting the stirrer, mass spectra were scanned after 1 min and periodically thereafter. The maximum peak height attained was considered to be equivalent to 1.0 ppm, and the subsequent concentrations were determined from the peak heights by assuming a linear relationship between peak height and concentration (26). The five chlorinated compounds were determined at the following

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m/e values: CHCl_3 , 83; CH_2Cl_2 , 84; CH_3CCl_3 , 97 (corrected for the contribution of the m/e 95 isotope peak due to the fragmentation of $\text{CHCl}=\text{CCl}_2$); $\text{CHCl}=\text{CCl}_2$, 130; $\text{CCl}_2=\text{CCl}_2$, 164. The solutions were at room temperature ($\sim 25^\circ\text{C}$), but were not in a constant temperature bath.

The sealed systems were stirred magnetically in a 250-ml Erlenmeyer flask (200 ml of solution) closed with a Teflon-covered rubber stopper. The hollow fiber probe was inserted through the stopper. The additives were introduced into the sealed system after the ion peaks had reached their maximum intensity and had leveled off for 2 or 3 min. The flask was lowered from the stopper around the probe for 0.5 min to carry out the addition. The blank runs also were opened for 0.5 min to have a valid comparison.

The evaporation rates of the other 22 chlorinated compounds from water were determined in a similar manner. Groups of 2 to 4 of the compounds were determined simultaneously in the same solution.

Reactivity Studies. The solution which contained 1.00 ppm each of CH_2Cl_2 , CHCl_3 , CH_3CCl_3 , $\text{CHCl}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$ was prepared as described in the previous section except that the water was purged with air for 15 min just prior to the addition of the chlorinated compounds. Aliquots (15 ml) of this solution were placed in 22-mm i.d. $\times$ 53-mm (after sealing the tube) quartz tubes and 18-mm i.d. $\times$ 150-mm (after sealing the tube) Pyrex tubes. The ice-cooled tubes, previously constricted at the neck, were sealed. The solutions occupied 28% of the volume of the quartz tubes and 51% of the volume of the Pyrex tubes.

The Pyrex tubes were placed in a light-proof container and kept in the laboratory at $\sim 25^\circ\text{C}$. These tubes were shaken every week or two. The quartz tubes were placed horizontally in a tray on the roof of the laboratory where they were exposed to the maximum amount of sunlight available. The tubes were washed to remove soot and (or) snow and shaken once a week for a period of one year. The temperature range of these tubes was estimated to be $\sim 20^\circ$ to $\sim 40^\circ\text{C}$ by periodic readings of a thermometer in the tray. Tubes were removed periodically for analysis.

Analyses were carried out as described above. The solutions were stirred in an open beaker, and spectra were scanned at 0.5, 1.0, 2.0, 3.0, and 4.0 min. The maximum peak heights attained (usually at 0.5–2.0 min depending on the compound) were taken as proportional to the concentration of that compound. A standard solution of 1.00 ppm of each of the five compounds was freshly prepared as above, except that the water was not aerated, and determined each time along with the unknown samples. An indication of the reproducibility of the analyses can be seen from the following two runs on freshly prepared standard solutions. Both samples were analyzed on the same day, one at the beginning of a set of analyses and the other at the end. The first number in each set is the m/e value, the next the peak height for the first standard, and the last the peak height for the second standard: 83, 135, 132; 84, 100, 98; 97, 106, 108; 130, 165, 165; 164, 128, 119. A standard for each compound analyzed had to be used since the permeabilities of the fiber (and probably the spectrometer sensitivity) to the various compounds were not always in the same ratio.

Results and Discussion

Evaporation Studies. The rates of evaporation of CH_2Cl_2 , CHCl_3 , CH_3CCl_3 , $\text{CHCl}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$ from water without any other additives were determined three times over a two-week period under conditions which were as nearly alike as possible. Typical data are shown in Figure 1. The evaporation rates of all five chlorinated compounds were nearly the same during any one run. The time

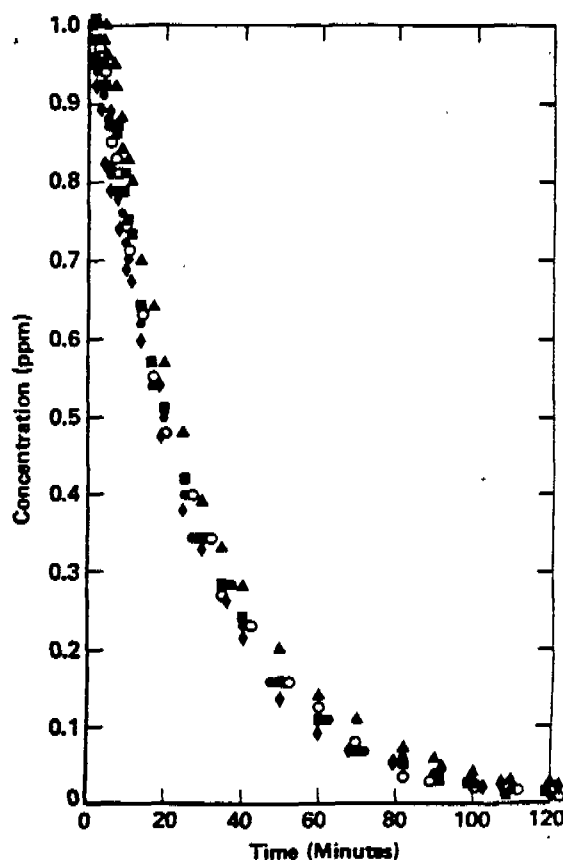


Figure 1. Evaporation rates of CH_2Cl_2 ($\diamond$), CHCl_3 ($\bullet$), CH_3CCl_3 ($\circ$), $\text{CHCl}=\text{CCl}_2$ ($\blacksquare$), and $\text{CCl}_2=\text{CCl}_2$ ($\blacktriangle$) from water

required for the chlorinated compound concentrations to be reduced by 50% varied from 21 ± 4 min to 26 ± 3 min, and to be reduced by 90% the time varied from 66 ± 6 min to 85 ± 5 min among the three runs (Table I). These variations apparently were due to some uncontrolled variable(s) in the experiments. The amount of water which evaporated from the solutions during these runs was not measured, but in blank runs an average value of 20 g/day was observed. The mass spectrometer sensitivity changed with time, and the appearance of the hollow fiber itself was altered, depending on the type of additives in the water which were brought into contact with the fiber in between these three standard runs. For these reasons it was deemed desirable to compare the effects of additives in the solution on the solvent evaporation rate only with the standard run closest in time to the additive experiment.

By using a sealed system, we showed that the loss of the chlorinated compounds, attributed to evaporation, could not have been due to depletion of these compounds through the hollow fiber sample probe into the mass spectrometer. There was no loss of the chlorinated compounds ($< 5\%$) within 2 hr.

The stirring speed had a marked effect on the evaporation rates. With no stirring, except for 15 sec every 5 min, the time required for 50% depletion was $> \sim 90$ min. The 15-sec stirring was required for proper operation of the hollow fibers.

Mackay and Wolkoff (10) have developed Equation 1 for

$$\tau = \frac{12.48 GP_w C_{12}}{10^6 EP_{12} M_i} \quad (1)$$

predicting the evaporation rate of slightly soluble organic compounds from water. In Table II are shown the solubility, vapor pressure, partition coefficients, and calculated and experimental half-lives for evaporation of five chlorinated compounds. In Equation 1, τ is the half-life in days,

Table I. Evaporation Rates of Chlorinated Compounds from Dilute Aqueous Solution

Compound	Time for evaporation from water, min	
	50%, τ	90%
CH ₂ Cl ₂	27	91
CH ₂ Cl ₂ , ^a	19	60
	19	67
	24	80
CHCl ₃ , ^a	18	62
	20	68
	25	83
CCl ₄	29	97
CH ₂ CH ₂ Cl	21	79
CH ₂ CHCl ₂	22	109
CH ₂ ClCH ₂ Cl	29	96
CH ₂ CCl ₃ , ^a	17	63
	20	65
	23	80
CH ₂ ClCHCl ₂	21	102
CH ₂ ClCCl ₃	43	>120
CHCl ₂ CHCl ₂	56	>120
CHCl ₂ CCl ₃	48	>140
CCl ₃ CCl ₃	45	>120
CH ₂ =CHCl	26	96
CH ₂ =CCl ₂	22	89
CHCl=CHCl (cis)	18	64
CHCl=CHCl (trans)	24	83
CHCl=CCl ₂ , ^a	19	63
	21	63
	24	80
CCl ₂ =CCl ₂ , ^a	24	72
	25	86
	28	90
CH ₂ ClCHClCHCl ₂	51	>120
CH ₂ ClCCl ₂ CH ₂ Cl	47	>120
CH ₂ =CHCH ₂ Cl	27	89
CH ₂ =CClCH ₂	29	110
CHCl=CHCH ₂	16	59
CH ₂ =CClCH ₂ Cl	20	68
CHCl=CHCH ₂ Cl	31	98
(cis and trans)		
CHCl=CClCH ₂ Cl	49	>140

^a Results of three separate runs are given.

G is the weight of water in grams (200 for our case), P_w is the partial vapor pressure of water (23.76 mm for our case), C_w is the solubility (mg/L) of the solute in water, E is the weight in grams of water which evaporates/day (20 for our case), P_s is the vapor pressure of the pure solute, and M_i is the molecular weight of the solute. The experimental evaporation half-lives are much longer than the calculated values. Part of the discrepancy may be due to nonuniform concentrations that arise because of depletion of the solute near the surface of the water. Uniform concentrations of solute at all times are required for Equation 1 to be valid. Faster stirring would likely lead to smaller τ values since slower stirring led to larger τ values. The sevenfold variation in the calculated τ values between the compounds predicted to evaporate the slowest, CH₂Cl₂, and the fastest, CH₃CCl₃, is not reflected in the experimental values. However the general conclusion of Mackay and Wolkoff (10) that the evaporation rates would be rapid is borne out.

To obtain more ecologically significant data, we studied the rate of evaporation or disappearance of the five chlorinated compounds under conditions more nearly like those found in the environment. The presence of sodium chloride

Table II. Physical Properties, Partition Coefficients, and Evaporation Rates from Water of Chlorinated Compounds

Compound	Solubility in water, ppm ^a (25°)	Vapor pressure, mm Hg ^a (25°)	Partition coefficient ^b		Evaporation half-life, min, τ	
			Calcd ^c	Found ^d	Calcd ^e	Found
CH ₂ Cl ₂	19,800	426	0.10	0.11	2.3	21 ± 3
CHCl ₃	7,950	200	0.16	0.13	1.4	21 ± 4
CH ₂ CCl ₃	1,300	123	0.68	—	0.34	20 ± 3
CHCl=CCl ₂	1,100	74	0.48	—	0.48	21 ± 3
CCl ₂ =CCl ₂	400	19	0.41	0.50	0.56	27 ± 3

^a Data from "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed., Interscience Publishers, New York, N.Y., 1964 (in some cases by interpolation). ^b $K = C_{air}/C_{water}$. ^c Conc'n in sat'd air/conc'n in sat'd water. ^d Data from E. J. Brown, Dow Chemical Co., Plaquemine, La. ^e Calculated from Equation 1.

(3.0%, as in seawater) may have caused about a 10% decrease in the chlorinated compound evaporation rate at 40% chlorinated compound depletion. The effect, if any, therefore, appears to be slight.

Addition of dry, granular bentonite clay (500 ppm) appeared to increase the rate of disappearance of the chlorinated compounds by 33% at 20 min (~65% solute depletion) (Figure 2). However, when the clay was allowed to stand in contact with purified water for several days and then added to a solution of chlorinated compounds, there was no change in rate from the standard (~50% solute depletion at 20 min). To determine whether the apparent increase in the disappearance rate with dry clay was due to adsorption of the material onto the clay surface, we carried out two closed system experiments where the only solute loss could be by adsorption. Dry clay (375 ppm) was intro-

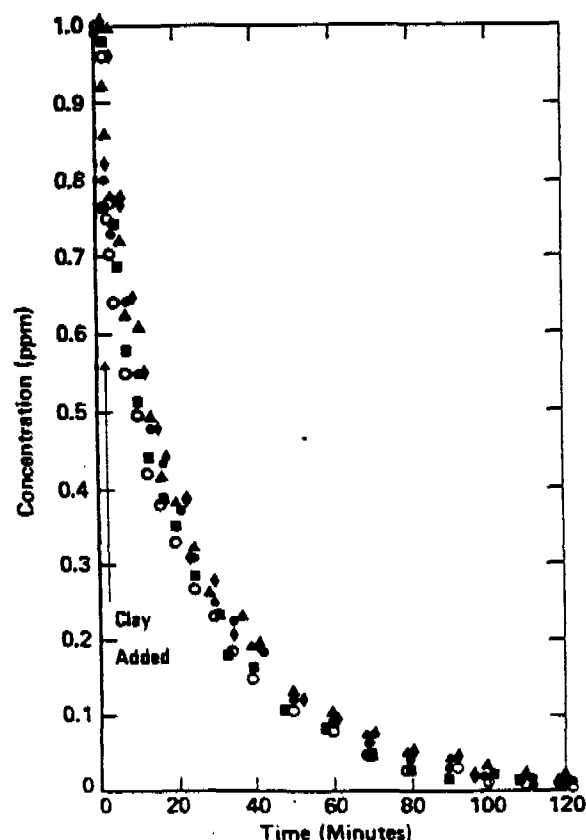


Figure 2. Disappearance rates of CH₂Cl₂ (♦), CHCl₃ (○), CH₃CCl₃ (■), CHCl=CCl₂ (▲), and CCl₂=CCl₂ (△) from water which contained 500 ppm bentonite clay (initially dry)

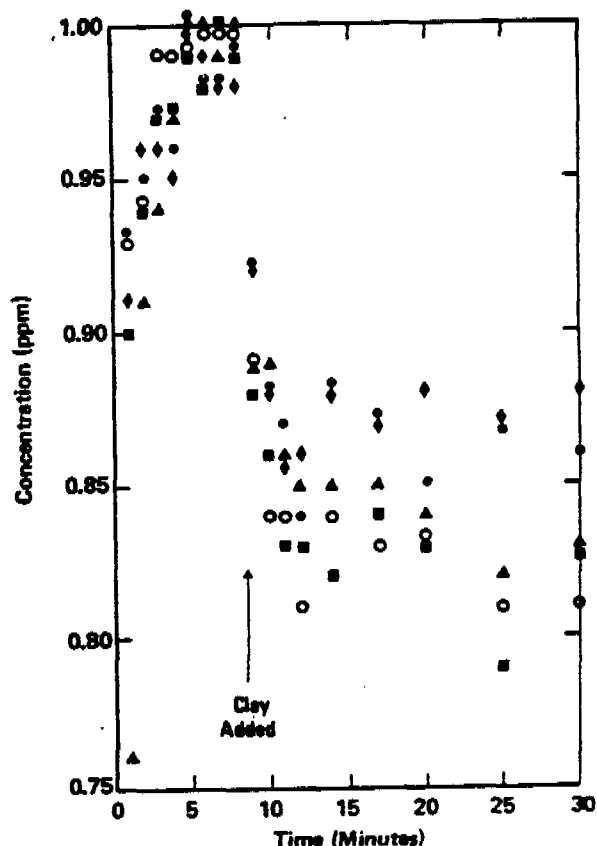


Figure 3. Disappearance rates of CH_2Cl_2 ($\blacklozenge$), CHCl_3 ($\bullet$), CH_3CCl_3 ($\blacksquare$), $\text{CHCl}=\text{CCl}_2$ ($\blacktriangle$), and $\text{CCl}_2=\text{CCl}_2$ ($\blacktriangledown$) from water which contained 375 ppm bentonite clay (initially dry) in a sealed system

duced into a sealed solution; in 10 min there was a ~10% adsorption of the chlorinated compounds by the clay (Figure 3) compared to a blank. When the amount of clay added to the closed system was doubled (750 ppm) there was 22% solute adsorption after 30 min. There was no further solute adsorption after this time. There appears to be relatively little selectivity among the various chlorinated compounds in the adsorption process.

Addition of dry powdered dolomitic limestone (500 ppm) caused a 50% depletion of the chlorinated compounds in 20 ± 2 min and a 90% depletion in 70 ± 2 min. Thus, these compounds probably are adsorbed slightly by the limestone, but without any selectivity as also was observed with bentonite clay. Ottawa silica sand (500 ppm) did not affect the disappearance rates of the chlorinated materials; 50% depletion was observed in 27 ± 2 min and 90% depletion in 88 ± 3 min.

Peat moss (~500 ppm), added to simulate a high organic content in water, appeared to accelerate the disappearance rate initially, but then to slow it down toward the end of the run (90% depletion in 120 ± 15 min). In the sealed system, ~500 ppm of peat moss adsorbed ~40% of the chlorinated compounds in 10 min. At longer times, no further solute removal was noted. Thus ~500 ppm of peat moss rapidly removed up to ~0.4 ppm each of the five chlorinated compounds when originally present at the 1-ppm level, and may account for the slight acceleration of solute loss in the open system at short times. The decrease in the rate of disappearance of the chlorinated materials at longer time periods may be due to a gradual release to the solution of these chlorinated compounds by the peat moss.

Propylene glycol (15 ppm), added to simulate a chemical plant waste effluent, had no appreciable effect on the evaporation rate of the five chlorinated compounds.

Addition of 1 ml of kerosene to the surface of the water

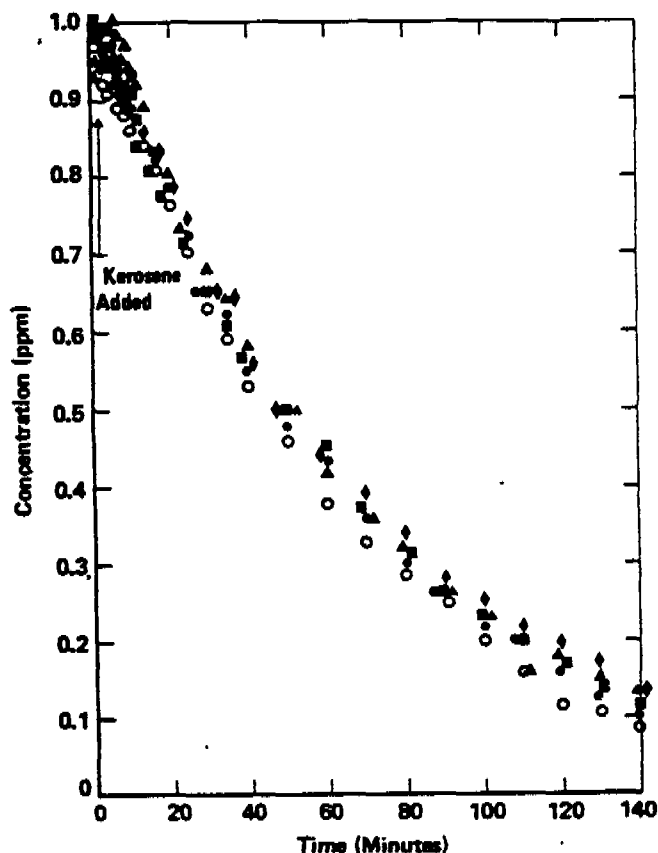


Figure 4. Disappearance rates of CH_2Cl_2 ($\blacklozenge$), CHCl_3 ($\bullet$), CH_3CCl_3 ($\blacksquare$), $\text{CHCl}=\text{CCl}_2$ ($\blacktriangle$), and $\text{CCl}_2=\text{CCl}_2$ ($\blacktriangledown$) from water under a layer of kerosene

caused a decrease in the rate of disappearance of the chlorinated compounds from water (Figure 4). After 30 min, the loss of chlorinated materials from water covered with a layer of kerosene, was ~47% less than that from the blank. In the sealed system, ~17% of the chlorinated compounds was removed by the kerosene in 5 min (only $\text{CHCl}=\text{CCl}_2$ and $\text{CCl}_2=\text{CCl}_2$ were measured because the ion peaks from the kerosene in the mass spectrum interfered with measurements of the other solvents). Since the kerosene retarded the disappearance rate in the open system, it follows that the chlorinated compounds pass into the air above the water at a faster rate than they pass into the kerosene layer above the water.

A 2.2 ± 0.1 mph wind (from a fan) across the surface of the water caused an increase in the evaporation rate as expected. After 20 min the solute evaporation was ~17% greater with the wind than in still air (0 ± 0.2 mph wind).

At $1\text{--}2^\circ\text{C}$ the solute evaporation rate was slower than at $\sim 25^\circ\text{C}$. After 30 min there was a 28% decrease in the amount of the chlorinated compounds which had evaporated from water at $1\text{--}2^\circ\text{C}$ compared with the blank at $\sim 25^\circ\text{C}$.

Thus the chlorinated compounds, CH_2Cl_2 , CHCl_3 , CH_3CCl_3 , $\text{CHCl}=\text{CCl}_2$, and $\text{CCl}_2=\text{CCl}_2$, evaporate rapidly from slowly stirred water in the presence of various natural and added contaminants. None of the contaminants examined changed the disappearance rate more than a factor of two. Thus evaporation is probably the major pathway by which these solvents are lost from water.

The rates of evaporation of the 22 chlorinated compounds mentioned in the introduction are listed in Table I. The concentration of all of these compounds decreased tenfold within about 3 hr. In general, the higher the molecular weight the slower the material evaporated although numerous exceptions were noted.

Table III. Decomposition Rates of Chlorinated Compounds in Aerated Water in the Dark and in Presence of Sunlight

Compound	Concentration, ppm						Dark Reaction	
	0 mo		6 mo ^a		12 mo ^b			
	Dark	Light	Dark	Light	Dark ^c	Light ^c	k, d mo ⁻¹	t _{1/2} , mo
CH ₂ Cl ₂	1.00	1.00	0.76 ^c	0.79	0.68, 0.70	0.64, 0.64	0.039 ± 0.008	~18
CHCl ₃	1.00	1.00	0.73	0.75	0.63, 0.65	0.56, 0.57	0.045 ± 0.008	~15
CH ₃ CCl ₃	1.00	1.00	0.46	0.46	0.26, 0.29	0.32, 0.25	0.12 ± 0.01	6
CHCl=CCl ₂	1.00	1.00	0.68	0.56 ^c	0.44, 0.48	0.21, 0.30	0.065 ± 0.001	10.7
CCl ₂ =CCl ₂	1.00	1.00	0.63	0.52	0.35, 0.41	0.24, 0.25	0.079 ± 0.002	8.8

^a June 22, 1971, to December 22, 1971. ^b June 22, 1971, to June 22, 1972. ^c Duplicate tubes run. ^d Calculated on the assumption of a first order reaction. ^e The second decimal place in each analysis is somewhat uncertain.

With respect to the recent findings of some of these compounds in drinking water (27), we note that the concentrations found were generally well below those used in this study. It is difficult to predict loss rates from water at these very low concentrations from our data. Also the amount of agitation and free air space above the water may be less in some portions of a drinking water system than in our experimental system.

Reactivity Studies. These results are shown in Table III. The half-lives for the saturated compounds were nearly the same in either sunlight or the dark. The half-lives of the olefinic materials were 1.5 to 2 times shorter in sunlight than in the dark. The products of these reactions were not determined but are probably the same as those noted in the introduction. Dichloroacetic acid and hydrogen chloride are likely products from CHCl=CCl₂ (28).

The concentration of oxygen in air-saturated water is 8.3 ppm at 25° (29). The concentrations of oxygen and the five chlorinated compounds in water were as follows: O₂, 260 μM; CH₂Cl₂, 11.8 μM; CHCl₃, 8.4 μM; CH₃CCl₃, 7.5 μM; CHCl=CCl₂, 7.6 μM; CCl₂=CCl₂, 6.0 μM. Thus there was about a sixfold molar excess of dissolved oxygen compared to the total amount of chlorinated compounds. In addition, the air space above the solution in the quartz tubes contained ~90 times as much oxygen as was present in the saturated solution. Thus, there was a great excess of oxygen present which would have been available for complete oxidation of all the chlorinated compounds present. Since these compounds are highly volatile from water, it is possible that part of the reaction occurred in the vapor phase.

Sunlight had the greatest effect on the reactivities of the unsaturated compounds, CHCl=CCl₂ and CCl₂=CCl₂. These findings are in agreement with predictions based on vapor phase photolysis studies where it was shown that these two compounds disappeared when irradiated with long wavelength light in the presence of nitric oxide or nitrogen dioxide (30-35). Thus, most of the disappearance of CHCl=CCl₂ and CCl₂=CCl₂ was probably due to oxidation and was probably free radical in character. In contrast, sunlight had relatively little effect on the reactivities of CH₂Cl₂, CHCl₃, and CH₃CCl₃. CH₂Cl₂ and CH₃CCl₃ in the vapor phase in air are known to be very unreactive with long wavelength light in the presence of nitric oxide or nitrogen dioxide (35). Thus the major reactions of CH₂Cl₂, CHCl₃, and CH₃CCl₃ probably were ionic hydrolyses.

From kinetic studies carried out at higher temperatures, it is known that the hydrolysis of CH₃CCl₃ (16) is faster than that of CH₂Cl₂ (13). This is also true at ~25°C. The extrapolated 6.9 months half-life for hydrolysis of CH₃CCl₃ at 25°C is in good agreement with our value of six months (Table III). Our experimental half-life for hydrolysis of CH₂Cl₂ of ~18 months is in poor agreement with the extrapolated value of ~680 years at 25°C. However it was re-

ported that the apparent activation energy for hydrolysis of CH₂Cl₂ was not constant, but was a function of temperature (13). Thus the reaction at 25°C may proceed by a different mechanism from that at 100-150°C, and the rate constant extrapolated to 25°C from data at 100-150°C may be meaningless.

Acknowledgment

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Literature Cited

- (1) Murray, A. J., Riley, J. P., *Nature*, **242**, 37-8 (1973).
- (2) Murray, A. J., Riley, J. P., *Anal. Chim. Acta*, **65**, 261-70 (1973).
- (3) Farber, H. A., "Chlorinated Solvents and the Environment," paper presented at AAPCC Symposium, Atlanta, Ga., January 10-11, 1973; "Textile Solvent Technology—Update '73," pp 6-12.
- (4) Hester, N. E., Stephens, E. R., Taylor, O. C., *J. Air Pollut. Control Assoc.*, **24**, 591-5 (1974).
- (5) Lillian, D., Singh, H. B., *Anal. Chem.*, **46**, 1060-3 (1974).
- (6) Simmonds, P. G., Kerrin, S. L., Lovelock, J. E., Shair, F. H., *Atmos. Environ.*, **8**, 209-16 (1974).
- (7) Kleopfer, R. D., Fairless, B. J., *Environ. Sci. Technol.*, **6**, 1036-7 (1972).
- (8) Lovelock, J. E., Maggs, R. J., Wade, R. J., *Nature*, **241**, 194-6 (1973).
- (9) Tardiff, R. G., Deinzer, M., "Toxicity of Organic Compounds in Drinking Water," paper presented at Fifteenth Water Quality Conference, Urbana-Champaign, Ill., February 7-8, 1973.
- (10) Mackay, D., Wolkoff, A. W., *Environ. Sci. Technol.*, **7**, 611-4 (1973).
- (11) Roka, K., Ger. Patent 467,234 (1922); *Chem. Abstr.*, **23**, 2191 (1929).
- (12) Carlisle, P. J., Levine, A. A., *Ind. Eng. Chem.*, **24**, 146-7 (1932).
- (13) Fells, L., Moelwyn-Hughes, E. A., *J. Chem. Soc.*, 1326-33 (1958).
- (14) Fells, L., *Fuel Soc. J. Univ. Sheffield*, **10**, 26-35 (1959); *Chem. Abstr.*, **54**, 12748-9 (1960).
- (15) Hardie, D. W. F., "Kirk-Othmer Encyclopedia of Chemical Technology," 2nd ed., Vol. 5, pp 111-19, Interscience Publishers, New York, N.Y. 1964.
- (16) Stowe, S. C., Raley, C. F., Dow Chemical Co., Midland, Mich., private communication, 1960.
- (17) Britton, E. C., Reed, W. R., U.S. Patent 1,870,601 (1932); *Chem. Abstr.*, **26**, 5578 (1932).
- (18) Ryan, R. F., Dow Chemical Co., Midland, Mich., private communication, 1954.
- (19) Howard, W. L., Burger, J. D., Dow Chemical Co., Freeport, Tex., private communication, 1965.
- (20) Howard, W. L., Moore, T. L., *ibid.*, 1966.
- (21) Howard, W. L., *ibid.*, 1967.
- (22) Carlisle, P. J., Levine, A. A., *Ind. Eng. Chem.*, **24**, 1164-8 (1932).
- (23) Shepherd, C. B., "Chlorine, Its Manufacture, Properties, and Uses," J. S. Sconce, Ed., pp 375-428, Reinhold Publishing Corp., New York, N.Y., 1962.
- (24) Archer, W. L., Dow Chemical Co., Midland, Mich., private communication, 1970.
- (25) Ref. 15, pp 195-203.

- (26) Westover, L. B., Tou, J. C., Mark, J. H., *Anal. Chem.*, **46**, 568-71 (1974).
- (27) *Chem. Eng. News*, p 18, April 28, 1975.
- (28) Dilling, W. L., Tefertiller, N. B., submitted for publication.
- (29) Lange, N. A., "Handbook of Chemistry," 10th ed., p 1091, McGraw-Hill, New York, N.Y., 1961.
- (30) Hamming, W. J., "Photochemical Reactivity of Solvents," paper presented at Aeronautic and Space Engineering and Manufacturing Meeting, Society of Automotive Engineers, Los Angeles, Calif., October 2-6, 1967.
- (31) Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., "Photochemical Reactivity of Trichloroethylene and Other Solvents," paper presented at 158th American Chemical Society National Meeting, New York, N.Y., September 7-12, 1969; Abstracts of Papers, ORPL 38.
- (32) Wilson, K. W., Doyle, G. J., Hansen, D. A., Englert, R. D., *Amer. Chem. Soc., Div. Org. Coat. and Plast. Chem. Preprints*, **29**, No. 2, 445-9 (1969).
- (33) Wilson, K. W., "Photoreactivity of Trichloroethylene," Summary Report for Manufacturing Chemists Association on SRI Project PSC-6687, Stanford Research Institute, South Pasadena, Calif., September 1969.
- (34) Altshuller, A. P., Bufalini, J. J., *Environ. Sci. Technol.*, **5**, 39-64 (1971).
- (35) Dilling, W. L., Bredeweg, C. J., Tefertiller, N. B., submitted for publication.

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Molecular Composition of Secondary Aerosol and its Possible Origin

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■ Several aerosol samples were collected during a diurnal period of inversion and aerosol production in Pasadena, Calif. Particles were collected in two size ranges: particles of diameters less than 1-2 μm and particles of diameters greater than 1-2 μm . Computer-controlled mass spectrometric thermal analysis was used for molecular organic and inorganic analysis. The results described in this paper are semiquantitative with a precision of $\pm 30\%$ on a relative comparison basis, but accuracies may range up to two times for some of the organic secondary aerosols with estimated response factors. X-ray fluorescence and atomic absorption were used to obtain inorganic elemental composition. The diurnal variation in aerosol composition was studied for the two size ranges and used to postulate the primary and/or secondary origin of the aerosol. The most probable precursors for the measured secondary aerosol products are presented in this paper and postulated from the results of smog chamber studies and the gaseous composition of gasoline, auto exhaust, and ambient air samples. The primary pollutants included alkanes, polycyclic aromatics, substituted phenols, and several elements. Organic secondary pollutants included acids, aldehydes, alcohols, chlorides, and nitrates. Inorganic secondary pollutants identified included sulfates, nitrates, and chlorides. The results are discussed with respect to meteorological conditions.

It has been suggested by several investigators that photochemical aerosol produced from reactions of hydrocarbons and oxides of nitrogen are major pollutants in Southern California (1). Insight into processes occurring to form aerosols have been made using smog chambers. The composition of aerosols formed during the photochemical oxidation of several alkanes in a smog chamber was first determined by Wilson et al. (2). O'Brien et al. (3, 4) have also found organic acids and nitrates in aerosols, formed from the smog chamber reactions of octadiene and NO_x . To

date, few measurements on the molecular organic composition of atmospheric aerosols have been made during periods of atmospheric stability and photochemical aerosol formation. Recently, new techniques have been established by Schuetzle (5-7) using computerized high-resolution mass spectrometry, which make such a study more feasible. Semiquantitative results on submicrogram quantities of pollutants were possible using this technique, which allowed pollutant concentrations to be followed using 2- or 3-hr sampling intervals.

The sampling of air particulate matter was made in conjunction with the 1972 California Aerosol Characterization Study (ACHEX) (8). Aerosol samples were collected over a two-month period from September 19, 1972, to November 25, 1972. Due to unusual meteorological conditions, there were few days during which the atmosphere was stable enough to allow the formation of photochemical aerosols. Fortunately, there was one three-day period of sampling, during which meteorological conditions were ideal for studying the molecular composition of aerosols before, during, and after photochemical smog production.

Experimental

Atmospheric Sampling. Air sampling techniques for particulate and gaseous pollutants were used which were compatible with a sampling probe designed for the mass spectrometer system. A single-stage impactor was designed which collects particles greater than 1-2 μm on 0.30-in. diam gold plates. Gold was used as a sampling medium because of its nonreactivity to acid aerosols. The remainder of the particulate matter was collected on a glass fiber filter. A mobile sampling van was equipped with a 20-ft mast upon which the sampling assembly could be hoisted and directed into the prevailing winds (Figure 1). After sampling, the filter and impactor plates were stored at dry ice temperature in glass containers sealed with a Teflon gasket to prevent losses due to volatilization and interreaction of pollutants. (Total particle concentrations were determined using a 37-mm Nuclepore filter.) Impactor plates and Nuclepore filters were weighed to $\pm 2 \mu\text{g}$ before and after sampling. Submicron particle concentrations were determined from the difference between total particle concentrations and the supermicron particle concentrations. An integrat-

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