OFFICE OF TOXIC SUBSTANCES REV. 7/27/82

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TOXICITY OF METHYLCHLOROFORM TO FRESHWATER ORGANISMS

Chemical Name (100 per name)	25	CAS No. (10)	26
METHYL CHLOROFORM		71-55-6	

AK 5/31/83

111

8782110 64

D555

TOXICITY OF METHYLCHLOROFORM TO FRESHWATER ORGANISMS

February 23, 1979

by

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ABSTRACT

Methylchloroform was evaluated for acute toxicity on a cold water (12°C) fish representative, a warm water (22°C) fish representative and a macroinvertebrate species in static water tests. The cold water fish species used was rainbow trout (*Salmo gairdneri* Richardson). The warm water fish species used was bluegill (*Lepomis macrochirus* Rafinesque). An aquatic invertebrate representative, *Daphnia magna* Straus, was tested at 20°C.

The 96-hour LC50 value for rainbow trout was 52(46-59)* mg/L and for the bluegill 58 (51-68) mg/L. The 48-hour LC50 for daphnids was 11.2 (9.7-12.8) mg/L.

*95% Confidence Interval

INTRODUCTION

Methylchloroform was evaluated for acute toxicity on a cold water (12°C) fish representative, a warm water (22°C) fish representative and a macroinvertebrate species in static water tests. The cold water fish species used was rainbow trout (*Salmo gairdneri* Richardson). The warm water fish species used was bluegill (*Lepomis macrochirus* Rafinesque). The acute fish and macroinvertebrate toxicity tests were run in static water for the purpose of pesticide registration.

MATERIALS & METHODS

Sample

The sample of methylchloroform used for these acute toxicity tests was identified as methylchloroform pesticide grade, Lot TA0#1681. Analysis of this product shows 96.37% of the active ingredient, 1,1,1-trichloroethane.

The test solutions were prepared just prior to the start of the test using methanol as the carrier solvent.

Water

Raw Lake Huron water was dechlorinated with activated carbon filtration prior to testing. This water exhibits chemical characteristics in the following ranges: dissolved oxygen (D.O.)[a], 7.4 mg/L; pH 8.0[b]; total alkalinity, 91.5 mg/L as $CaCO_3$; total hardness, 128 mg/L as $CaCO_3$; specific conductivity, 200 µmhos/cm; and resistivity[c], ~570 ohms/cm. Other data for raw Huron water prior to dechlorination by activated carbon are in Table I[2].

The static water acute toxicity tests follow the test methods described in the EPA publication, "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians"[3].

Fish

1. Rainbow Trout

The test fish, rainbow trout, were reared in our laboratory. Trout eggs for rearing were received from Mt. Lassen Trout Farm, Red Bluff, CA, on 7/25/78. When tested, the fish had an average weight of 1.1 g and an average standard length of 38.3 mm. The average loading per aquarium was 0.55 g/L.

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[a]Yellow Springs Instruments Model 54 - Oxygen Meter

[b]Sargent-Welch pH Meter - Model LS

[c]Yellow Springs Instruments Model 31 - Conductivity Bridge

TABLE I

RAW LAKE HURON WATER ANALYSES

Turbidity as ppm SiO_2	2.3
Color, APHA	<3
Alkyl benzene sulfonate, ppm	<0.1
Arsenic, ppm	<0.005
Barium, ppm	*(1.0)
Cadmium, ppm	*(0.01)
Chlorine, ppm	7.0
Chromium ppm	*(0.05)
Copper, ppm	0.03
Cyanide, ppm	*(0.01)
Fluoride, ppm	0.07
Iron, ppm	0.1
Lead, ppm	*(0.05)
Magnesium ppm	7.0
Manganese, ppm	*(0.05)
Nitrate, ppm	*(0.1)
Phenols, ppm	*(0.001)
Selenium, ppm	*(0.01)
Silver, ppm	*(0.05)
Sulfate, ppm	12
Total dissolved solids, ppm	110
Zinc, ppm	*(0.3)
PCB's, ppm	*(0.02×10^{-3})
Mercury, ppb	*(5)

*Parameter was below the limits of detection which are included in parentheses.

The fish were kept in a 16-hr light/8-hr dark cycle. A synthetic diet[4] was fed to all specimens. Feeding was stopped three days prior to the test to empty the digestive tract. Test fish were placed into the bioassay vessels 24 hours before adding the test compound.

Tests were conducted by placing 8 liters of dechlorinated Lake Huron water in each vessel, a round glass aquarium measuring 22 cm deep with a 24.5 cm diameter, adding the fish, then aerating. If no deaths occurred in 24 hours, aeration was stopped and the test solution added with two liters of water for mixing, making a total of 10 liters. Any vessel containing dead fish was cleaned, reset, and observed for another 24 hours prior to compound addition. Constant temperature water troughs maintained the temperature at 12°C ± 1°C. Ten fish were exposed to each concentration of the compound. Observations were made and recorded, and dead fish removed at the same time for four days (96 hours). Death was used for the effect criterion.

2. Bluegill

Bluegill were received from the Hebron National Fish Hatchery, Hebron, Ohio, on September 9, 1978. When tested, the average weight of each fish was 1.1 g and an average standard length of 33.7 mm. The average loading per aquarium was 0.53 g/L.

The bluegill were acclimated for ten days at 22°C before testing. They were kept in 16-hr light/8-hr dark cycle. The same synthetic diet was fed to all fish during acclimation.

Testing procedures of bluegill follow that described for the trout except temperature was maintained at 22 ± 1°C.

Daphnids

The static acute toxicity consisted of exposing daphnids reared in our laboratory to various concentrations of the material being tested in dechlorinated Lake Huron water at a temperature of 20°C.

Stock solutions of methylchloroform were prepared using methanol as a carrier solvent. The concentration of the stock solution was 200 mg/mL. Stocks older than 48 hours were discarded.

The required amount of stock solution was combined with sufficient dechlorinated Lake Huron water to make a final volume of 200 mL in the 250 mL test beaker. A control was set using dechlorinated Lake Huron water. Because methanol was used in the stock solution, a second series of beakers were exposed containing the largest amount of solvent used in any concentration to act as a solvent control. The concentration of solvent in any beaker did not exceed 0.5 mL/L. Ten first instar daphnids were then added to each beaker and the beakers set in a constant temperature incubator. Three beakers were used for each exposure concentration

and each control. The standard exposure time was 48 hours. Mortality data were recorded at 24 and 48 hours. Death was defined as no response to a gentle prodding. Dead daphnids were not removed from any beaker during the test.

Statistical Calculations

For each set of mortality data, the LC values and their 95% confidence intervals are given. The LC 50 is the estimated concentration of the test material at which 50% of the test organisms are dead at a specified time interval. This value is determined using Finney's probit analysis[5] with a computer program.

RESULTS

Fish

The 96-hour LC 50 values of the two test species are: rainbow trout, 52 (46-59) mg/L, and bluegill, 58 (51-68) mg/L.

Statistical data for the different fish species used in these acute toxicity tests are included in Table II for rainbow trout data and in Table III for bluegill data. The 24, 48, 72 and 96 hour data is the same for the rainbow trout, therefore, only the 96 hour data is shown in Table II. No mortality occurred in the control fish.

Daphnids

The 48-hour LC 50 for daphnids was 11.2 (9.7-12.8) mg/L. The 48-hour LC 50 with its 95% confidence interval and slope were determined on *Daphnia magna* using the computer program for Finney's probit analysis. The 24 and 48-hour data is shown as Table IV. The 24-hour data is insufficient for a valid probit analysis. Control daphnids exhibited a 7% mortality during the test. This meets the acceptable criteria of the EPA publication "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians."[3]

Wanda M. McCarty 2/26/79

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TABLE II

TOXICITY OF METHYLCHLOROFORM TO RAINBOW TROUT

AND STATISTICAL DATA

METHYL CHLOROFORM STATIC ACUTE RAINBOW TROUT 12C 11-21-78 96 HR

CONCENTRATION UNITS ARE MG/ML

PROBIT SLOPE(USING LOG CONC.)= 11.21. 95% C.I.=(5.69, 16.72)

CHI-SQUARE FOR LACK OF FIT IS 2.49 WITH 3 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 7.81

THERE WERE 10 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
100.00	2.00	100.	*****	8.186
75.00	1.88	90.	6.282	6.786
56.00	1.75	80.	5.841	5.364
42.00	1.62	10.	3.718	3.964
32.00	1.51	0.	*****	2.640

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	39.95	29.75	45.45
50	51.97	45.74	59.18
90	67.60	59.33	91.36

TABLE III

TOXICITY OF METHYLCHLOROFORM TO BLUEGILL AND STATISTICAL DATA

METHYL CHLOROFORM STATIC ACUTE BLUEGILL 22C 11-21-78 24 HR

CONCENTRATION UNITS ARE MG/ML

PROBIT SLOPE(USING LOG CONC.)= 17.05. 95% C.I.=(7.01, 27.09)

CHI-SQUARE FOR LACK OF FIT IS 0.02 WITH 2 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 5.99

THERE WERE 10 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
100.00	2.00	100.	*****	7.993
75.00	1.88	80.	5.841	5.862
56.00	1.75	10.	3.718	3.699
42.00	1.62	0.	*****	1.568

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	56.16	42.18	62.14
50	66.76	59.56	74.68
90	79.35	71.77	109.20

METHYL CHLOROFORM STATIC ACUTE BLUEGILL 22C 11-21-78 48 HR

CONCENTRATION UNITS ARE MG/ML

PROBIT SLOPE(USING LOG CONC.)= 8.24. 95% C.I.=(4.92, 11.95)

CHI-SQUARE FOR LACK OF FIT IS 16.53 WITH 4 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 9.49

THERE WERE 10 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
100.00	2.00	100.	*****	6.615
75.00	1.88	80.	5.841	5.586
56.00	1.75	10.	3.718	4.540
42.00	1.62	0.	*****	3.511
32.00	1.51	10.	3.718	2.538
24.00	1.38	0.	*****	1.508

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	44.53	32.05	52.04
50	63.08	55.15	74.24
90	91.06	77.33	129.98

TABLE III (Cont.)

TOXICITY OF METHYLCHLOROFORM TO BLUEGILL AND

STATISTICAL DATA

METHYL CHLOROFORM STATIC ACUTE BLUEGILL 22C 11-21-78 72 HR

CONCENTRATION UNITS ARE MG/ML

PROBIT SLOPE(USING LOG CONC.)= 8.09. 95% C.I.=(4.50, 11.68)

CHI-SQUARE FOR LACK OF FIT IS 10.82 WITH 4 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 9.49

THERE WERE 10 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
100.00	2.00	100.	*****	6.679
75.00	1.88	80.	5.841	5.668
56.00	1.75	20.	4.159	4.642
42.00	1.62	0.	*****	3.631
32.00	1.51	10.	3.718	2.675
24.00	1.38	0.	*****	1.665

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	43.08	31.06	50.42
50	62.01	53.66	72.30
90	89.27	75.72	126.94

METHYL CHLOROFORM STATIC ACUTE BLUEGILL 22C 11-21-78 96 HR

CONCENTRATION UNITS ARE MG/ML

PROBIT SLOPE(USING LOG CONC.)= 7.90. 95% C.I.=(4.49, 11.31)

CHI-SQUARE FOR LACK OF FIT IS 6.79 WITH 4 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 9.49

THERE WERE 10 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
100.00	2.00	100.	*****	6.842
75.00	1.88	90.	6.282	5.855
56.00	1.75	20.	4.159	4.853
42.00	1.62	10.	3.718	3.867
32.00	1.51	10.	3.718	2.934
24.00	1.38	0.	*****	1.948

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	40.24	29.11	47.20
50	58.42	50.52	68.08
90	84.89	71.96	119.65

TABLE IV

TOXICITY OF METHYLCHLOROFORM TO DAPHNIDS

AND STATISTICAL DATA

METHYL CHLOROFORM STATIC ACUTE DAPHNIA MAGNA 20C 12-19-78 24 HR

CONCENTRATION UNITS ARE MG/L

PROBIT SLOPE(USING LOG CONC.)= 2.20. 95% C.I.=(1.52, 2.89)

CHI-SQUARE FOR LACK OF FIT IS 36.92 WITH 3 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 7.81

THERE WERE 30 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
56.00	1.75	67.	5.430	6.278
32.00	1.51	97.	6.834	5.743
18.00	1.26	83.	5.967	5.193
10.00	1.00	33.	4.570	4.630
5.60	0.75	3.	3.166	4.076

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	3.66	1.88	5.78
50	14.72	11.32	18.64
90	56.10	39.28	104.17

METHYL CHLOROFORM STATIC ACUTE DAPHNIA MAGNA 20C 12-19-78 48 HR

CONCENTRATION UNITS ARE MG/L

PROBIT SLOPE(USING LOG CONC.)= 5.19. 95% C.I.=(3.68, 6.69)

CHI-SQUARE FOR LACK OF FIT IS 2.98 WITH 3 DEGREES OF FREEDOM
CRITICAL VALUE(ALPHA = .05) IS 7.81

THERE WERE 30 OBSERVATIONS AT EACH CONCENTRATION

CONC.	LOG(CONC.)	% RESPONSE	OBS. PROBIT	EXP. PROBIT
56.00	1.75	100.	*****	8.634
32.00	1.51	97.	6.834	7.374
18.00	1.26	90.	6.282	6.078
10.00	1.00	43.	4.832	4.754
5.60	0.75	3.	3.166	3.448

LC	ESTIMATE	LOWER C.I.	UPPER C.I.
10	6.32	4.73	7.57
50	11.19	9.65	12.84
90	19.69	16.54	25.93

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1. Gerard, D. S., Texas Division, Quality Assurance, Nov. 17, 1978.

2. Hunemorder, E. J., et al. [redacted]

3. Committee on Methods for Toxicity with Aquatic Organisms. 1975. Methods for Acute Toxicity Tests with Fish, Macro-invertebrates, and Amphibians. Ecological Research Series, EPA-660/3-75-009.

4. Mehrle, P. M., Mayer, F., and Johnson, W. Aquatic Toxicology and Hazard Evaluation, ASTM STP634, 1976.

5. Finney, D. J. 1952. Statistical methods in biological assay. Cambridge University Press.

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Contractor

Doc Type: • R.I • U.P • H.E.A.S.D B.D. 3.U H.S F.N

Doc Title: INDUSTRIAL HYGIENE SURVEY AT THE STYRON SPECIALTY PRODUCT PLANT MICHIGAN DIVISION MIDLAND MICHIGAN 1978

Chemical Name (100 per name)	CAS No. (10)
CHLOROTHENE	71-55-6

AK 5/21/83

1/1

878211065

D-565

R & D REPORT

DOW CHEMICAL U.S.A.

RESTRICTED: for use within The Dow Chemical Company only.

[redacted]

DATE ISSUED: January 29, 1979

[redacted]

DEPARTMENT: HDBS, USA Industrial Hygiene Laboratory

[redacted]

TITLE: INDUSTRIAL HYGIENE SURVEY AT THE STYRON* SPECIALTY PRODUCTS PLANT, MICHIGAN DIVISION, MIDLAND, MICHIGAN, 1978

AUTHOR(S) (SIGNATURE): S. L. S. Dombrowski [signature] 2/1/79

REVIEWER'S (SIGNATURE): E. J. Schneider [signature] 2/1/79

DESCRIPTIVE SUMMARY WITH CONCLUSIONS: (Include in this space references to data books, and to earlier related reports, patents and publications.)

Employee exposures to all materials measured were acceptable for normal operations [redacted]

[redacted]

bjd

[redacted]

[redacted]

*Trademark of The Dow Chemical Company

CRI NUMBER

[redacted]

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PROBLEM

An industrial hygiene survey was requested by plant supervision to evaluate employee exposures during operation of the Styron Specialty Products Plant of the Michigan Division. [redacted]

CONCLUSIONS & RECOMMENDATIONS

1. Employee time-weighted average (TWA) exposures to all materials measured were acceptable for normal operations.

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PROCESS DESCRIPTION

[redacted]

EVALUATION CRITERIA

Dow Industrial Hygiene Guides (IHGs) are concentrations of airborne substances to which nearly all employees may be repeatedly exposed throughout a working lifetime without adverse effect. IHGs are established by the health professionals of the Dow Industrial Health Board for chemicals (raw materials, intermediates, byproducts, wastes, and products) handled within The Dow Chemical Company. Published exposure criteria are available for many industrial chemicals; examples include the Threshold Limit Values (TLVs) of the ACGIH (American Conference of Governmental Industrial Hygienists), the ANSI standards of the American National Standards Institute, and the OSHA standards of the Occupational Safety and Health Administration of the United

States Department of Labor. For most of these chemicals, the Industrial Health Board has adopted the published exposure criteria as the Dow IHGs. In a few instances the IHG set by the Industrial Health Board differs from the published exposure criteria. In establishing IHGs for chemicals which lack published exposure criteria, the Industrial Health Board considers toxicological information, occupational exposure data, and medical experience.

Industrial Hygiene Guides do not represent fine lines between safe and dangerous exposures. As the name indicates, IHGs are properly used as guides for plant design and for evaluating occupational exposures. IHGs for gases and vapors are usually expressed in parts per million (ppm, volume/volume; for dusts, fumes, aerosols, and mists, IHGs are usually expressed in milligrams of contaminant per cubic meter of air (mg/m^3).

Most IHGs are time-weighted average (TWA) concentrations for an 8-12 hour workday and a 40 hour workweek. Limited excursion exposures to concentrations exceeding the IHG are permitted, provided that the TWA exposure for the entire workday is acceptable and the consequences of exposure, within the excursion limit, are minimal and reversible. For most chemicals, excursion limits are calculated from the IHGs and the excursion factors recommended by the ACGIH. Ceiling IHGs are assigned to those materials which cause significant or irreversible effects at concentrations exceeding the IHG. For these chemicals, no excursion exposures are allowed.

The following exposure criteria currently apply to the airborne contaminants measured during this survey:

Compound or Material	IHG	Excursion Limit
Methylene chloride	200 ppm	300 ppm
Toluene	100 ppm	150 ppm
Chlorothene	350 ppm	500 ppm

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AIR SAMPLING & ANALYSIS METHODS

Methylene chloride, [redacted] toluene, [redacted] Chlorothene [redacted] were collected on glass tubes containing 1 gram of Pittsburgh coconut base (PCB) charcoal each. The samples were obtained using battery operated pumps to draw air through the tubes. Samples taken for 6-8 hours to evaluate TWA exposures were collected at flowrates of 90-100 cc/minute using a soap bubble flowmeter for the calibrations (Figure 5). Short term samples taken to evaluate peak exposures were collected at flowrates of 1-2 liters/minute determined using a calibrated rotameter.

The charcoal tubes were submitted to the Industrial Hygiene Laboratory where the charcoal was desorbed in dry ice chilled carbon disulfide and analyzed by gas chromatography. The analysis was performed by [redacted] of the Industrial Hygiene Laboratory and the results were reported in reports [redacted]

PRESENTATION OF DATA

Table 1 is a summary of employee exposures to chemical and physical agents by various job classifications. The degree of exposure, hazard rating and measured results are shown.

The measured concentrations that appear in Table 1 are 6-8 hour TWA exposures determined by personal monitoring unless noted otherwise. Many materials on the table have exposures that were judged acceptable (JA). These judgments were based on physical properties, toxic properties, frequency and duration of use, and the specific job classifications, operations and how they apply to the exposures. In all cases the employees' consequences of overexposure were low and a potential hazard to health was minimal.

Employee exposures to methylene chloride, [redacted] toluene, [redacted] Chlorothene and Dowtherm A were also evaluated. Personal sampling was performed for the job classifications of the laboratory technician, plant mechanic, spare, and head operator. These job classifications were chosen to represent the highest exposure potentials for each of the respective materials evaluated. The 6-8 hour TWA exposures to all materials for all the job classifications monitored were found to be acceptable (Table 3). Job classifications for which personal monitoring was not performed were judged acceptable based on these results.

In addition to personal sampling, excursion sampling was performed to evaluate peak exposures. [redacted] toluene, [redacted] were the airborne materials evaluated in this manner. [redacted]

Toluene exposures ranged from less than 0.01 ppm up to less than 0.63 ppm and all excursion exposures were "acceptable" (Table 4).

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Figure 1.

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Figure 3.

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Figure 4.

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Figure 5. AIR SAMPLING SET UP USED FOR AIRBORNE VAPOR SAMPLING AT THE MICHIGAN DIVISION STYRON SPECIALTY PRODUCTS PLANT, JULY 6-7, 1978

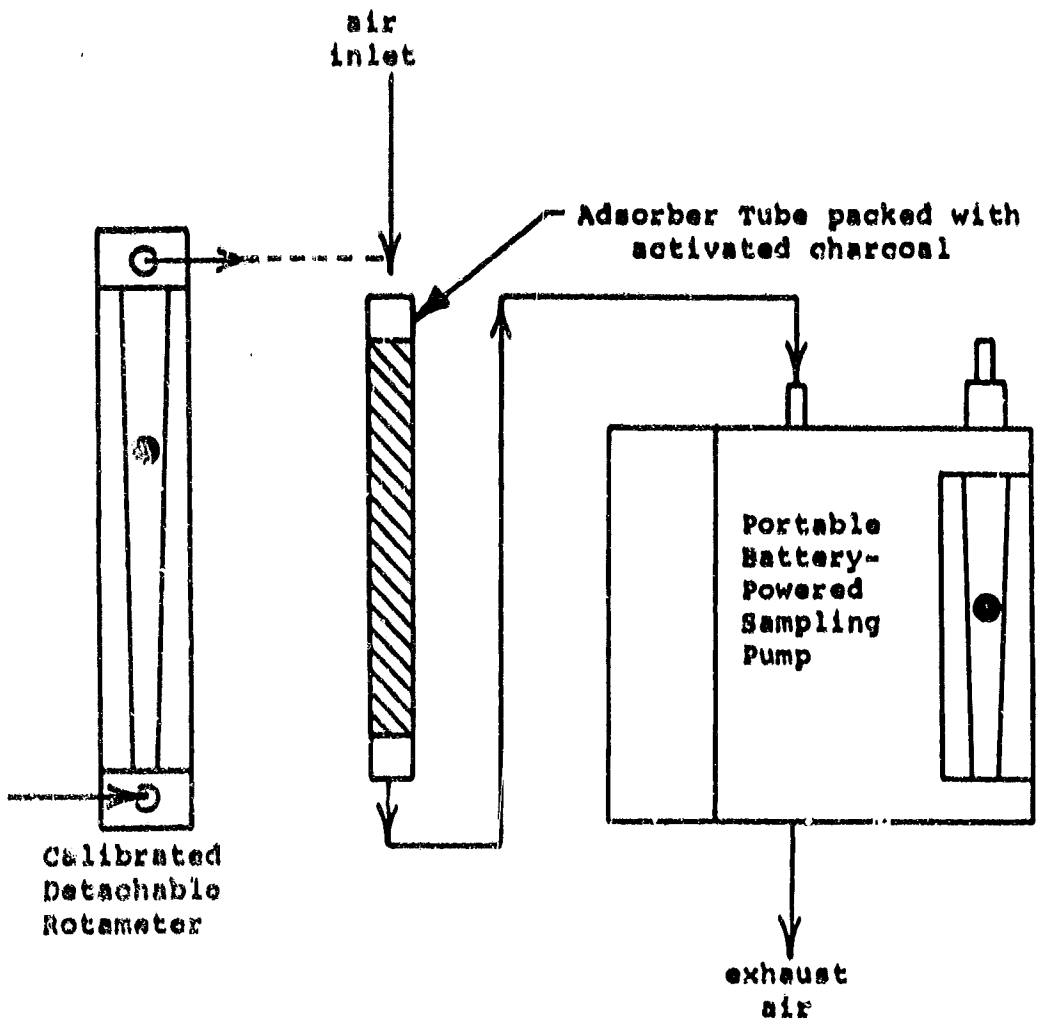

Table 1. SUMMARY OF INDUSTRIAL HYGIENE HAZARD EVALUATIONS PERFORMED AT THE NEOCHEM DIVISION STORE SPECIALTY PRODUCTS PLANT IN 1978

Chemical/Physical Agent	Industrial Hygiene Guide	Head Operator, Spare, Alternate			Plant Mechanic			General Foreman			Prod. Dev. Eng., Prod. Supr., Prod. Supt., Janitor/Housekeeper			Office Supr.			Lab Technician		
		Degree of Exposure	Hazard Rating	Measured Exposure	Degree of Exposure	Hazard Rating	Measured Exposure	Degree of Exposure	Hazard Rating	Measured Exposure	Degree of Exposure	Hazard Rating	Measured Exposure	Degree of Exposure	Hazard Rating	Measured Exposure	Degree of Exposure	Hazard Rating	Measured Exposure
Chloroform [illegible]	550 ppm	II	4	2A	II	2	*.4 ppm	II	4	2A	II	4	2A	II	4	2A			
[illegible]																			
1,2,4-Trichlorobenzene	5 ppm	I	5	2A	I	4	2A	II	5	2A	II	5	2A	I	5	2A	II	[illegible]	2A
Toluene	200 ppm	II	3	0.08 ppm	I	4	2A	II	5	2A	II	5	2A	I	5	2A	III	1	0.[illegible] ppm
[illegible]																			
Methylene chloride	500 ppm																III	[illegible]	0.[illegible] ppm

*50 mg/m^3 - suggested IHG based on workplace data

**Represent average of concentrations samples from Table 2

(1) 2A - judged acceptable
(2) ND - not detected at analytical sensitivity [illegible]
(3) NE - not evaluated

Table 2.

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Table 3 RESULTS OF 6-8 HOUR PERSONAL MONITORING DONE IN THE MICHIGAN DIVISION STYRON SPECIALTY PRODUCTS PLANT, A. A. MICH, JULY 6-7, 1978. RESULTS ARE REPORTED IN PARTS PER MILLION (VOLUME/VOLUME IN AIR)

Job Classification	Date	Sample Number	Methylene Chloride	Toluene	Chloroform
Lab technician	07/06/78	14	ND*(0.07)	0.04	--
Lab technician	07/05/78	20	ND(0.17)	0.11	--
Plant Mechanic	07/05/78	1	ND(0.15)	ND(0.03)	1.4
Spare "Lab"	07/06/78	24	--	0.01	--
Spare "Lab"	07/05/78	3**	--	ND(0.11)	--
Spare "Grinder"	07/06/78	21	--	0.04	--
Head Operator	07/06/78	22	--	0.21	--
Head Operator	07/05/78	2**	--	ND(0.16)	--
IDLH			2000	1000	3500
EXCURSION LIMIT			500	150	500

*ND - not detected at analytical sensitivity indicated in parenthesis
**Pumps failed after 4 hour sample time
***NE - not established

Table 4. RESULTS OF EXCURSION SAMPLES TAKEN DURING SPECIFIC OPERATIONS OCCURRING IN 131C WING, JULY 6-7, 1978. RESULTS ARE REPORTED IN PARTS PER MILLION (VOLUME/VOLUME IN AIR)

Date	Sample Description	Sample Number	Toluene
07/05/78	Breathing zone of head operator while taking first stage solids sample	4	ND*(0.63)
07/05/78	Breathing zone of head operator while taking second stage solids sample	5	ND(0.63)
07/05/78	Breathing zone of head operator while cleaning rubber grinder	6	ND(0.17)
07/05/78	Breathing zone while operator checks restart rubber grinder	7	ND(0.59)
07/05/78	Breathing zone while head operator obtained [redacted] sample	8	ND(0.25)
07/05/78	Area sample while operator opened valve mixing tank #2	9	ND(0.27)
07/05/78	Area sample next to extruder bath die end [redacted]	10	ND(0.01)
07/05/78	Area sample taken on desk top in panel room	11	0.01
07/06/	Area sample taken out in process area directly south of panel room	12	0.01
07/06/78	Breathing zone sample while pumping catalyst	13	0.06
07/06/78	Breathing zone sample while draining recycle from run off tank	15	0.09
07/06/78	Breathing zone sample while alternate changed feed filter	19	0.06
	TLV		100
	EXCURSION LIMIT		150

*ND - not detected at analytical sensitivity indicated in parenthesis

OFFICE OF TOXIC SUBSTANCES REV. 7/27/82

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Microfiche No. (7) 206125 | No. of Pages 2

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Organ. Name DOW CHEM CO

Dept/Div —

P.O. Box | Street No./Name

City MIDLAND | State MI | Zip 48640 | Country

MID No. (7) | D & B No. (10)

Contractor

Doc Type • R.I • U.P • H.E.A.S.D 8.D. SU H.S F.N

Doc Title SOLVENT OPTION TO MEET EPA AIR QUALITY REGULATIONS

Chemical Name (100 per name) 1,1,1-TRICHLOROETHANE | CAS No. (10) 71-55-6

A.K. 5/31/83

D-567

8782/1066

SOLVENT OPTION TO MEET EPA AIR QUALITY REGULATIONS

Solvent-borne coatings for the rail car industry are currently being confronted with air quality regulations mandating severe reductions in volatile organic compound (VOC) emissions. The EPA guidelines for the emissions of VOC relative to this industry are a maximum of 3.6 pounds of solvent per gallon of paint at the spray gun.[1] In the past several years, new coating technologies, such as high solids and waterborne, have been developed to meet these regulations. An additional option is the use of compliance chlorinated solvents, 1,1,1-trichloroethane and methylene chloride. The physical properties of these solvents often allows them to be formulated in many coatings, using the same resins and pigments. These solvents are fast drying solvents and, with no flash point, may reduce fire hazards. Coatings formulated with chlorinated solvents will be similar in overall performance to conventional solvent-borne coatings, using the same press resins, using the same application methods, and providing additional flexibility in meeting air compliance.

Air Quality Regulations

As a part of its guidelines of VOC emissions, the EPA has published a list of compounds which have been shown to be of negligible photochemical reactivity (or nonsmog producing), and thus do not need to be regulated or inventoried as VOC. The exempt compounds are methane, ethane, trichlorotrifluoroethane, 1,1,1-trichloroethane, and methylene chloride. Due to this definition, the solvents--1,1,1-trichloroethane and methylene chloride--may be placed in coating formulations and not increase the VOC emission rate.[1-7]

The exemption of these two solvents from air regulations is not present in some states. Following the EPA guidelines, however, over 80% of those states having VOC emissions plans, have exempted 1,1,1-trichloroethane, and over 60% have exempted methylene chloride (See Table 1).

Toxicological Data

1,1,1-Trichloroethane and methylene chloride are among the few solvents that have been widely investigated from a toxicity standpoint due to their history of use in areas such as metal degreasing, adhesives, and aerosol formulations. Studies in the area of mutagenicity, teratogenicity, carcinogenicity, chronic toxicity, epidemiology, and environmental effects lead to a favorable position for these products. Specifically, evaluation of the data to date does not indicate carcinogenic, mutagenic, or teratogenic risk to humans.

As a means of providing a guideline of health hazard, the Occupational Safety and Health Administration (OSHA) has set the current maximum exposure levels for [illegible] compounds. For the solvents of interest, these are shown in [illegible] These values are the maximum concentrations of the compound allowed for an eight-hour per day, five-day per week average known as time-weighted average (TWA). It can be seen that the TWA for chlorinated solvents [illegible] as conventional solvents.

[illegible] level is a federal CTG guideline; state VOC emission levels may be [illegible] 02 [illegible]

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DEC 20 1982

Flammability

Due to concerns of flammability, chlorinated solvents have replaced flammable solvents to reduce fire hazards of coatings. Both 1,1,1-trichloroethane and methylene chloride show no flash point by either open or closed cup test methods, in contrast to conventional solvents, as can be seen in Table 3.

In many cases, chlorinated solvents, particularly methylene chloride, have been responsible for a substantial increase in flash point, thus reducing the risk of fire. Use of such coatings may lead to increased insurability.

Physical Properties

Aside from the flammability characteristics of these two solvents, a knowledge of the physical properties is important in formulating. The physical properties of various solvents are given in Table 4.

1,1,1-Trichloroethane and methylene chloride both have specific gravities of 1.3, which enables pigments to be suspended longer and makes resuspension easier after settling. These solvents have high evaporation rates. These rates may be controlled by the addition of slower evaporating cosolvents, such as a glycol ether.

The solubility parameters are similar to conventional solvents, such that with cosolvents, they may be used to formulate with many common resin families, such as alkyds, acrylics, epoxies, urethanes, chlorinated rubber, etc.

The chlorinated solvents should not be grossly contaminated with water. Chlorinated solvents thermally degrade above 400°F to hydrochloric acid. These do not pose a problem in many rail car paint shops. The compatibility of chlorinated solvent should be evaluated in each paint operation.

In general, with low solids formulation, these solvents can replace the conventional solvents. The remaining VOC can be modified to optimize evaporation and [illegible]. With high solids formulations, the chlorinated solvents may be [illegible] thinners for viscosity adjustment.

[illegible] Equipment Not Recommended

Galvanized [illegible] coating systems should not be used with chlorinated solvent-based coating. [illegible] is a reactive metal and has been shown to be an [illegible] material of construction for equipment handling a variety of materials [illegible], alcohols, soil water, acids, bases, halogenated solvents, [illegible] formulated with these products. Aluminum should not be used as material of construction for pumps, valves, nozzles, and other [illegible] equipment, nor should it be used for storage containers for chlorinated solvents or chlorinated solvent-based formulations.

Recommended materials of construction are regular steel, stainless steel, or black [illegible]. Some spray equipment manufacturers have pumps and many other

components currently available which are compatible with 1,1,1-trichloroethane and methylene chloride. Replacing aluminum equipment is a limitat for chlorinated solvents. As with any new compliance coating option, some component changes are required.

Cost/Effectiveness

1,1,1-Trichloroethane-based or methylene chloride-based coatings are expected to be slightly higher in cost compared to low solids coatings. They should be cost competitive with low VOC compliance systems, such as high solids coatings. Several factors should be considered when comparing cost of different compliance coating systems. These are:

1. Coating Performance - The coatings formulated with chlorinated solvent are essentially equivalent to the low solid coatings. This is due to formulating with the same resins and pigments. These coatings can achieve desirable film properties, such as good gloss and adhesion. Because of solvency characteristics, it has been noted that these coatings have high dirt tolerance and adhere better to poorly cleaned surfaces.

2. Equipment Costs - The chlorinated solvents usually require no change in fluid handling equipment but, as mentioned earlier, aluminum equipment should not be used. With these coatings, high pressure spray equipment and in-line heaters are not required. Due to evaporation rate, coatings may not require baking ovens to decrease dry time.

3. Energy - The chlorinated solvent-based coatings may be applied and allowed to dry essentially at ambient temperatures, therefore, minimizing the need for heaters. The viscosity adjustment available with this compliance solvent option eliminates the need for in-line heaters, thus an energy savings.

4. Training - Retraining of shop personnel and changes made to application procedures are expected when converting to low VOC coatings. Chlorinated solvent coatings may be applied as low solids coatings were; therefore, minimal retraining is required. Additional information regarding to solvent characteristics and proper handling should be given to all those involved with these solvents.

Certainly other cost considerations may prove important, but these vary from location to location.

Conclusion

1,1,1-Trichloroethane and methylene chloride as paint solvents offer the railroad industry the ability to comply with air quality regulations safely. Resin systems, familiar to the end user, can still be utilized providing a proven performance and fast dry times. There is no need for major procedural changes or extensive retraining of operators on new equipment. The use of 1,1,1-trichloroethane or methylene chloride may be the most feasible and economical means to obtain air quality compliance.

REFERENCES

1. Federal Register, 42(131), 35314, July 8, 1977.

2. "Workshop on Requirements for Nonattainment Area Plans," Environmental Protection Agency, April, 1978.

3. Gallagher, Vera, letter to J. C. Barry, "Definition of Volatile Organic Compound," Environmental Protection Agency, June 1, 1978.

4. "Control of Volatile Organic Compounds from Existing Stationary Sources; Volume 2, Surface Coating of Cans, Coils, Paper, Fabrics, Automobiles, and Light-Duty Trucks," Environmental Protection Agency, May, 1977.

5. Federal Register, 44(11), 3274, January 16, 1979.

6. Federal Register, 44(108), 32042, June 4, 1979.

7. Federal Register, 45(97), 32424, May 16, 1980.

8. Archer, W. L., and Stevens, V. L., "Comparison of Chlorinated Solvents, Aliphatic, Aromatic Oxygenated Hydrocarbons as Solvents," I&EC Product Research and Development, Vol. 16, December, 1977, Pages 319-326.

TABLE 1

STATUS OF 1,1,1-TRICHLOROETHANE AND METHYLENE CHLORIDE IN VOC SIP EXEMPTIONS

(the following data is subject to change)

	1,1,1	Methylene Chloride
Alabama	+	-
Alaska	0	0
Arizona	0	0
Arkansas	+	+
California		
Bay Area	+	+
Southcoast	+	+
Colorado[a]	-	-
Connecticut[b]	-	-
Delaware	+	+
D of Columbia	+	+
Florida	+	+
Georgia	+	-
Hawaii	0	0
Idaho	0	0
Illinois	-	-
Indiana	+	+
Iowa	0	0
Kansas	+	+
Kentucky	-	-
Louisiana	+	+
Maine	0	0
Maryland	+	-
Massachusetts	+	-
Michigan[c]	-	-
Minnesota	+	+
Mississippi	+	+
Missouri	+	-
Montana	+	-
Nebraska	+	-
Nevada	0	0
New Hampshire	+	+
New Jersey	-	-
New Mexico	0	0
New York	+	+
N. Carolina[d]	(+)	(+)
N. Dakota	0	0
Ohio	+	+
Oklahoma	+	+
Oregon	+	+
Pennsylvania[e]	+	+
Rhode Island	-	-
S. Carolina	+	+
S. Dakota	0	0
Tennessee	+	-
Texas	+	-
Utah	+	+
Vermont	-	-
Virginia	+	+
Washington	+	+
W. Virginia	0	0
Wisconsin	(+)	(+)
Wyoming	0	0

+ = Exempt
- = Not Exempt
( ) = Tentative
0 = No VOC SIP Necessary

[a]Colorado exempts for degreasing and cleaning only.
[b]Connecticut exempts for metal cleaning only.
[c]Michigan exempts both solvents for new sources only.
[d]N. Carolina's exemption is not across-the-board, but does include coating of miscellaneous metal parts and products, flat wood paneling, and graphic arts.
[e]Pennsylvania exempts for coatings, but not metal cleaning.

02/02

TABLE 2

Current Maximum Exposure Levels
of Various Solvents

Solvent	OSHA TWA 8-Hour ppm
1,1,1-Trichloroethane	350
Methylene Chloride	500
n-Hexane	500
Toluene	200
Methyl Ethyl Ketone	200
Acetone	1000
Ethyl Acetate	400

TABLE 3

Flammability Hazards

Solvents	Flash Point Open Cup (°F)	Flash Point Closed Cup (°F)	Flammable Limit In Air 20°C (Volume %) Upper	Lower
Methylene Chloride	NF	NF	None*	
1,1,1-Trichloroethane	NF	NF	10.5	8.0
n-Hexane	--	-7	6.9	1.26
Toluene	45	40	7.0	1.3
Methyl Ethyl Ketone	--	30	11.5	1.81
Methanol	54	60	36.5	6.72
Ethyl Acetate	30	24	11.0	2.26

*12-19% (volume) in air at 30°C

8782/1066

TABLE 4

Physical Properties

Solvents	bp (°C)	Sp. Heat (cal/g/°C)	Heat of Vaporization	Evaporation Rate (n-butyl Acetate) = 1
Methylene Chloride	40.0	0.24	78.7	14.6
1,1,1-Trichloroethane	74.0	0.28	56.7	6.0
n-Hexane	68.7	0.53	82.0	0.1
Toluene	110.6	0.39	86.0	1.6
Methyl Ethyl Ketone	79.6	0.498	106.0	7.7
Methanol	64.6	0.607	262.8	3.6
Ethyl Acetate	77.2	0.478	87.63	4.1

Solubility

Solvents	Solubility Parameter δ	H Bonding (k)	(g) H_2O Soluble in 100g Solvent (25°C)
Methylene Chloride	9.7	2.7	0.20
1,1,1-Trichloroethane	8.6	2.6	0.05
n-Hexane	7.3	2.1	0.01
Toluene	8.9	3.3	0.05
Methyl Ethyl Ketone	9.3	6.0	11.0
Methanol	14.6	8.6	--
Ethyl Acetate	9.1	6.2	3.3

Physical Properties

Solvents	Specific Gravity	Pounds/Gallon 20°C	dyn/cm Surface Tension
Methylene Chloride	1.336	10.98	26.52
1,1,1-Trichloroethane	1.3249	10.99	25.56
n-Hexane	0.6594	5.66	17.91
Toluene	0.860	7.26	30.00
Methyl Ethyl Ketone	0.8051	6.71	24.6
Methanol	0.7924	6.60	22.69
Ethyl Acetate	0.9020	7.51	23.9

OFFICE OF TOXIC SUBSTANCES REV. 7/27/82

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MID No. (7) 19 D & B NO. (11) 20

Contractor 21

Doc Type 22
*R.I.*W.P* MEASD BD. 9U HS EN

Doc Title 23
TOXICITY OF TRICHLOROETHANE AS COMPARED WITH OTHER CHLORINATED COMPOUNDS

Chemical Name (300 per name) 25	CAS No. (10) 26
1,1,1-TRICHLOROETHANE	71-55-6

AK 5/31/83

878211382

Biochemical Research Laboratory
THE DOW CHEMICAL COMPANY

Subject: TOXICITY OF TRICHLOROETHANE AS COMPARED WITH OTHER CHLORINATED COMPOUNDS

To

From

File
Chg.
Rec'd. 10-5-38
Fin'd. 10-6-38
By H. C. Spencer
H. C. Spencer
Checked
10-7-38

A survey of the literature reveals very little direct experimental data concerning the toxicity of trichloroethane.

Tables I and II give the relative toxicity of various chlorinated compounds as determined by Lazarew (1929) and as cited by Browning ("Toxicity of Industrial Organic Solvents"). It will be noticed that there is a difference in the relative toxicity depending on whether it is estimated by the "narcotic" action or by the "lethal" action.

Table I

Relative Toxicity of Certain Chlorinated Compounds as Estimated by "Narcosis". (Browning)

(Arranged according to increasing toxicity)

1. Ethyl chloride
2. Carbon tetrachloride
3. 1;1;1-trichloroethane
4. Ethylidene chloride
   Methylene dichloride
5. Trichloroethylene
6. Chloroform
7. Ethylene dichloride (dichloroethane)
8. Perchloroethylene
9. 1;1;2-trichloroethane
10. Tetrachloroethane
11. Pentachloroethane

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Table II.

Relative Toxicity of Certain Chlorinated Compounds as Estimated by "Lethal" Results (Browning)

(Arranged according to increasing toxicity)

1. Ethyl chloride
2. Ethylidene chloride
3. Carbon tetrachloride
4. 1:1:1-trichloroethane
5. 1:1:2-trichloroethane
6. Methylene dichloride
7. Trichloroethylene
8. Perchloroethylene
   Tetrachloroethane
9. Chloroform
10. Ethylene dichloride (dichloroethane)
    Pentachloroethane

A study of the vapor toxicity of 1:1:1-trichloroethane (methyl chloroform) on guinea pigs was made a few years ago in the Biochemical Research Laboratory (T5.3-1).
It was found that:

Animals exposed to an atmosphere 85% saturated with methyl chloroform will become unconscious in a short time. If removed to fresh air at once they will survive.

Animals exposed to an atmosphere 17% saturated with methyl chloroform show drowsiness and a definite intoxication, but remain conscious.

Two animals exposed to an atmosphere 17% saturated for 7.5 hours per day for two consecutive days showed the usual intoxication while in the chamber but recovered at once when removed. Two days after removal they appeared in excellent condition.

Table III presents data cited by McNally ("Toxicology") plus an indication of the position that trichloroethane probably holds in this table, as judged by these experimental results. For comparative purposes the approximate position of tetrachloroethane is also indicated.

Table III.

Comparative Data on Familiar Compounds (McNally).
Concentration Expressed in Volume of Gas per Million Volumes of Air (ppm).

Substance	Fatal with 5-10 minute exposure	Dangerous (toxic) 1/2 - 1 hr. exposure	Endurable 1/2 - 1 hr. exposure
Chlorine	500	50	5
Carbon disulfide	2,000	1,000	500
Tetrachloroethane *	—	—	
Benzene	20,000	7,500	3,000
Chloroform	25,000	15,000	5,000
Carbon tetrachloride	50,000	25,000	10,000
Trichloroethane*	—	—	

* = Estimated position in this table.

JR

Physical Research Laboratory
THE DOW CHEMICAL COMPANY

File
Chg.
Rec'd.
File'd. 7-12-34
By D.D.I.

Subject TOXICITY OF METHYL CHLOROFORM.

To

From

CH_3-CCl_3 $C_2H_3Cl_3$

The toxicity was determined by exposing guinea pigs to controlled concentrations of methyl chloroform vapir in air.

An atmosphere saturated with methyl chloroform will cause the animal to become unconscious in a very short time. If removed at once to fresh air the animal may survive. One animal so treated could not be revived by artificial respiration.

Animals exposed to an atmosphere 75% saturated with methyl chloroform will become unconscious in a short time. If removed to fresh air at once, they will survive.

Animals exposed to an atmosphere, 17% saturated with methyl chloroform, show drowsiness and a definite intoxication, but remain conscious.

Two animals exposed to an atmosphere, 17% saturated for 7-1/2 hours per day for two consecutive days, showed the usual intoxication while in the chamber but recover at once when removed. Two days after being removed from the chamber the last time, they appear in excellent condition.

The methyl chloroform produces anesthesia in concentrations slightly above 17% saturated. At that concentration definite narcosis is produced, but not anesthesia. 15 hrs. exposure at 17% saturation, interrupted by one rest interval of 16 hours, showed no evidence of accumulative toxic effect.

Respectfully submitted,

MR

I am an author of and have read this report comprising 2 pages with 3 pages of drawings, photographs, graphs, and checked the data herein against the original entries under Biochemical Laboratory File Number T 3.4-19-1

Signature W. K. Rose Date 9-2-45

Signature _____ Date _____

I finished typing this report on 8-31-45 comprising 2 pages and placed therewith 0 pages of drawings, photographs, graphs from an original draft given me by W. K. Rose on 8-1-45. I have placed in the plant mail 3 copies of this report for transmittal to Dale Report

Signature Jean Franck Date 8-31-45

O. R. Frick 9-19-45
Edwin Eckman 11-21-45

000006

Biochemical Research Laboratory
THE DOW CHEMICAL COMPANY

File
Chg.
Rec'd 5-9-45
Fin'd 8-8-45
Work By C.H. Geisel
C.H. Swenson

Subject RANGE FINDING TESTS RELATIVE TO THE TOXICITY OF METHYL CHLOROFORM.

To File Report Check [illegible] 9-9-45 Rept. By [illegible] 8-7-45

PROBLEM

Since the Dow Company is advertising the subject material for sale, some toxicological information was desired.

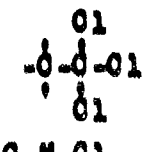
MATERIAL

Name - Methyl Chloroform
- 1,1,1-Trichloroethane

K-No. -

Formula -

Structural -



Empirical - $C_2H_3Cl_3$

Source - Texas Division
Received 6-9-45.

EXPERIMENTAL RESULTS

Acute Oral -

Doses of methyl chloroform were suspended in 5-10% gum arabic solution and fed to rats by means of a stomach tube. The material was found to be low in acute oral toxicity, doses of 5.0 g./kg. being survived.

Skin Irritation -

Ten applications of the undiluted material to both the rabbit ear and shaven belly produced only a very slight simple irritation characterized by hyperemia and exfoliation.

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CONCLUSIONS

Methyl chloroform is low in acute oral toxicity and does not possess unusual skin irritating properties.

Information relative to the vapor toxicity of this material is lacking.

Because methyl chloroform is similar in structure to other chlorinated hydrocarbons whose vapors are known to be quite hazardous, particularily upon repeated or prolonged exposure, we would recommend that this material be handled with care. Concentrations in the air having a definite odor should be avoided.

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• P.I. • L.E. • HEADQ. 8D. SU HS FN

Doc Title 23
ENVIRONMENTAL FATE OF CHLORINATED SOLVENTS - SOLUBILITY AND RATE OF EVAPORATION FROM WATER

Chemical Name (300 per name) 25	CAS No. (10) 24
1,1,1-TRICHLOROETHANE	71-55-6

A.K. 5/31/83 1A

D-600

87821386

THE DOW CHEMICAL COMPANY

March 31, 1971

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FROM: M. J. Mieta, N. B. Tefertiller, D. J. Kallio, and W. L. Dilling

SUBJECT: Environmental Fate of Chlorinated Solvents - Solubility and Rate of Evaporation from Water

In order to understand the interaction of chlorinated solvents with the environment it is necessary to know something about the dynamics of these compounds in the ecosystems of concern. For example, little useful fit is to be derived from a study of solvent metabolism by aquatic plants if the solvents transfer rapidly and irreversibly from water to air.

In order to qualitatively assess the rate of evaporation from water of the four most important chlorinated solvents (methyl chloroform, methylene chloride) the hollow fiber mass-spec technique

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APR 2 1971

CRI MIDLAND

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March 31, 1971

CHLORINATED SOLVENTS IN WATER

Compound	Solubility[a] in H_2O (g/100g, 20°C)	Vapor Pressure[a] mm Hg (20°C)	Partition Coefficient[b] $K = C_{vac(g)}/C_{vac(w)}$
CH_2Cl_2	1.32 [1.20 (25°C)][c]	349	0.218
CH_3CCl_3	0.095 (37°C)[0.130 (25°C)]	100	0.828

---

[a] J. G. Renfro, "Physical Properties for Some Chlorinated Hydrocarbons," October 31, 1967.

[b] Calculated by using technique described by C. McAuliffe, Science, 163, 478 (1969).

[c] Seidell, "Solubilities of Organic Compounds," D. Van Nostrand Co., New York (1941).

was applied. Two hundred ml of a solution 1 ppm in each solvent was placed in a 250 ml beaker equipped with a glass covered magnetic stirring bar. A hollow fiber membrane probe was immersed in the solution and a spectrum was taken every 5 minutes for 2 hours. It is rather important to note that the water used in these experiments was free of organics and that the relative rate of evaporation from waters high in organics (eg. Mississippi River) would probably be a great deal slower.

With only mild agitation all four solvents rapidly evaporate, with concentrations dropping 10-100 fold within 2 hours (Figures 1 and 2). Increasing the agitation (only stirring for 15 seconds before sampling) produced a marked decrease in the rate of evaporation (Figure 3) but the solvents were still about half gone in 1 1/3 hours. It is also apparent that all four solvents evaporate at about the same rate even though they have rather different solubilities, vapor pressures and partition coefficients.

While there doesn't appear to be any literature on the environmental mobility of chlorinated solvents, the literature is replete with corresponding studies on chlorinated pesticides (eg. dieldrin, lindane). Some of the most important work related to our needs is that done by Spencer (Persistence of Soil Pesticides, Decomposition and Movement."

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proceedings of an International Symposium on Pesticides in the Soil held at Michigan State University, February 25-27, 1970) who observed that "soil-water content effects on volatilization are due to an increased vapor density resulting from displacement of the pesticide from the soil surface by water and not due to evaporation of water by 'co-distillation.'" He also noted that "in all soils, vapor densities increased linearly with concentration, but were inversely related to the soils' organic matter content." While these observations may not extrapolate directly to chlorinated solvents they do suggest both the type of data we need to generate and their interpretation. Thus the extrapolation of the latter observation from soil to water, including both dissolved and suspended organic matter, would predict an inverse relationship of vapor density above the water to the organic matter content.

Based on these results we can conclude that chlorinated solvents should not present a problem in relatively pure waters since they would be rapidly transferred to the atmosphere. Thus hydrolysis and related studies in "distilled water" probably have little value for providing ecologically significant information. Future studies involving chlorinated solvents in water should be carried out using natural waters.

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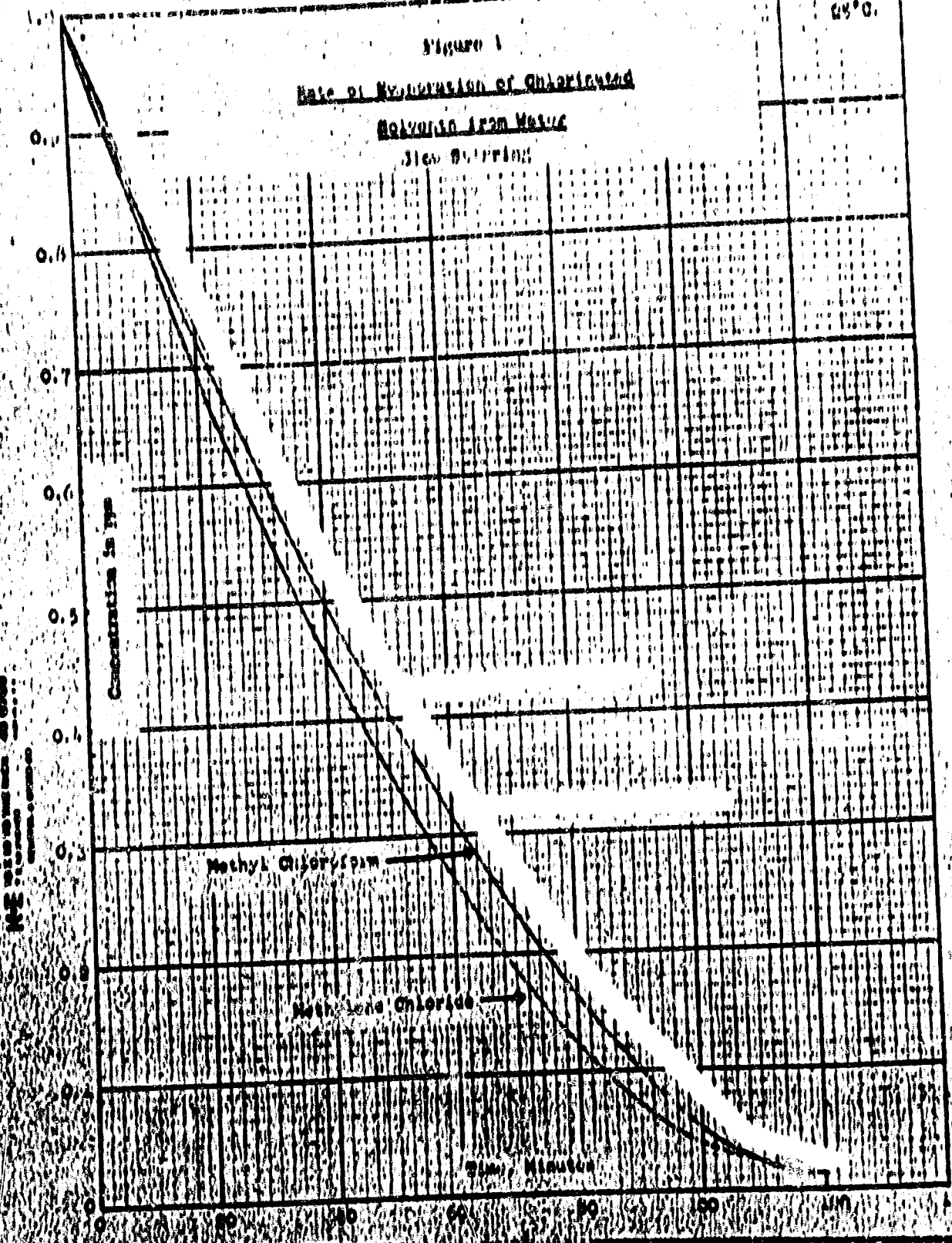
Figure 1

Rate of Volatilization of Chlorinated Solvents from Water

Stirred Solutions



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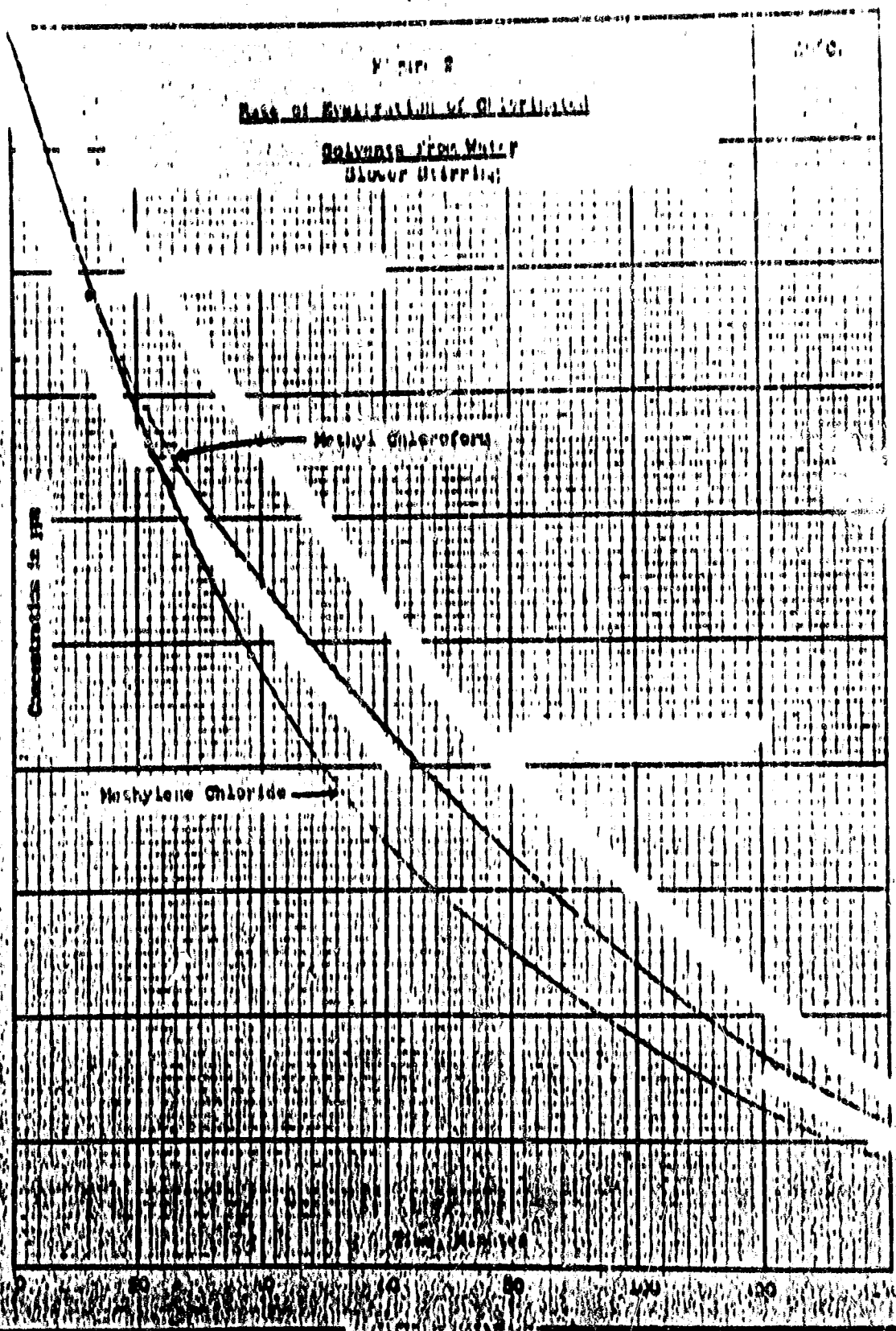
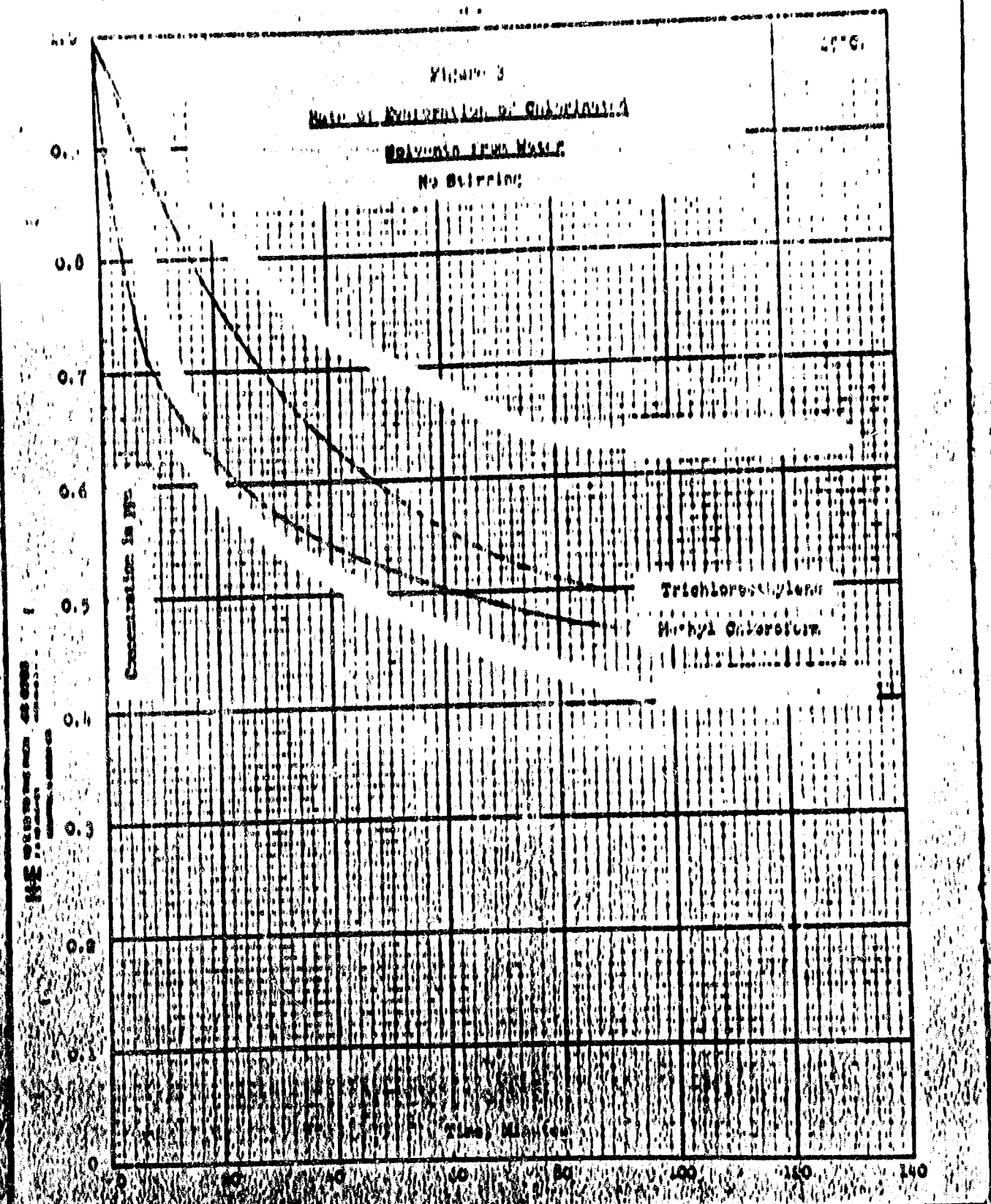

Rate of Evaporation of Chlorinated
Solvents from Water
Methyl Chloroform
Methylene Chloride
Concentration in ppm
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50
100
150
200

8788/1386



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Doc Title 23
THE SIMULATED ATMOSPHERIC PHOTOREACTIVITY OF METHYL CHLOROFORM METHYLENE CHLORIDE AND CARBON TETRACHLORIDE

Chemical Name (300 per name) 25	CAS No. (10) 24
1,1,1-TRICHLOROETHANE	71-55-6

A.K. 5/21/83

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MIDLAND, MICHIGAN

Nancy L. Jefferiller and Wendell L. Dilling

"The Simulated Atmospheric Photoreactivity of Methyl Chloroform, Methylene Chloride, and Carbon Tetrachloride"

The ultimate fate of chlorinated solvents discharged to the environment is of increasing concern, as ecological considerations are leading to tighter governmental regulation of these materials. Methyl chloroform and methylene chloride have been reported to be stable to photochemical degradation for short periods of time when irradiated with sea level type irradiation ($\lambda > 295$ nm). If these materials are persistent, the question can be raised as to whether, with continued release to the atmosphere, they will accumulate at high altitude and be a cause of future environmental problems.

This study was undertaken to determine over what periods of time methyl chloroform and methylene chloride were stable under environmentally simulated conditions at sea level, then how rapidly they, along with CCl_4, would disappear when exposed to simulated high altitude type irradiation ($\lambda > 254$ nm).

Methyl chloroform (50 ppm) did not react when irradiated with sunlamps ($\lambda > 295$ nm) for 4 weeks in the presence of SO_2 (~ 10 ppm) and moisture (35% RH). Methylene chloride was found to be stable under the same conditions for approximately 6 days, then it rapidly disappeared. All 3 solvents were at least 90% reacted within 10 min, however, when irradiated with light typical of that found at high altitude. Therefore a buildup of these materials in the upper atmosphere does not appear likely.

* Organic Photochemistry, XX.

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I. INTRODUCTION[1]

It had been reported by Corwin Fredewell[2] that methyl chloroform (10 ppm) in air containing 35% relative humidity and 5 ppm NO reacted less than 5% in 23.5 hr when irradiated with sunlamps (λ > 295 m) emitting sea level type irradiation. Similarly, in the presence of 16.8 ppm NO_2 it reacted less than 5% in 8 hours. Methylene chloride under the same conditions showed less than 5% reactivity either in 21 hours in the presence of 5 ppm NO or in 7.5 hours in the presence of 16.8 ppm NO_2. Further work by Arrington and Minz[3,4] confirmed that methyl chloroform (10 ppm and 50 ppm) and methylene chloride (10.5 ppm and 50 ppm) were unreactive photochemically when irradiated 15 and 15 hours respectively in the presence of NO_2 and moisture and that neither exhibited oxidant forming potential.

The present study was undertaken to determine whether methyl chloroform and methylene chloride would be stable under prolonged irradiation by sunlamps under simulated sea-level atmospheric conditions and to determine whether there was any possibility of their buildup at higher altitudes should they prove to be persistent at sea level. Carbon tetrachloride was included in the study using simulated high altitude irradiation (λ 254 m), as it has been observed by scientists in remote areas of the world, leading to questions of its persistence in the environment.

II. RESULTS AND CONCLUSIONS

Methyl chloroform (50 ppm) in air containing 35% relative humidity and 10 ppm NO_2 at ~ 27°C was stable for 4 weeks when irradiated with GE sunlamps emitting low altitude light (> 295 m) (Figures 1 and 2). When irradiated at 33°C with a Hanovia low pressure mercury arc lamp (λ = 254 m) simulating high altitude irradiation, the methyl chloroform was 94% gone in 10 minutes (Figure 3). The presence of NO_2 and moisture in the air were not necessary to the reactivity of the methyl chloroform (Figures 4 and 5), and the solvent was stable in the presence of ozone in the dark. There appeared to be no adsorption of methyl chloroform onto the reactor walls.

FIGURE 1

UV LEVEL IRRADIATION
OF METHYL CHLOROFORM

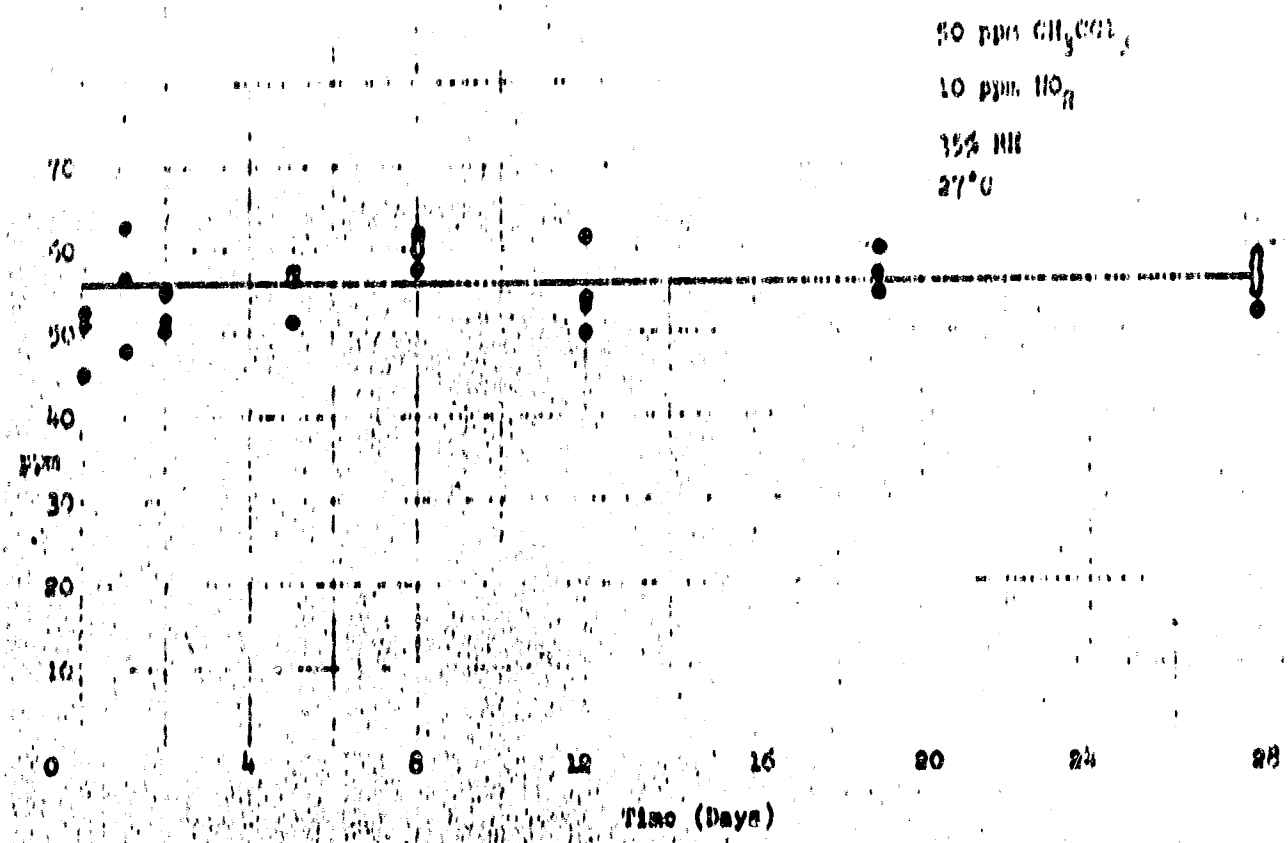

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FIGURE 2

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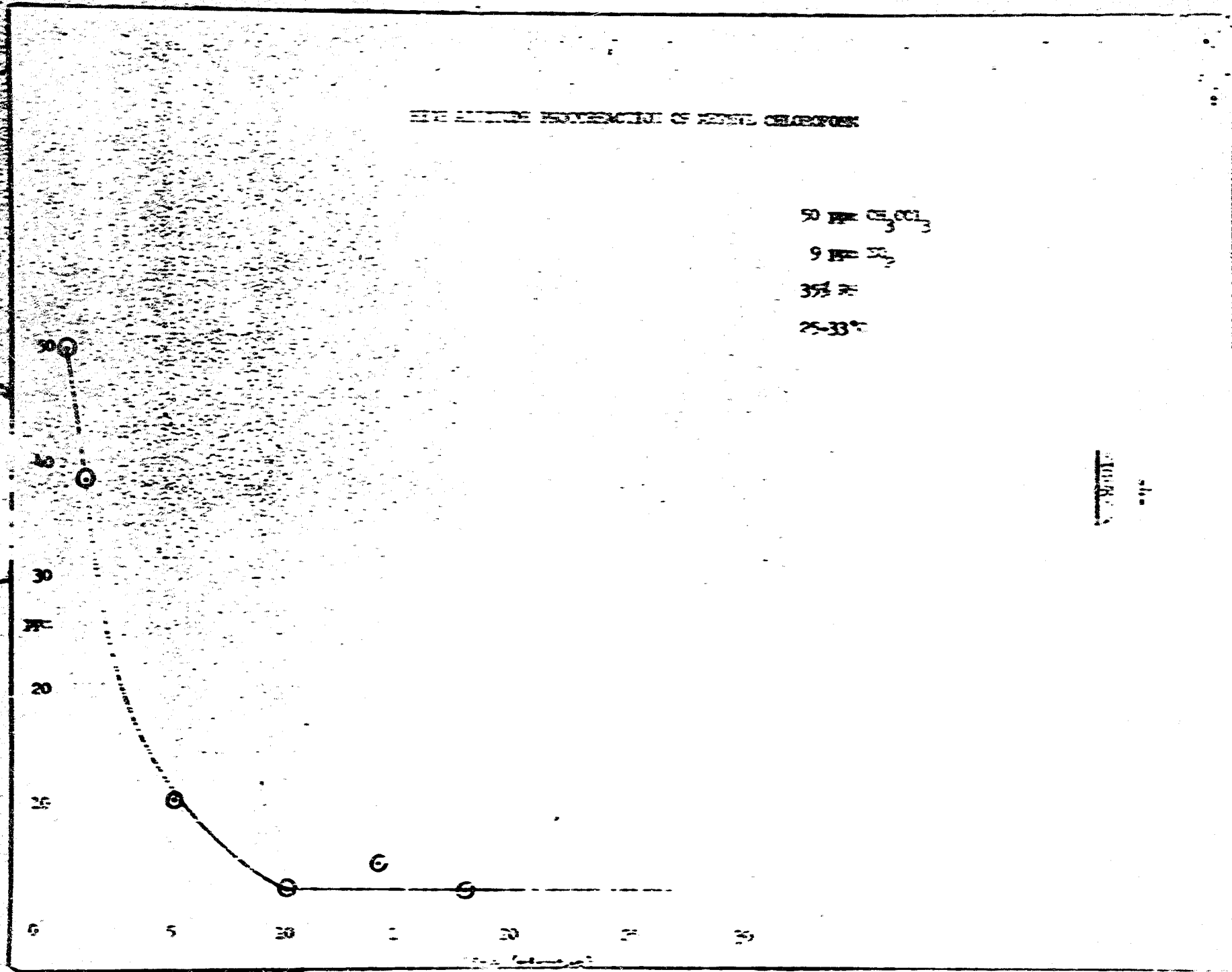

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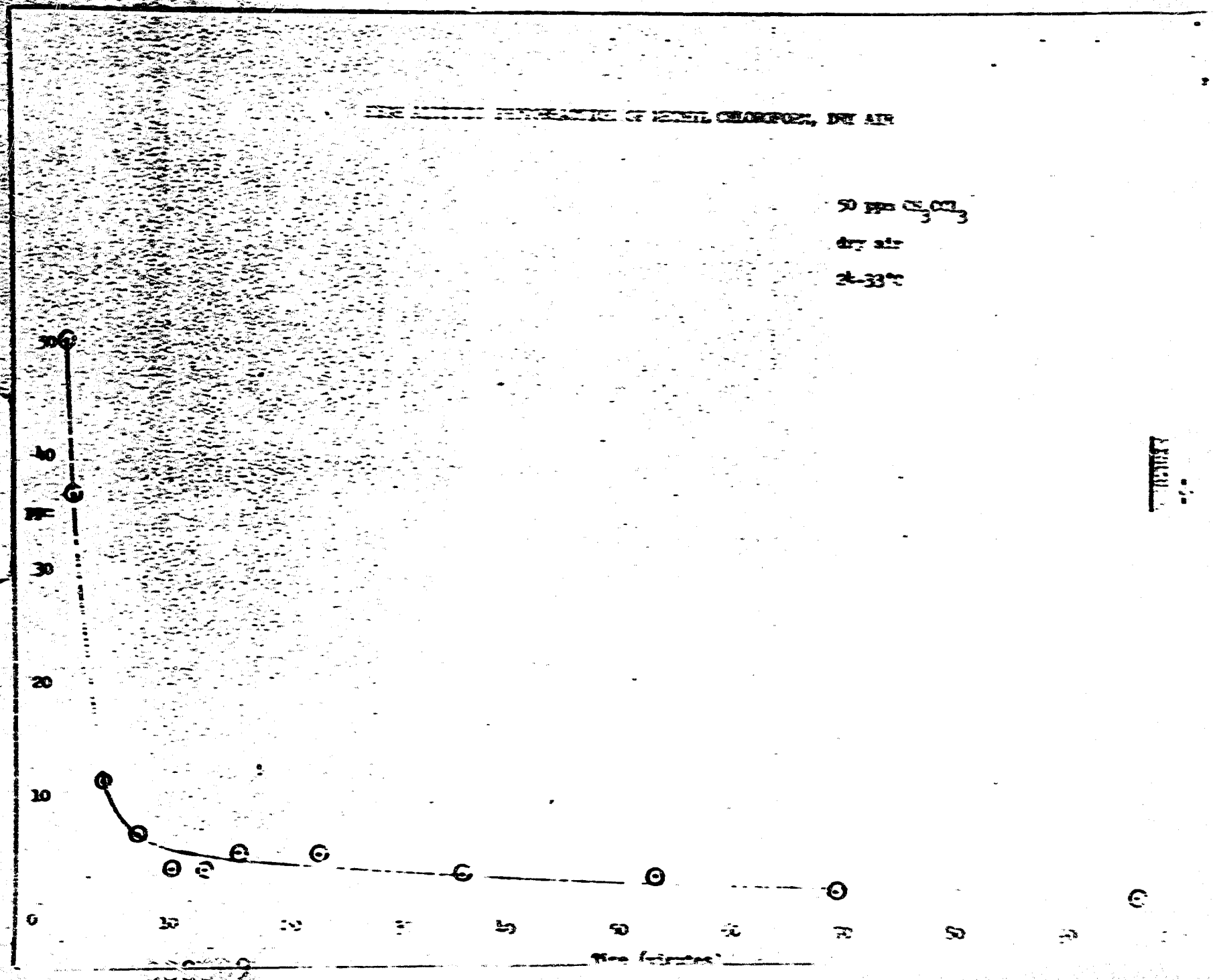

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Methylene chloride (50 ppm) in air at 20-30°C containing 3[illegible] relative humidity and 10.5 ppm NO_2 was stable for approximately 6 days under sea-level irradiation, then rapidly disappeared (Figures 6 and 7). It was possible to account for 77% of the chlorine from the CH_2Cl_2 as inorganic Cl^- after rinsing the reactor with dilute NaOH solution. With high altitude irradiation, it too, was 95% reacted in 10 minutes in dry air with no NO_2 present (Figure 8).

Carbon tetrachloride was not studied under low altitude conditions, but was found to be 96% photodegraded in 10 minutes at a level of 50 ppm in dry air with high altitude irradiation (Figure 9).

Some unidentified photoproducts were observed in the high altitude irradiation of all three solvents . These were generally of a low concentration with the exception of one product from CCl_4 which reached a concentration of about a third (as area %) of the starting CCl_4, and then disappeared with further irradiation.

III. DISCUSSION

Both methyl chloroform and methylene chloride appear to be stable in air when irradiated with sunlamps which simulate sunlight at sea level. Methyl chloroform, in particular, showed no activity in four weeks. The sharp disappearance of the methylene chloride after several days irradiation is unexplained. It can be theorized that an impurity in the CH_2Cl_2, as yet unidentified, inhibited the reaction until the impurity itself had been photoreacted; that a product was formed at an extremely low level which catalyzed the reaction; or that there was an agent on the surface of the glass which effected a delayed reaction. The fact that at the completion of the reaction 77% of the Cl_2 from the CH_2Cl_2 could be accounted for by $AgNO_3$ titration as Cl^-, however, indicates that reaction did occur, rather than an accident to the system (such as a leak) which might have caused the CH_2Cl_2 to be lost.

FIGURE 4

SEA LEVEL PHOTOREACTION OF METHYLENE CHLORIDE

50 ppm CH_2Cl_2

10.5 ppm NO_2

39% RH

25-26°C

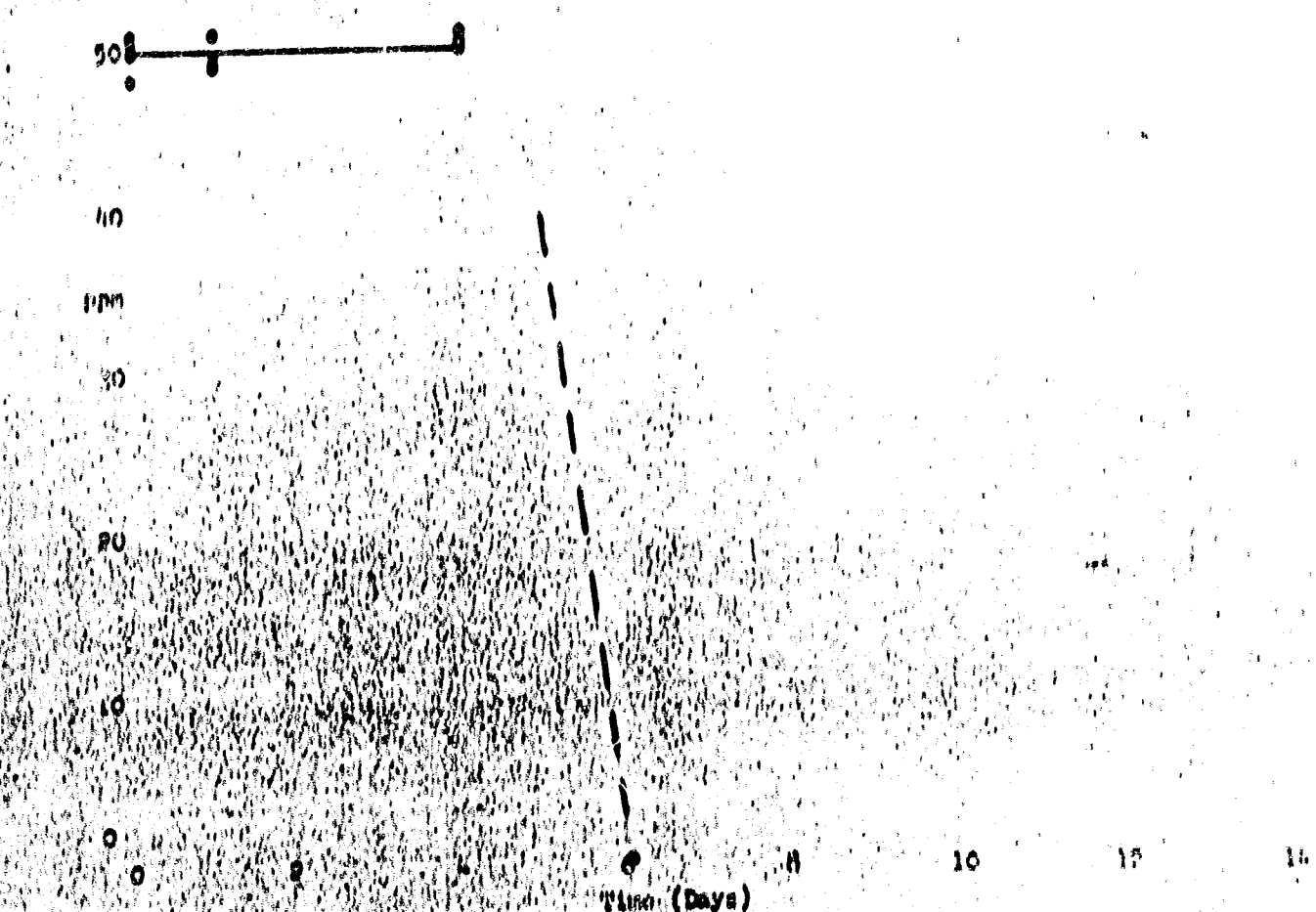

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FIGURE 7

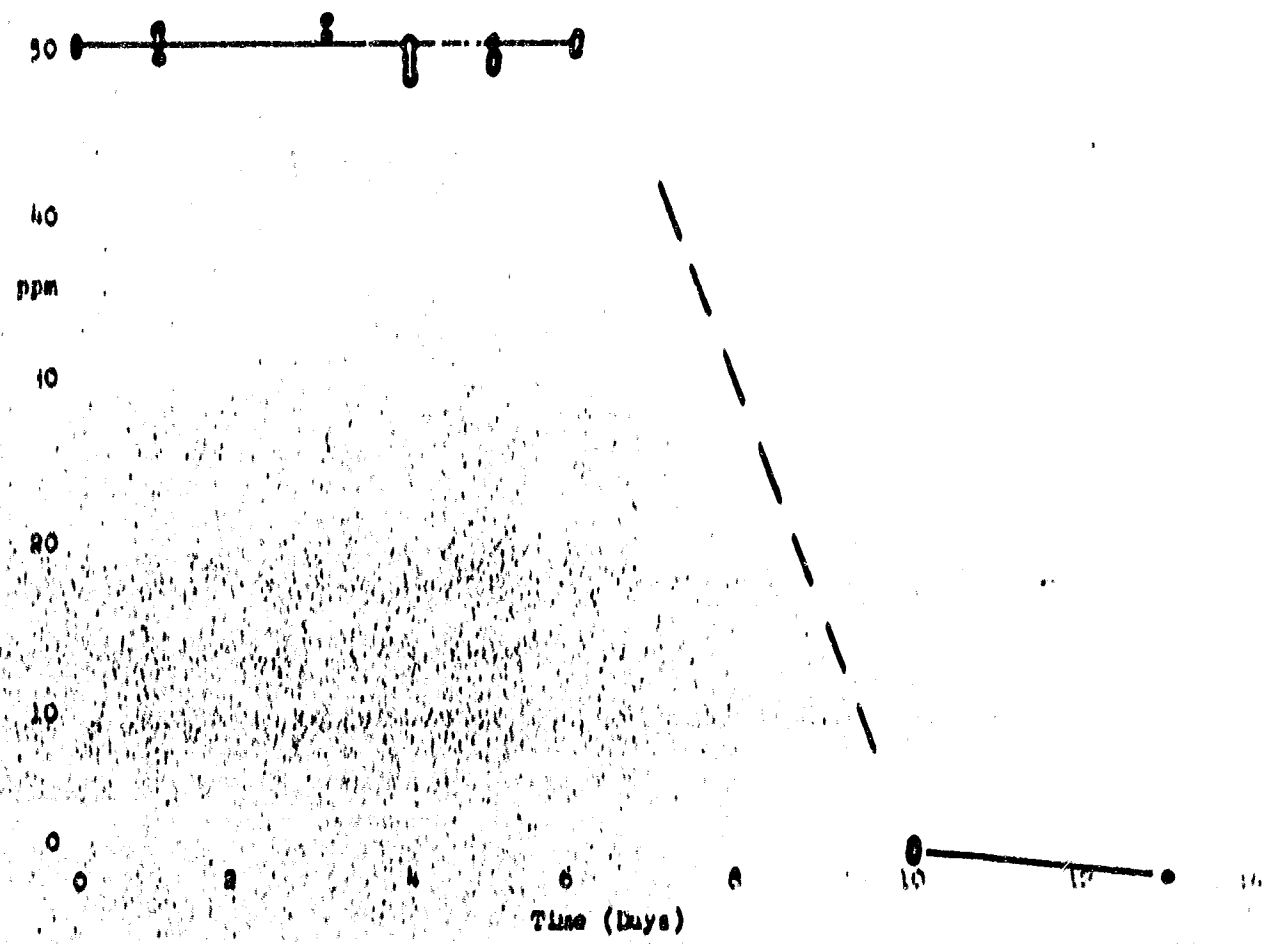
SEA LEVEL PHOTOREACTION OF METHYLENE CHLORIDE

50 ppm CH_2Cl_2

10 ppm NO_2

65% RH

25-27°C



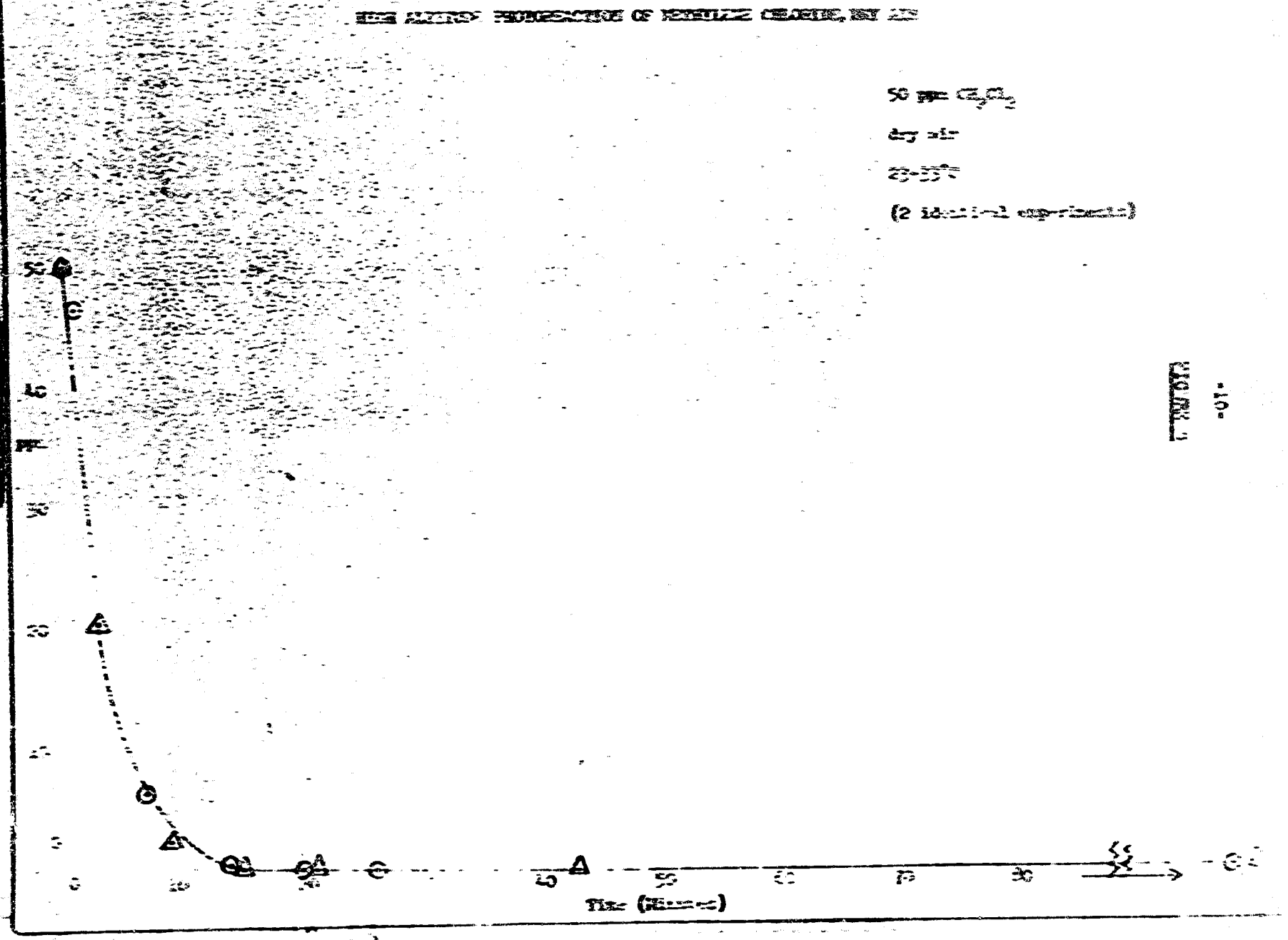


FIGURE 1

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[illegible] ALTITUDE PHOTOLYSIS OF CARBON TETRACHLORIDE

50 ppm CCl_4

dry air

23-33°C

50

40

30

20

Time (Minutes)

Sunlight which reaches the surface of the earth has been filtered through the earth's ozone layer (5-20 mi in depth) where the short wavelength ultraviolet radiation is absorbed.[5] Consequently, it is of longer wavelength (> 290 m) and lower energy than that radiation in the upper regions of the atmosphere (~ 25 mi) which still contains the high energy, short wavelength UV light. Even though the spectral distribution from sunlight is a continuum while the emission from a medium pressure mercury arc lamp such as the sunlamps used in this work is a series of lines, the overall spectral output from the two sources parallel each other rather closely in this region of the spectrum (> 290 m).[6] Therefore the sunlamp equipped with a Pyrex filter should be a reasonably good simulator of sunlight in this spectral region. It is not surprising that methyl chloroform and methylene chloride were not reactive when irradiated with sunlamps as their ultraviolet spectra show no absorption in that spectral region. Apparently these solvents are unreactive toward the radicals derived from the photolysis of nitrogen dioxide.

The high energy radiation observed at higher altitudes would be expected to cause a more efficient photoreaction of the chlorinated solvents which have been studied in this work. The Hanovia low pressure mercury arc lamp used to simulate high altitude radiation has 90% of its emitted light at 254 m where the solvents still have tailing absorption.[7] The lamp's intensity (see Appendix) as measured by Roger Bredewog of the Analytical Lab., is 30-120 times that of sunlight just inside the earth's atmosphere at an altitude of ~ 25 miles (see Appendix). While more intense than naturally occuring sunlight, the rapidity with which the chlorinated solvents were photolysed allows one to draw a crude extrapolation as to how long these solvents would exist should they manage to reach the upper regions of the earth's atmosphere. Based only on lamp intensity, one would expect at least a 90% photoreaction of the solvents with 5-20 hours irradiation. There appears to be little danger of their accumulation under these conditions.

The exact temperature of the atmosphere at the altitude which the lamp is simulating an unknown; at 11 kilometers (~ 7 mi) the temperature is -50 to -60°C and rises to about 0°C at 50 km (~ 30 mi).[8] The photoreactions described in the work were run close to room temperature; temperature often has little effect on the rate of photoreactions. The photoreactions were run at 740-750 mm. pressure; the pressure at high altitudes is lower. Pressure probably has an effect on the rate of these photoreactions. The rate could be either increased or decreased with a decrease in pressure depending on the mechanism of the photodecompositions.

010000

There is probably not much water in the atmosphere at higher altitudes, most being found in the troposphere (< 11 km).[8]

IV. EXPERIMENTAL

A. General Techniques

a) Low level irradiation - The photochamber used in this work was designed to minimize the possibility of leakage from the chamber during extended photoreactions. Consequently, there were only two openings, a 4 mm teflon stopcock and a capillary tubing sample port which was sealed with a silicone rubber septum. The chamber was a flat-ended pyrex cylinder of 11.6 liters capacity. At each end was positioned a sunlamp. Between each lamp and the end of the reactor was a 3/8" thick quartz plate to reduce warming of the photoreactor by the sunlamps. The ends of the reactor were further cooled by forced air which had been passed over a cold water cooling coil. The entire system was placed in a hood to maintain adequate air flow to dissipate generated heat. The temperature was measured by a thermocouple taped to the outside of the reactor near the center of the cylinder. (Figure 10)

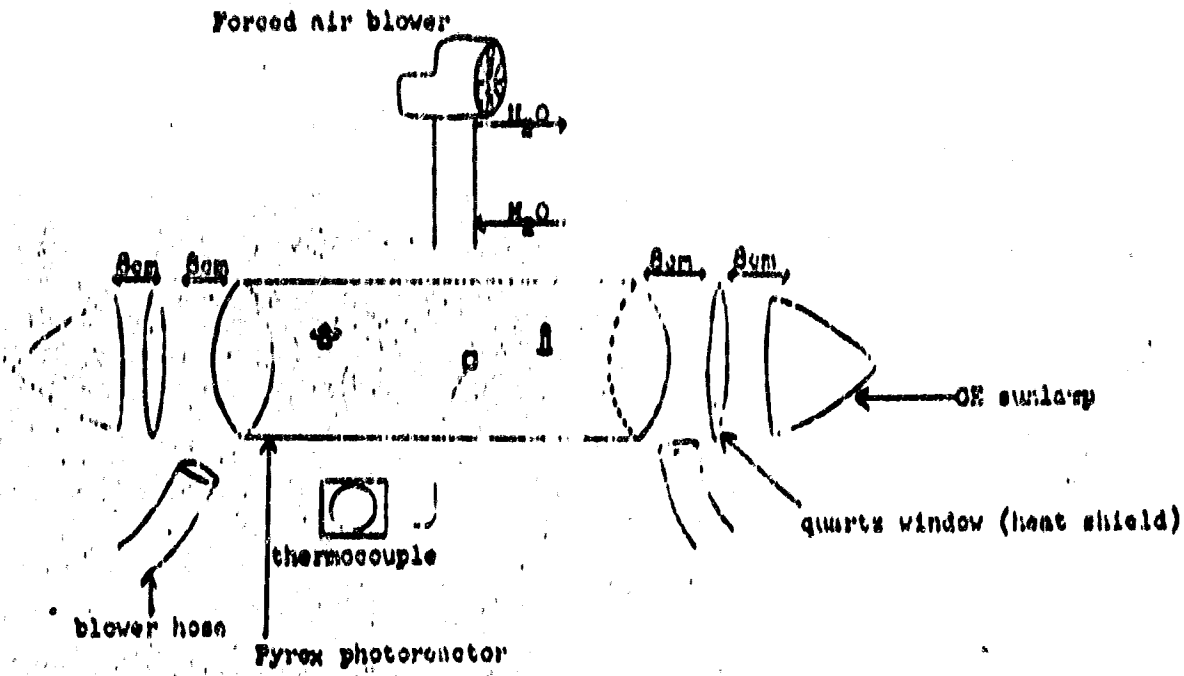
Irradiation was provided by 2 GE RS-275W sunlamps with an intensity of 1 to 2 times that of sunlight[9] and wavelengths greater than 295 m.

The hood in which the apparatus was placed was covered by black cloth to eliminate the possibility of eye injury from the ultraviolet irradiation.

b) High altitude irradiation - The photochamber for these experiments was a Pyrex sphere of 12.1 liters capacity having a 4 mm teflon stopcock and a capillary tubing sample port closed by a silicone rubber septum. The photoreactor had a ground glass joint into which was fitted the ultraviolet lamp. A silicone grease seal was used to eliminate the possibility of leakage from the reactor. The system was proven capable of holding a vacuum for several days. Blowers were directed at the top and bottom of the photoreactor to dissipate the small amount of heat generated by the lamp. The temperature of this system was measured by a thermocouple taped to the outside of the flask near the middle between the blowers.

FIGURE 10

SEA LEVEL IRRADIATION APPARATUS



As a high voltage existed across the leads of the lamp, the entire apparatus was enclosed in a wire mesh, grounded cage with safety switches which would turn off the lamp if the doors were opened accidentally while the lamp was on. The entire cage was covered by black cloth to prevent escape of short wavelength UV radiation which is potentially damaging to the eyes. The cage was ventilated into a nearby hood by an auxiliary blower, as the lamp generated ozone during its operation. (Figure 11)

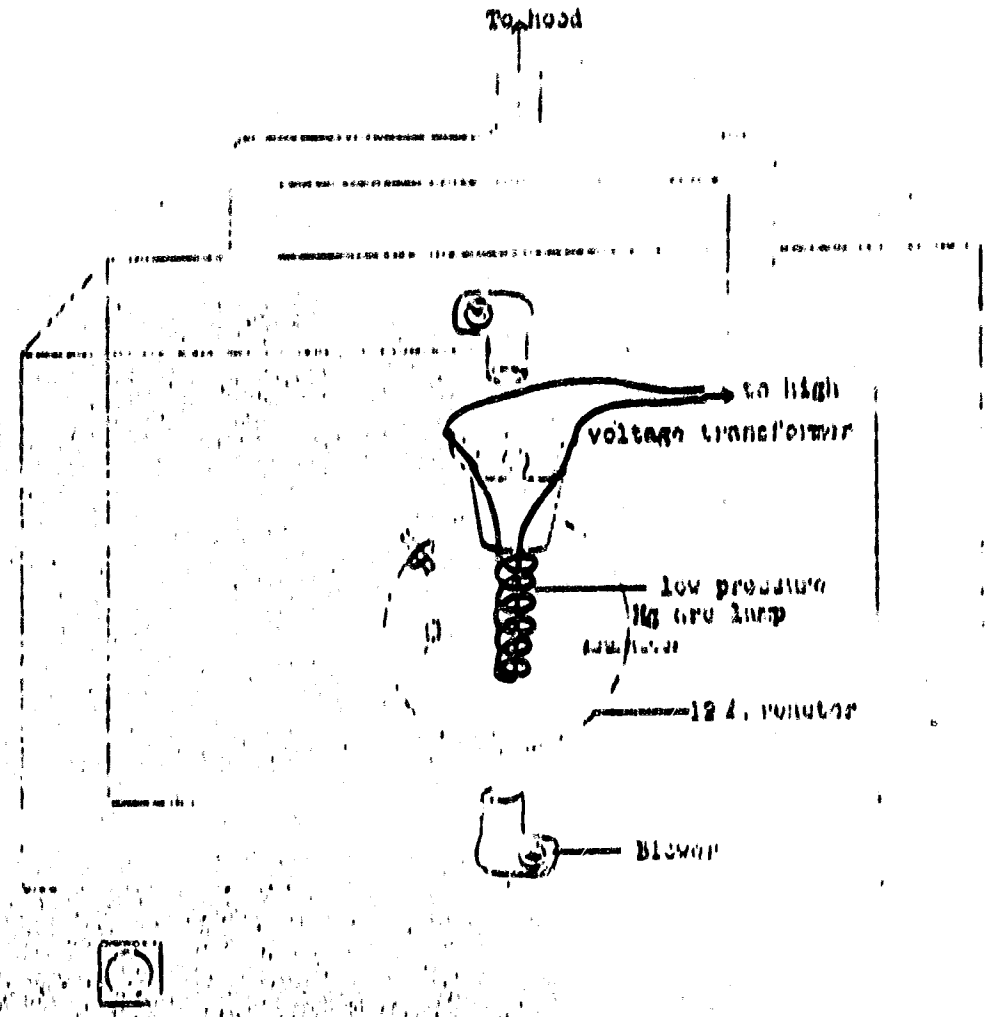
Irradiation was provided by a Hanovia low pressure mercury arc lamp (see Appendix). Approximately 90% of its emitted wavelength was at 2537 Å.[7] There may also be emitted a shorter wavelength line at 1849 Å which would cause the generation of the ozone observed each time the lamp was used. The lamp can be said to approximate the sun's emission. It is 10-40 times as intense as the sun's radiation would be just outside the earth's atmosphere. Just within the earth's atmosphere (at ~ 25 miles) where the sun's intensity is cut to ~ 1/3 of its original intensity in the 2000-3000 Å range by absorption of its short wavelength radiation by ozone, the lamp would be 30-120 times as intense as sunlight at that altitude.

c) Gas mixture - The simulated atmosphere used in the photoreactions was obtained by premixing to the desired proportions a dry air stream with an air stream saturated with water and one containing a known amount of NO_2. The gas streams were monitored by flowmeters and the photochamber was flushed with the gas mixture for a period of time calculated to replace 99.9% of the ambient air in the photochamber.[3] A sample of the gas mixture was then removed and analyzed for ppm NO_2 using a modified Saltzman procedure and a calibration curve prepared by M. J. Mintz.[9] Finally a quantity of chlorinated solvent calculated to give 50 ppm (on a molar basis) in air was injected through the septum into the reactor. The system was allowed to equilibrate overnight, blanks (0 time) were analyzed, and the photoreactions were run for varying lengths of time with the two types of irradiation. Gas samples (2 or 10 ml) were removed at specific intervals by gas-tight syringe and analyzed by gas-liquid chromatography.

d) Analysis - Two gas chromatography systems were used to analyze for chlorinated solvent concentration. The first was by thermal conductivity GC analysis using a F & M 500 instrument equipped with a 10' x 1/4" 20% aplezon L column

FIGURE 1

HIGH ALTITUDE IRRADIATION APPARATUS



on chromosorb WAW and a column temperature of 160°. The detector temperature was 300°, the injector was 140° and the helium flow rate through the column was 45 cc/min. A 3.0 cc gas sample was used, and while it was possible to increase the sensitivity of the filaments by increasing the filament current to 175 milliamps (vs. 150 under typical operating conditions), the resultant peak size was quite small. The peak area of all gas samples was measured by planimeter. There was observed considerable scatter in the data and the best that was hoped for was 10% reproducibility. A liquid standard consisting of methyl chloroform in trichlorethylene was used to calibrate the GC sensitivity with each gas run.

During the course of this work a hydrogen flame ionization gas chromatography system became available which allowed much greater sample reproducibility, usually within 4%. It consisted of an Aerograph Hy-Fi Model 550-B with a Bendix electrometer equipped with a 10' x 1/8" N,N-bis(2-cyanoethyl)formamide column 20% on chromosorb W. The column temperature was generally 97° and the carrier gas was nitrogen. It was possible to use a 2 cc gas sample size with this system.

A gas standard bulb was used to calibrate the H_2 flame GC. It consisted of 50 ppm chlorinated solvent in a 12.6 liter glass sphere having only two openings, a 4 mm stopcock and a capillary sampling port closed by a silicone rubber septum. Samples from this bulb were reproducible over at least 6 weeks, indicating no leakage from the bulb.

B. Reagents

Carbon tetrachloride and methylene chloride, Burdick & Jackson, distilled in glass; methyl chloroform, Dry-distilled, center cut BP 74° at 760 mm; air, dry cylinder air from Matheson Gas Products, NO_2 in air, made to specification by Matheson Gas Products, analyzed to be 25 ppm in air by the modified Saltzman procedure.

C. The Photoreaction of Methyl Chloroform

a) Simulated sea level environment - Methyl chloroform (50 ppm) in the presence of 10 ppm NO_2 and 35% relative humidity at 27° was irradiated for 28 days using the OE apparatus (Figure 1). The methyl chloroform was analyzed by thermal conductivity GC and found to be stable under these conditions.

The above experiment was repeated under the same conditions using the flame-ionization GC method of analysis in order to reduce the scatter in the data and was found to be stable when irradiated for 16 days (Figure 3).

b) Simulated high altitude irradiation - Methyl chloroform (50 ppm) in the presence of 9 ppm NO_2 and 35% RH at 25-33°C was 94% photoreacted within 10 minutes when irradiated with the low pressure Hg arc lamp (Figure 3). Analysis was by thermal conductivity and, while the CH_3CCl_3 was difficult to distinguish from background noise after 5 minutes, it appears that there is a residual amount (~ 3 ppm) which remains in the system. This is probably an artifact of the system (i.e. CH_3CCl_3 may have dissolved into the rubber septum and is slowly being released back into the reactor), and later experiments with CCl_4 using the more sensitive flame-ionization GC indicate that the small residuals observed in several reactions will eventually disappear with further irradiation.

Effect of NO_2 - The above reaction was repeated with no NO_2 present. The CH_3CCl_3 appeared to be completely gone within 6 min. (Figure 4). The apparent complete reaction of the CH_3CCl_3, compared to that run in the presence of NO_2, is probably not significant because of the analytical uncertainty.

Effect of moisture - CH_3CCl_3 (50 ppm) in dry air (obtained by running Matheson dry cylinder air through a drying tower filled with Drierite interspersed with P_2O_5) was irradiated for 96 min. at 24-33°C. The CH_3CCl_3 was approximately 90% reacted in 10 min. (Figure 5). Flame-ionization GC was used and confirmed a low residual of CH_3CCl_3 in the reaction. It also indicated the appearance, then subsequent disappearance of a possible very low level unidentified photoproduct.

Stability of methyl chloroform in the presence of ozone - CH_3CCl_3 (50 ppm) was added to an ozone-filled photoreactor and held in the dark for 4 days. The CH_3CCl_3 was analyzed after 1 day and 4 days. There was no decrease in the concentration of CH_3CCl_3 as compared to previous samples with no ozone present.

Adsorption of methyl chloroform on the reactor walls - CH_3CCl_3 (50 ppm) was allowed to equilibrate overnight in the photoreactor and its GC peak area measured. A second addition of 50 ppm CH_3CCl_3 was made to the photoreactor and this was also allowed to equilibrate overnight. The subsequent peak area was about double that of the first CH_3CCl_3 injection (within experimental error) indicating no significant adsorption of the first addition of CH_3CCl_3 onto the reactor walls.

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D. The Photoreaction of Methylene Chloride

Simulated sea level environment

Methylene chloride (50 ppm) in the presence of 10.5 ppm NO_2 and 35% RH was irradiated at 25-26° for 6 days. The CH_2Cl_2 was stable for 4 days, then disappeared completely by the sixth day (Figure 6).

The above reaction was repeated. The CH_2Cl_2 was stable for 6 days, almost completely gone by 10 days and totally reacted in 13 days (Figure 7). The photoreactor was rinsed with 20 ml of 0.01N NaOH and 40 ml of DI water. The rinses were evaporated to a small volume, acidified and titrated with N/10 $AgNO_3$. It took 0.36 ml N/10 $AgNO_3$ to reach an end point, a recovery of 76.6% of the chlorine from the initial CH_2Cl_2 (1.51 mg or 0.0470 mmol Cl^-) as Cl^-.

Simulated high altitude irradiation

Methylene chloride (50 ppm) in dry air was irradiated for approximately 2.5 hours with the low pressure Hg arc lamp. The CH_2Cl_2 was 95% reacted within 10 minutes and completely reacted within 40 minutes (Figure 8). The experiment was repeated in order to observe the behavior of an impurity which appeared in the equilibrated gas mixture only after the CH_2Cl_2 had been injected into the reactor (perhaps a residue coming off the reactor walls from previous photoreactions?) and which disappeared rapidly upon irradiation. A small photoproduct then formed having the same retention time, but it, too, disappeared with further irradiation. A second, even smaller unidentified photoproduct may have been observed.

A GC peak identified as water was confirmed in these experiments. The source of this moisture is unknown, as the air in these reactions is dry cylinder air further treated in a drying tower as described.

E. The Photoreaction of Carbon Tetrachloride

Simulated high altitude irradiation

CCl_4 (50 ppm) in dry air was irradiated at 23-31°C for 320 minutes. The CCl_4 was 70% reacted within 10 minutes, leaving a low level of CCl_4 (~ 2 ppm)

[illegible] disappeared over the next [illegible] (Figure 7). A photoproduct [illegible] the same retention time as that seen in the CH_2Cl_2 photoreaction was observed. At the greatest concentration (~[illegible] min. exp) it represented [illegible] of [illegible] CCl_4. The product is unidentified. It is not propene, formed with [illegible] hexachloroethane or tetrachloroethylene. It gradually disappeared with continued irradiation, with most of it being photoreacted within one hour. There may have been one other, very small photoproduct observed in the reaction.

V. ACKNOWLEDGEMENTS

The authors wish to thank Michael J. Mintz of Organic Chemicals Production Research for the design of the photoreactors and many helpful discussions.

VI. TOXICITY AND HANDLING PRECAUTIONS

The chlorinated solvents used in this work did not present a health hazard at the levels used. Routine precautions were taken in their handling. Care was taken to avoid accidental release of potentially eye damaging ultraviolet radiation by covering both apparatus with black cloth. The ozone generated by the low pressure mercury arc lamp was monitored by Richard Olson of Chemical Biology Research (Industrial Hygiene Section)[10] and the level found to be far less than the Threshold Limit Value (0.1 ppm) outside the cool and work cage. The ozone inside the work cage (~ 0.2 ppm) was forced into a nearby hood by an auxiliary blower, having an alarm to indicate blower failure.

VII. REFERENCES

The data in this report was gathered in order to learn more about the interaction of the above solvents with the environment and to prevent the development of future problems. While CH_3CCl_3 and CH_2Cl_2 appear to be stable at low altitudes, they previously have been shown not to lead to oxidant formation and therefore not to contribute to photochemical smog.[3,4] At higher altitudes, as indicated, the solvents would not be persistent.

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[illegible]

1. [illegible] Dow Chemical Company Report [illegible] (1971).

2. [illegible]

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5. Lewis Katter, "Ultraviolet Radiation and Second Edition, John Wiley and Sons, Inc., New York, 1965, pp. 118-120.

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9. M. J. Hintz, Dow Chemical Company

10. R. Olson, Dow Chemical Company

Appendix

Relative Energy of Hanovia Low Pressure Mercury Arc Lamp Emission and Solar Irradiation Outside Earth's Atmosphere

Hanovia Low Pressure Mercury Arc Lamp

Wavelength (Å)	Intensity (in watts/cm²) at 24 inches from Lamp
2537	3.9 (275)
2654	0.016
2967	0.018
3100	0.11
3341	0.004
3657	0.053
4047	0.055
4358	0.063
5461	0.034

Total energy at 2537 Å = 2.5 watts; lamp assumed to be a cylinder (10 cm. long x 1.8 cm. diameter) (actually a coil); light intensity (power) = 11.7 milliwatts/cm² at surface of lamp.

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[illegible]

[illegible] Radiation Outside Earth's Atmosphere
(Calculated from data in ref. 5, p. [illegible])

Wavelength range (m)	Power in wavelength range (milliwatts/cm²)	
140-145	0.00001	
145-150	0.00007	
150-155	0.00018	
155-165	0.00041	
165-175	0.00001	
175-185	0.00001	
185-195	0.0017	
195-202.5	0.00225	
202.5-207.5	0.0025	
207.5-212.5	0.0050	
212.5-217.5	0.0070	
217.5-222.5	0.015	
222.5-227.5	0.021	
227.5-232.5	0.026	
232.5-237.5	0.027	
237.5-242.5	0.029	
242.5-247.5	0.034	
247.5-252.5	0.032	
252.5-257.5	0.050	
257.5-260	0.0325	Total, 140-260 m = 0.267
260-262.5	0.0325	
262.5-267.5	0.10	
267.5-272.5	0.105	
272.5-277.5	0.11	
277.5-280	0.060	Total, 140-280 m = 0.714
280-282.5	0.060	
282.5-287.5	0.17	
287.5-292.5	0.26	
292.5-297.5	0.315	
297.5-300	0.1525	Total, 140-300 m = 1.672

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Doc Type 22
• R.I • U.P • H.E.A.S.D B.D. S.U H.S F.N

Doc Title 23
ATMOSPHERIC FLUOROCARBONS AND METHYL CHLOROFORM AT THE SOUTH POLE

Chemical Name (300 per name)	25	CAS No. (10)	24
1,1,1-TRICHLOROETHAN		71-55-6	

A.K. 5/31/83

D-623

8782/1.388

Abstract for Library of Congress

Antarctic Bibliography

TITLE: Atmospheric Fluorocarbons and Methyl Chloroform at the South Pole.

AUTHORS: R. A. Rasmussen and M. A. K. Khalil

The aim of our research is to unravel exactly how human activities are modifying the present composition of the earth's atmosphere and what effect this change will eventually have on the global environment. It is feared that accumulation of man-made gases in the atmosphere will warm the earth and consequently cause climatic changes or that certain chlorine-containing gases will destroy the stratospheric ozone layer, allowing high doses of the sun's ultraviolet radiation to reach the earth, causing harm to living organisms. At the south pole our experimental and theoretical work has included eight years of measurements of man-made trace gases which might contribute to these global problems (CCl_3F, CCl_2F_2, $CHClF_2$, $C_2Cl_3F_3$ and CH_3CCl_3). Fluorocarbons 11 and 12, active in the destruction of the ozone layer, are no longer increasing as rapidly as in the earlier years. However, steady increases of new man-made fluorocarbons (22 and 113) have now been observed at the south pole and elsewhere. Based on these data the global sources and sinks (lifetimes) have been determined and are reported in the literature.

Atmospheric fluorocarbons and methyl chloroform at the south pole

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The aim of our research is to unravel exactly how human activities are modifying the present composition of the earth's atmosphere, and what effect this change will eventually have on the global environment. It is feared that long-lived gases such as CO_2 released into the atmosphere by industrial processes and other human activities may eventually increase the surface temperature of the earth by enhancing the natural greenhouse effect. Chlorine- (and Bromine-) containing gases such as CCl_3F and CCl_2F_2 may deplete the stratospheric ozone layer, thus allowing more ultraviolet radiation to reach the earth's surface and harm living organisms (NAS, 1979; Barney, 1980).

In this paper we will discuss the changes in the atmospheric abundances of the man-made gases CCl_3F (F-11), CCl_2F_2 (F-12), $CHClF_2$ (F-22), $C_2Cl_3F_3$ (F-113), and CH_3CCl_3 over the past eight years. These gases may not only deplete the ozone layer but may also add to global warming. The very presence of these gases at the south pole, at concentrations not much less than in the northern hemisphere, attests to their

long atmospheric lifetimes and great potential for accumulating in the environment. Steady increases of F-22 and F-113 at the south pole are being reported for the first time in addition to the latest observations of F-11, F-12, and CH_3CCl_3. Analyses of the results shows that the latter gases are no longer increasing as rapidly as in earlier years.

We started observing the concentrations of CCl_3F, CCl_2F_2, and CH_3CCl_3 at the south pole in January 1975 and have continued these measurements every January since then. The eight years of data set comprise the longest systematic and internally consistent measurements currently available. It is being recognized that $CHClF_2$ (F-22) and $C_2Cl_3F_3$ (F-113) may also be important environmental contaminants. Techniques for the atmospheric measurement of these extremely rare fluorocarbons have been developed only recently. The measurements of these gases at the south pole since January 1979 are the first and only ones currently available. To provide a contrast for the antarctic measurements, the concentrations of these gases were also measured in the Pacific Northwest (45°N) during January of every year. Concentrations of all the gases mentioned so far are measured by electron capture gas chromatography techniques (EC/GC). Discussions of the early data on F-11, F-12, and CH_3CCl_3 and on the analytical techniques can be found in the references (Rasmussen, 1978; Rasmussen and Khalil, 1980; Rasmussen et al., 1980, 1981; Khalil and Rasmussen, 1981).

The observational results are shown in Figures 1 and 2 represented by solid circles (●). $(1/C)\ dC/dt = \beta(t)$ is the rate of change of concentration C with time t. This relative expression is used because it does not depend on knowing the absolute concentration of a

trace gas (accuracy) but only of relative changes (precision). The precision of measurements for these gases is very high (< 2%). It is known that the global yearly emissions of CCl_3F and CCl_2F_2 have not changed much since 1975, whereas before 1975 they had been increasing very rapidly. The yearly increase in the global emissions of CH_3CCl_3 has also slowed since 1975. A simple global mass balance model reveals that $\beta(t) = 1/C\ dC/dt$ would not remain constant but would gradually decline. We therefore adopted the following model for $\beta(t)$:

$$(1/C)\ \frac{dC}{dt} = \beta(t) = \bar{\beta}_o + \bar{\gamma}t \qquad \bar{\gamma} < 0 \tag{1}$$

or

$$C = C_o \exp\left[\bar{\beta}_o t + \frac{1}{2}\ \bar{\gamma}t^2\right] \tag{2}$$

The most suitable values of C_o, $\bar{\beta}_o$, and $\bar{\gamma}$ were determined by a non-linear least squares criterion and are reported in Table 1 and equation (2) is shown as a solid line in Figures 1 and 2 for CCl_3F, CCl_2F_2 and CH_3CCl_3. In these equations, C_o represents the concentration during 1/1975, $\bar{\beta}_o$ the rate of increase during 1975, and $\bar{\gamma}$ the gradual decline in the increase with time since 1975. The results imply that F-11, F-12, and CH_3CCl_3 are no longer increasing as rapidly as they were during the 1970's, and that this observation is consistent with the current knowledge of the global anthropogenic sources.

Much less is known about the global sources and sinks of $CHClF_2$ (F-22) and $C_2Cl_3F_3$ (F-113). It is certain, however, that their atmospheric concentrations are rising rapidly, as shown in Figure 2 and Table 1, and is cause for concern for the future global environment (see also Khalil and Rasmussen, 1981; Rasmussen et al., 1980b).

In addition to the fluorocarbons and CH_3CCl_3, concentrations of fifteen other trace gases were measured at the south pole and Pacific Northwest since 1979 or earlier; namely CCl_4, N_2O, CH_3Cl, SF_6, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6, C_7H_8, C_3H_8, CH_3I, $CHCl_3$, and C_2HCl_3. Results of these measurements are reported elsewhere (Rasmussen et al., 1981; Rasmussen and Khalil, 1982).

This work was supported in part by the National Science Foundation (NSF DPP 8108684). We thank NOAA/GMCC personnel, especially Lts. R. Williscroft and C. McPee for collecting the air samples at the south pole, and R. W. Dalluge, R. Gunawardena, J. Wiederholt, D. Stearns, and R. Watkins for laboratory work at OGC.

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Figure Captions

Figure 1. Observed concentrations of flucrocarbons 11 and 12 (CCl_3F and CCl_2F_2) at the south pole (lower lines) and the Pacific Northwest (45°N; upper lines). The solid line is the function $C = C_o \exp[\bar{B}_o t - \frac{1}{2} \bar{\gamma} t^2]$ where C_o, $\bar{B}_o$, and $\bar{\gamma}$ were determined from a least squares principle.

Figure 2. Observed concentrations of fluorocarbons 22 and 113 ($CHClF_2$ and $C_2Cl_3F_3$) and of methyl chloroform (CH_3CCl_3) at the south pole (lower lines) and the Pacific Northwest (upper lines). The solid line is the function $C = C_o \exp[\bar{\beta}_o t - \frac{1}{2} \bar{\gamma} t^2]$ for CH_3CCl_3 and $C = C_o \exp \bar{\beta}_o t$ for F-22 and F-113.

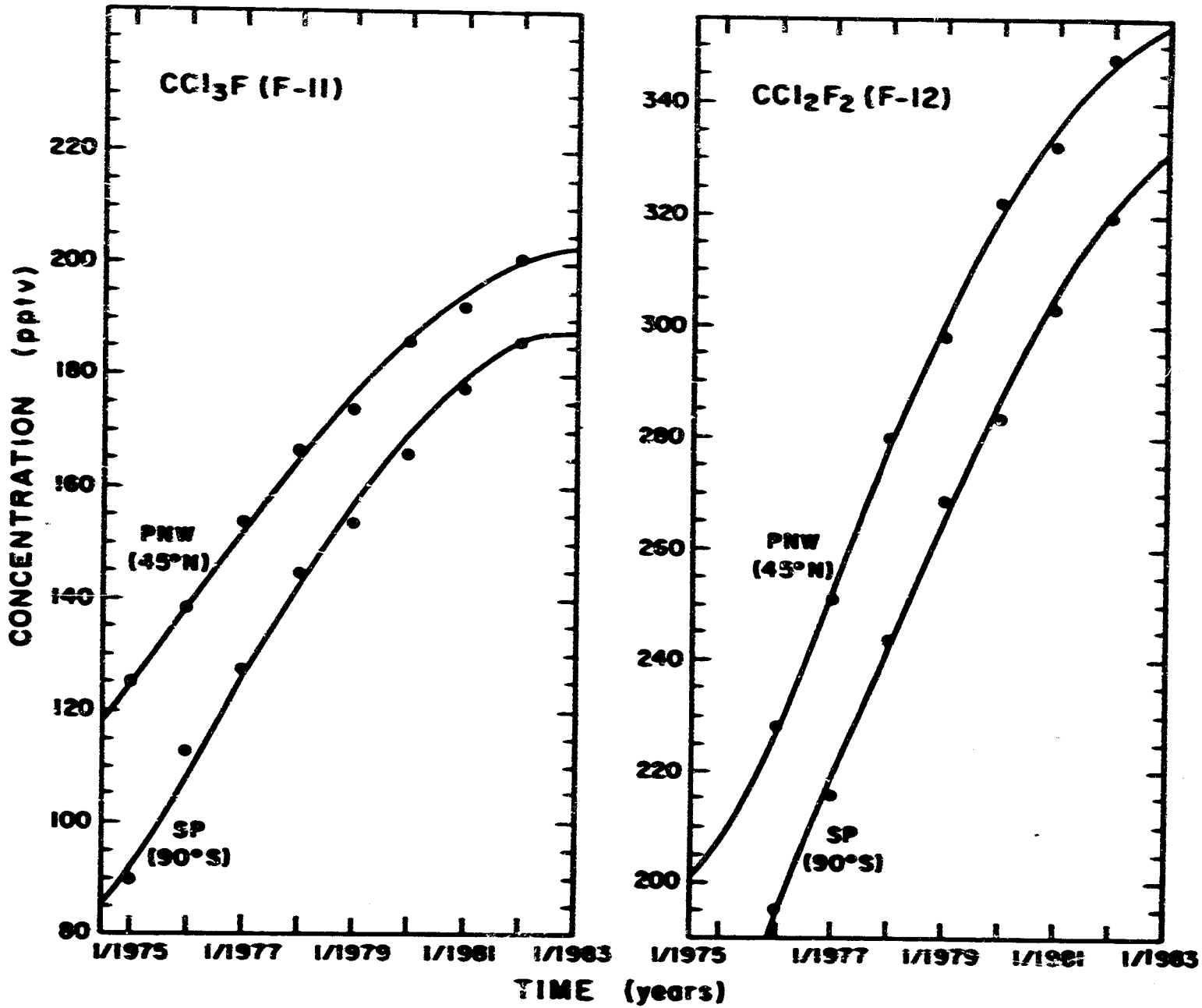
CCl3F (F-11)
CCl2F2 (F-12)
CONCENTRATION (pplv)
PNW (45°N)
SP (90°S)
PNW (45°N)
SP (90°S)
80
100
120
140
160
180
200
220
200
220
240
260
280
300
320
340
1/1975
1/1977
1/1979
1/1981
1/1983
1/1975
1/1977
1/1979
1/1981
1/1983
TIME (years)

Figure 1

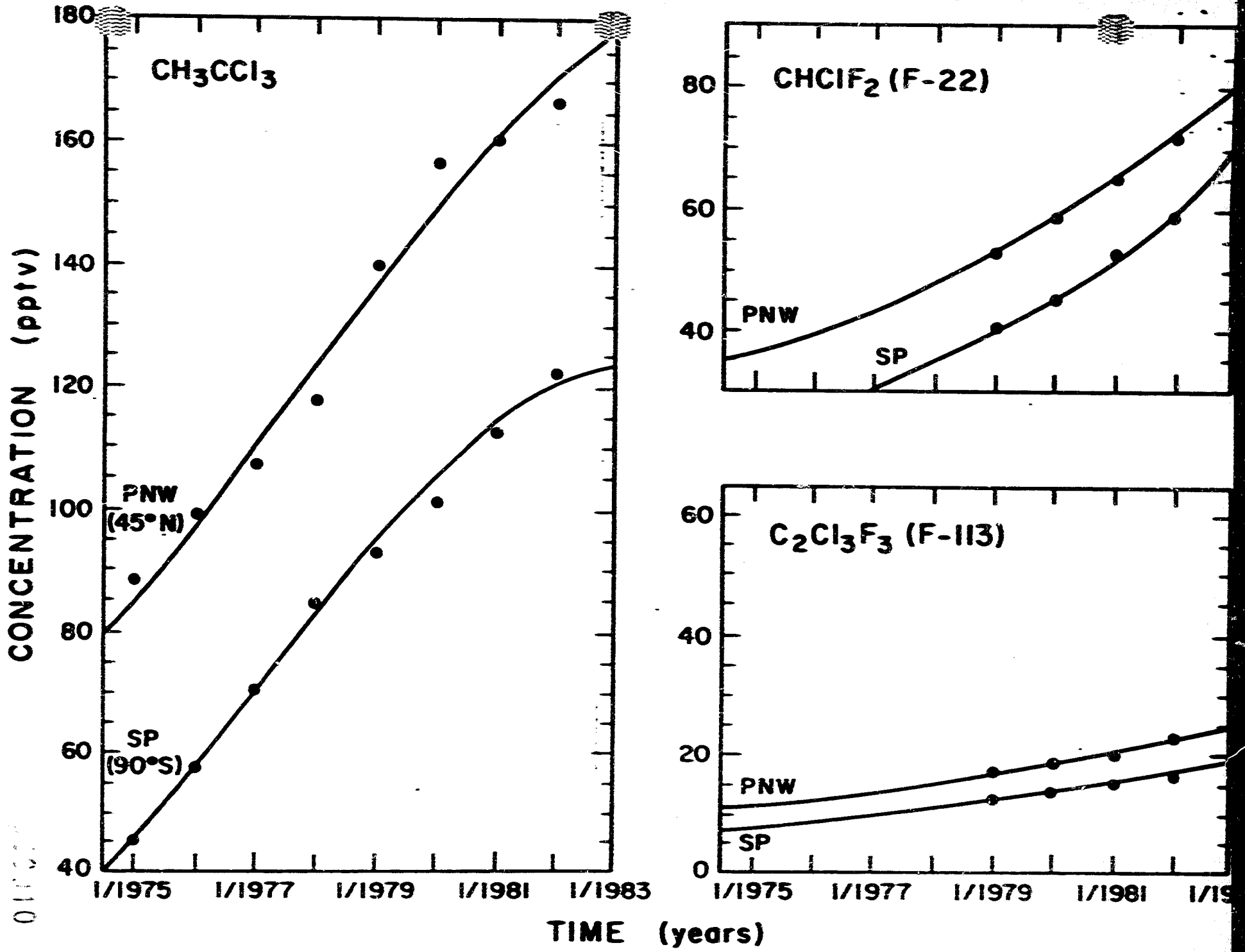
CH3CCl3
CHClF2 (F-22)
C2Cl3F3 (F-113)
PNW
(45°N)
SP
(90°S)
PNW
SP
PNW
SP
CONCENTRATION (pptv)
TIME (years)
180
160
140
120
100
80
60
40
80
60
40
60
40
20
0
1/1975
1/1977
1/1979
1/1981
1/1983

Figure 2

8782/1388

TABLE 1

The yearly increase of halocarbon concentrations and the slowdown of atmospheric accumulation at the south pole (SP, 90°S) and the Pacific Northwest (PNW, 45°N).

Gas	C_o (pptv)	β_o (% yr^{-1})	δ (% yr^{-2})	r	n
CCl_3F					
SP (90°S)	92	18	-2.4	0.997	8
PNW (45°N)	125	11	-1.2	0.999	8
Global	109	14	-1.8	0.999	8
CCl_2F_2 F-12)					
SP (90°S)	170	13	-1.4	0.999	7
PNW (45°N)	201	12	-1.6	0.999	7
Global	186	12	-1.4	0.999	7
CH_3CCl_3					
SP (90°S)	46	24	-2.8	0.997	8
PNW (45°N)	84	15	-1.6	0.991	8
Global	65	18	-1.8	0.999	8
$CHClF_2$ (F-22)					
SP (90°S)	40	13		0.999	4
PNW (45°N)	53	10		0.996	4
Global	46	11		0.996	4
$C_2Cl_3F_3$ (F-113)					
SP (90°S)	12	9		0.974	4
PNW (45°N)	16	10		0.986	4
Global	14	10		0.991	4

The rate of change of trace gas concentration is assumed to follow the equation $\frac{1}{C}\frac{dC}{dt} = \bar{\beta}_o - \bar{\delta}t$. $\beta_o = 100\,\bar{\beta}_o$ (% yr^{-1}) and $\delta = 100\,\bar{\delta}$. Concentrations of F-11, F-12, and CH_3CCl_3 started rising at β_o% per year around 1975, but this rate declined on the average by δ% per yr^2 since then. C_o is the average concentration of F-11, F-12, and CH_3CCl_3 during January 1975 and of F-22 and F-113 during January 1979. r = correlation and n - number of years measurements were made.

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Doc Type 22
• R.I • U.T • H.E.D.S.D B.D. S.U H.S F.N

Doc Title 23
ATMOSPHERIC TRACE GASES AT POINT BARROW AND ARCTIC HAZE

Chemical Name (300 per name) 25	CAS No. (10) 24
METHYL CHLOROFORM	71-55-6

A.K. 8/31/83

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ATMOSPHERIC TRACE GASES AT POINT BARROW AND ARCTIC HAZE

by

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For several decades a winter haze has appeared in the arctic, thousands of miles from the nearest area of dense human population or major industrial activity. Yet there is considerable evidence that this sub-micron-sized haze aerosol consisting of sulfate, soot, and organics results from human activities (Rahn & McCaffery, 1980; Weschler, 1981; Rosen et al., 1981a,b). The small ratios of primary to secondary components, combustion-derived soot and Vanadium, and the presence of excessive amounts of man-made gases all attest to the distant origin of arctic haze (Rosen et al., 1981a; Rahn & Heidam, 1981; Ottar, 1981; Husar & Patterson, 1979; Rahn & McCaffery, 1980; Shaw, 1981; Khalil & Rasmussen, 1982). Although current knowledge favours Eurasia as the dominant source, significant contributions from other industrialized and populated areas, including the United States, cannot be ruled out (Rahn, 1981a; Barrie et al., 1981; Reiter, 1981; Patterson & Husar, 1981). Except for a consensus that the presence of soot can heat the lower atmosphere of the arctic, the possible environmental effects of continued or increased arctic air pollution have yet to be worked out (see also Borys & Rahn, 1981; Rahn, 1981c; Rahn & Heidam, 1981; Rosen et al., 1981b).

It stands to reason that many exotic trace gases which are produced at the same mid-latitude regions of the northern hemisphere as the precursors of arctic haze will also be transported to the arctic. Such inert gaseous tracers can be used to identify the origins of arctic haze in much the same way as the ratios of elemental tracers (Rahn, 1981b).

In this paper we report data on eight potential man-made gaseous tracers of arctic haze, namely CCl_3F, CCl_2F_2, $CHClF_2$, CH_3CCl_3, C_2Cl_4, C_2HCl_3, CO, and CH_3Cl. We discuss the criteria for a gas to be a tracer of arctic pollution and finally review the conclusions which can be drawn from the trace gas studies. Further details of most topics discussed here are presented in the paper of Khalil & Rasmussen (1982).

1. The Data and Their Analysis

Since August 1980 samples of arctic air have been collected by NOAA/GMCC at Pt. Barrow, Alaska (~72°N). Each week three samples were collected, one immediately after the other, in specially prepared internally SUMMA® polished stainless steel 0.8 L flasks, with an ultra clean Metal Bellows MB-158 pump. This equipment was designed and supplied by our laboratory at the Oregon Graduate Center (OGC). The samples are sent by air to OGC where they are analyzed, usually within a week after being collected. Well-established gas chromatography techniques are used for the analyses as described in our earlier papers (Rasmussen & Khalil, 1980; Rasmussen et al., 1982). Each flask was analyzed twice, thus providing six determinations of each trace gas every week. In related laboratory studies it has been established that the trace gases we measured are inert in the sampling flasks for periods of many months. The precision of analysis of the fluorocarbons is <1% and <5% for other gases. In all, the results of analyzing about 240 samples are reported here, constituting about 80 different sets of samples and spanning over 1½ years.

As discussed earlier, the concentrations of six man-made halocarbons, CO and CH_3Cl showed markedly high concentrations during winter compared to other seasons. The monthly average concentrations of the man-made halocarbons, CO and CH_3Cl are listed in Table 1 along with 90% confidence limits of the means.

The data for fluorocarbons 11, 12, 22 and methyl chloroform were analyzed by first subtracting the annual trends of atmospheric concentrations according to the formula:

$$C_{ijk_*} = C_{ijk} - bt_{ijk} \qquad (1)$$

where C = concentration (pptv), ijk index time with i = week (1, 2, 3, 4), j = month, 1, . . . , 12, and k = year 1, 2 or 3, thus t_{111} is August 1980. These monthly averages with trend subtracted were used to construct Figure 1 showing high winter concentrations of these gases compared to other seasons. After the trend had been subtracted, data for the same month but

different years were pooled together by forming the average $C_{j*} = 1/N \Sigma_{ik} C_{ijk}$. These data were analysed statistically and the results were reported in detail in the paper of Khalil & Rasmussen (1982). The largest difference between such monthly means (δ^*) is given in Table 2 along with other calculations based on the data.

The case of methyl chloride (CH_3Cl) and CO is further complicated by natural seasonal cycles in their concentrations. Still, when the concentrations found at Pt. Barrow were compared with extensive measurements made at Cape Meares, Oregon (45°N), it turned out that large excesses of these gases were present at the arctic site only during winter. These tracers are important because they are released from specific combustion processes and could therefore aid in identifying the origins of arctic air masses when the haze is present (see Rasmussen et al., 1980; Crutzen et al., 1979; Logan, 1980; Rasmussen et al., 1982; Khalil & Rasmussen, 1981).

2. Criteria for Gaseous Tracers

As Table 2 shows, some tracers have more prominent winter maxima compared to others. Such tracers are desirable since their measurements can be used to more accurately estimate the contributions of various source regions. Based on the data discussed earlier, the criteria for gases to be tracers of arctic haze have been developed by Khalil & Rasmussen (1982) and are summarized next.

In general (a) the gases must be entirely man-made or must have large mid-latitude anthropogenic sources; (b) they must have long enough lifetimes in winter to survive transport to the arctic; and (c) their seasonal patterns must repeat year after year whenever arctic haze is present. The seasonal pattern in condition (c) should mirror the seasonal pattern of arctic haze aerosol; thus, maximum trace gas concentrations must occur during the arctic winter half year (see Rahn, 1981b; Rahn et al., 1977). To satisfy the last condition we chose the following quantitative criteria:

(i) $\bar{C}_{max} > \bar{C}_{min}$ $(\alpha < 0.01)$

(ii) $\bar{C}_{max} > \bar{C}_{1}$ $(\alpha < 0.01)$

where $\bar{C}_{max}$ is the average concentration of the trace gas in the arctic during three successive winter months between December and May when maximum concentrations are observed, $\bar{C}_{min}$ is the average concentration during the three months of summer (June to August), $\bar{C}_1$ is the average concentration for the nine months other than the three chosen to define $\bar{C}_{max}$, and α is the level of significance at which the hypotheses $\bar{C}_{max} = \bar{C}_{min}$ and $\bar{C}_{max} = \bar{C}_1$ can be rejected. It has been assumed that $\bar{C}_{max}$, $\bar{C}_{min}$ and $\bar{C}_1$ are calculated after any detectable long-term trends have been subtracted from the data. The criteria establish the high probability that wintertime concentrations of a trace gas are significantly greater than during summer or the rest of the year.

The trace gases listed in Tables 1 and 2 satisfy the criteria. Generally, the background concentrations of long-lived gases tend to be large compared to seasonal emissions, thus making it difficult to detect seasonal variations. Thus, gases with global lifetimes of less than 5 years or with concentrations far less than those expected from equilibrium with current yearly emissions were found to be the most suitable tracers.

3. Conclusions and Results Supported by Tracer Gases

The measurements of trace gases at Pt. Barrow support several conclusions of previous studies of the arctic haze aerosol. In particular the following conclusions may be drawn.

The six man-made halocarbons ($CHClF_2$, CCl_3F, CCl_2F_2, C_2Cl_4, C_2HCl_3, CH_3CCl_3), carbon monoxide (CO) and methyl chloride (CH_3Cl) are produced at the same mid-latitude regions as the precursors of arctic haze. Their maximum concentrations in the arctic occur during winter, closely following the occurrence of arctic haze. These gases can therefore serve as quantitative tracers of the distant origins of arctic haze.

Since these gases are produced in industrialized and populated regions of the world, their greater concentrations during the arctic winter can occur only because of long distance transport. This result provides additional and independent support to previous studies indicating that the sources of arctic haze aerosol are anthropogenic and located in the mid-latitudes of the northern hemisphere (Rahn, 1981b).

Several of the halocarbon tracers are released throughout the year and are so inert that their lifetimes do not vary significantly during the year. Their observed seasonal patterns are consistent with a faster transport during winter from polluted mid-latitude locations to the arctic. Such transport patterns may also contribute to the occurrence of arctic haze.

Differences in the seasonal pattern of F-11 and F-12 in the arctic may indicate either the seasonal variations in the use patterns of these gases or the contributions of different sources to the arctic atmosphere. Further studies may resolve whether there is a predominant location from which the arctic haze aerosol originates or if pollution from a few seperated locations combines to produce arctic haze.

More recent studies on the variation of tracer gas concentrations with height suggest that polluted air may be transported in a layer between 1 and 2 km and perhaps in higher layers as well. Figure 2 shows an example of a height profile of perchloroethylene, C_2Cl_4 (see also Rahn & Heidam, 1981).

Currently studies of the seasonal cycles of trace gases at Pt. Barrow are continuing and are being supplemented with studies of the abundances of unique exotic gases in transit from specific industrialized areas of the world to the arctic. It is hoped that this information will reveal the origins of arctic haze.

TABLE 1

Barrow, Alaska

Monthly averaged concentrations of man-made halocarbons, CH_3Cl and CO

Time	$CHClF_2$ (F-22)	CCl_2F_2 (F-12)	CCl_3F (F-11)	CH_3CCl_3	C_2Cl_4 (PCE)	C_2HCl_3 (TCE)	CH_3Cl	CO
8/1980	65 (4)	321 (12)	192 (5)	155 (4)				96 (5)
9	66 (1)	327 (4)	192 (4)	155 (3)			545 (51)	107 (5)
10	66 (1)	331 (3)	194 (2)	159 (3)			542 (40)	96 (11)
11	68 (2)	332 (1)	195 (1)	162 (5)			561 (13)	113 (11)
12	71 (6)	336 (4)	195 (4)	171 (18)			581 (11)	153 (21)
1/1981	81 (3)	334 (3)	193 (2)	185 (17)			627 (34)	149 (18)
2	69 (1)	337 (5)	147 (8)	166 (6)	145 (6)	51 (–)	608 (15)	174 (27)
3	67 (2)	333 (4)	198 (1)	167 (2)	96 (7)	15 (14)	623 (15)	157 (10)
4	69 (1)	331 (5)	199 (1)	166 (2)	104 (8)	12 (9)	623 (7)	160 (13)
5	69 (1)	336 (1)	200 (1)	167 (3)	75 (13)	9 (–)	639 (21)	146 (12)
6	69 (1)	335 (6)	200 (2)	165 (4)	74 (3)	6 (–)	621 (38)	106 (12)
7	69 (2)	337 (6)	200 (2)	162 (1)	62 (3)	4 (2)	565 (33)	78 (6)
8	70 (1)	340 (2)	199 (2)	162 (3)	62 (3)	8 (2)	541 (28)	70 (9)
9	71 (1)	338 (4)	198 (1)	168 (6)	56 (3)	6 (3)	506 (40)	83 (4)
10	71 (4)	345 (3)	197 (1)	166 (2)	75 (–)	11 (–)	536 (14)	107 (9)
11	73 (14)	348 (4)	200 (3)	189 (71)			587 (0)	123 (5)
12	79 (10)	349 (1)	204 (1)	182 (25)	106 (20)	34 (20)	587 (10)	116 (27)
1/1982	75 (3)	350 (3)	205 (1)	181 (16)	111 (10)	31 (9)	583 (5)	146 (78)
2	77 (1)	354 (2)	208 (3)	176 (9)	120 (8)	37 (4)	646 (–)	183 (8)
3	77 (–)	354 (–)	205 (–)	177 (–)				

Concentrations are in pptv (1 pptv = 10^{-12}) except CO which are in ppbv (10^{-9}).

( ) = 90% confidence limits based on the t-statistic.

TABLE 2. Comparison of the highest and lowest monthly concentrations of the Arctic Haze tracers ($\delta^* > 0$: $\alpha < 0.01$; Welch test)

Gas	Months of maximum and minimum concentrations								C_{max} ($\pm\delta C_{max}$)	C_{min} ($\pm\delta C_{min}$)	δ^* ($\pm\delta\delta^*$)	δ^* ($\pm\delta\delta^*$) %
	Max				Min							
	D	J	F	M	J	J	A	S				
$CHClF_2$ (F-22)		X				X			62.5 (±3.9)	55.3 (±0.9)	7.2 (±3.9)	13.0 (±7)
CH_3CCl_3		X				X			172.1 (±11.2)	149.7 (±1.0)	22.4 (±11.2)	15.0 (±7)
C_2Cl_4 (PCE)			X					X	128 (±11)	56 (±3)	72 (±11)	129 (±20)
C_2HCl_3 (TCE)			X			X			40 (±7)	4 (±2.5)	36 (±7)	850 (±400)
CCl_2F_2 (F-12)	X				X				326.7 (±1.7)	318.7 (±4.6)	8.0 (±4.7)	2.5 (±1)
CCl_3F (F-11)			X			X			202.6 (±3.4)	192.3 (±2.1)	10.3 (±3.7)	5.4 (±2)
CO (ppmv)			X			X			179 (±11)	78 (±7)	101 (±11)	130 (±18)
CH_3Cl				X				X	623 (±19)	523 (±22)	100 (±26)	19 (±5)

C_{max}, C_{min} are the average monthly highest and lowest concentrations during the year. δC are the 90% confidence limits of C. $\delta^* = (C_{max} - C_{min})$ and $\pm\delta\delta^*$ = 90% confidence limits of δ^*. $\delta^* > 0$ at α 0.01 (Welch test). $\delta^*\% = 100(C_{max} - C_{min})/C_{min}$: $\delta\delta^*\%$ are approximate 90% confidence limits.

Figure 1. Three-month running averages of the monthly average concentrations of eight gaseous tracers of arctic haze (Pt. Barrow, Alaska). This result provides evidence that the seasonal variations of these eight gases have repeated themselves over the two winters of observation. (From Khalil & Rasmussen, 1982).

Figure 2. The concentration of trichloroethylene as a function of height on two different days (⊢—●—⊣ : 5/7/82; (⊢—○—⊣ : 5/13/82). Polluted air occurs between 1 and 3 kilometers.

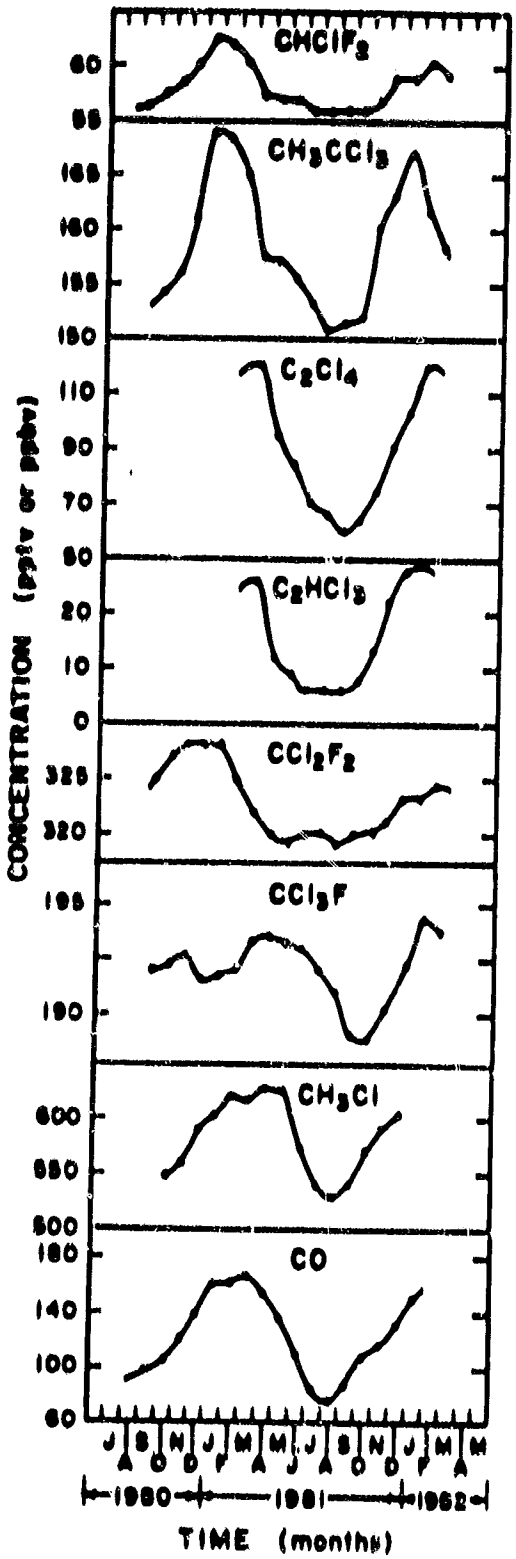
CHClF2
CH3CCl3
C2Cl4
C2HCl3
CCl2F2
CCl3F
CH3Cl
CO
CONCENTRATION (ppbv or pptv)
TIME (months)
1980
1981
1982

FIGURE 1

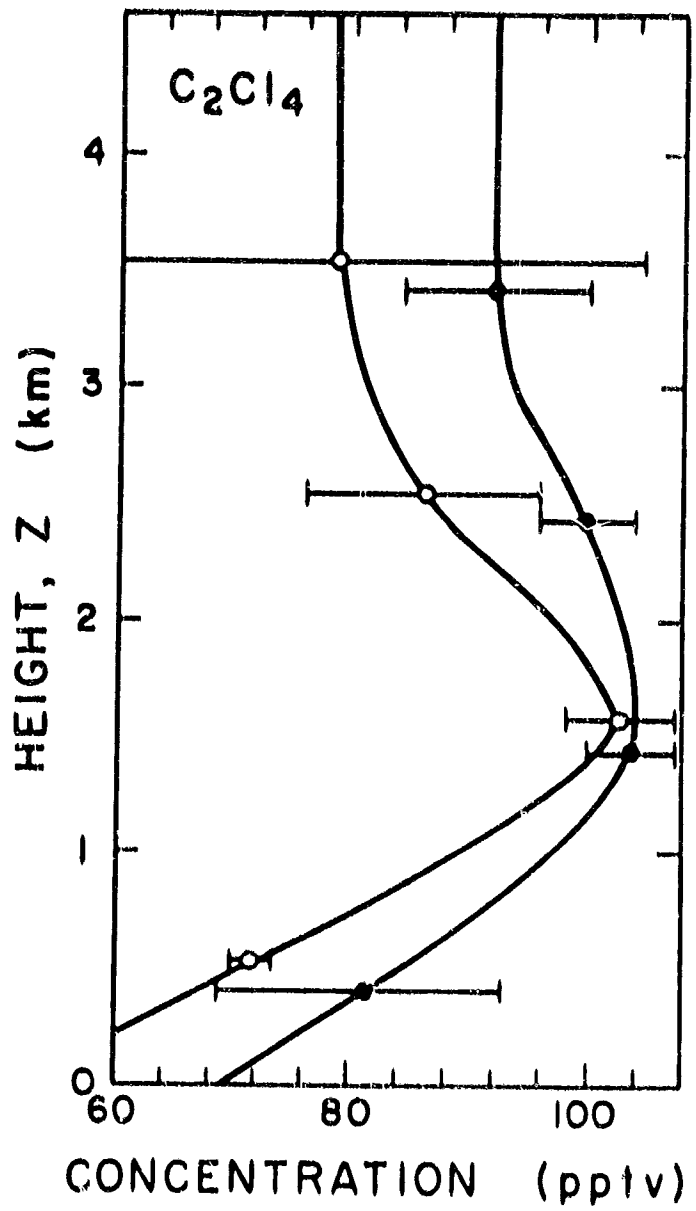

FIGURE 2

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1,1,1-TRICHLOROETHANE	71-55-6

A.K. 5/31/83

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The Atmospheric Lifetime Experiment VI: Results for CH_3CCl_3 based on three years of data

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Abstract

We present gas chromatographic determinations of the concentrations of CH_3CCl_3 at Adrigole (Ireland), Cape Meares (Oregon), Ragged Point (Barbados), Point Matatula (American Samoa), and Cape Grim (Tasmania) for the three-year period July, 1978 through June, 1981. The determinations involve approximately four measurements each day with on-site calibration. The absolute values and trends for these observed concentrations are interpreted in terms of the industrial production, global circulation rate, and atmospheric lifetime of CH_3CCl_3 using an optimal estimation technique incorporating a 9-box model of the atmosphere. The globally and annually-averaged trend in the lower troposphere at the mid-point of the second year of the experiment is 8.7% per year and the inferred global atmospheric content of CH_3CCl_3 at this mid-point is 2.58×10^9 kgm. The global atmospheric lifetime of CH_3CCl_3 deduced from its trend is $10.5^{+6.2}_{-2.8}$ years while the lifetime deduced from its global content is $9.6^{+4.5}_{-2.3}$ years.

1. INTRODUCTION

The compound 1,1,1-trichloroethane (methyl chloroform) is a relatively long-lived atmospheric constituent with a predominantly or exclusively anthropogenic origin. The reaction of CH_3CCl_3 with the OH radical is its principal recognised atmospheric sink (Yung et al., 1975; Cox et al., 1976). It has therefore been proposed as a potentially accurate indicator of tropospheric OH concentrations (Singh, 1977a; Lovelock, 1977). It has also been identified as a potentially significant source of reactive chlorine compounds in the stratosphere (McConnell and Schiff, 1978; Crutzen et al., 1978). It is therefore important to understand the global mass balance for this species and in particular to reconcile its observed atmospheric concentrations with its anthropogenic sources and globally-averaged atmospheric lifetime.

Estimates of the globally-averaged atmospheric lifetime τ of CH_3CCl_3 have varied considerably over the past few years. Estimates using horizontally-averaged models include those of Yung et al. (1975), Cox et al. (1976), Singh (1977a), Crutzen and Fishman (1977), McConnell and Schiff (1978), Rasmussen and Khalil (1981), and Makide and Rowland (1981) who estimated τ values of 3, 1.1, 7.2 ($\pm$ 1.2), 6 - 10.7, 8, 6 - 10 and 6.9 ($\pm$ 1.2) years respectively. In addition, using two-dimensional box models of varying complexity, Lovelock (1977), Neely and Plonka (1978), Singh (1977b), Chang and Penner (1978), Singh et al. (1979), Chameides and Tan (1981), and Logan et al. (1981) deduced τ values of 5 - 10, 3.3 ($\pm$ 0.7), 5.3, 11.3, 8 - 10, 4.6 - 15, and 5 years respectively. Finally, using a two-dimensional grid model, Derwent and Eggleton (1978, 1981) computed τ values of 5.4 and 3.6 - 6 years respectively. These various lifetime estimates have been obtained either

by specifying the atmospheric concentrations of the presumed principal scavenger of CH_3CCl_3 (namely OH), or by a consideration of the global mass balance between CH_3CCl_3 sources and sinks, or by a combination of both approaches. The lifetime estimates vary due to these differing basic approaches. They also vary due to differences in estimates of the tropospheric concentrations of OH and its rate of reaction with CH_3CCl_3, due to uncertainties in the industrial emissions, concentrations and spatial and temporal trends of CH_3CCl_3, and finally due to the varying complexity of the atmospheric models involved.

The approach which utilizes considerations of global sources and sinks is clearly the more direct for deducing CH_3CCl_3 lifetimes and provides atmospheric OH concentrations as an important corollary. Some of the problems associated with this approach, in particular systematic errors in industrial emissions and absolute atmospheric concentrations, can be alleviated through sufficiently accurate determinations of the global trend in CH_3CCl_3 concentrations. The use of trend measurements for determining atmospheric lifetimes has been discussed in detail by Cunnold et al. (1978) with specific application to the compounds $CFCl_3$ and CF_2Cl_2. By analogy with these latter compounds, we expect that measurements of CH_3CCl_3 trends at several globally-distributed sites should provide an accurate determination of the CH_3CCl_3 lifetime unaffected by systematic errors of the aforementioned type.

The "Atmospheric Lifetime Experiment" (ALE) was instigated to measure accurately the rates of increase of the atmospheric concentrations of the five long-lived atmospheric constituents $CFCl_3$, CF_2Cl_2, CH_3CCl_3, CCl_4, and N_2O (Prinn et al., 1982). One of the goals of the

experiment was to use the observed trends in concentration to deduce, where possible, the atmospheric lifetimes of these constituents. In this paper we present absolute concentrations and trends in CH_3CCl_3 concentrations obtained during ALE in the period July, 1978 through June, 1981. These observations are then interpreted in terms of the industrial emission, global circulation, and atmospheric lifetime of CH_3CCl_3.

The ALE utilizes automated dual-column electron capture gas chromatographs which sample the background air about four times daily at the following five globally-distributed sites: Adrigole, Ireland (52°N, 10°W); Cape Meares, Oregon (45°N, 124°W); Ragged Point, Barbados (13°N, 59°W); Point Matatula, American Samoa (14°S, 171°W) and Cape Grim Tasmania (41°S, 145°E). Details concerning the instrumentation and station operation are provided by Simmonds et al. (1982). Methyl chloroform is analysed using a silicone column with either a constant frequency (Ireland; Barbados; Nov. 10, 1978 to May 8, 1979 at Samoa) or constant current (Oregon; Samoa except Nov. 10, 1978 to May 8, 1979; Tasmania) detector. Details concerning the technique for absolute and relative calibration of the data are given by Rasmussen and Lovelock (1982). Reference cylinders of air which are analysed relative to a primary standard, are shipped to the ALE sites, where they are used for approximately 3 months and then returned for re-analysis. The primary standard for CH_3CCl_3 is described by Rasmussen and Lovelock (1982). Details concerning data processing including formuli used for data calibration and methods used for discerning locally polluted air from clean background air are provided in Prinn et al. (1982). Periods in which local pollution is unambiguously indentified are omitted from the data presented in

this paper. Such pollution periods are largely restricted to the Adrigole ALE station and their inclusion in the data would make this station non-typical of the 30°N-90°N atmospheric mass (Prinn et al. 1982).

The CH_3CCl_3 data are analysed in this paper using a 9-box model (8 tropospheric boxes and 1 stratospheric box) of the global atmosphere and an optimal estimation technique for calculating lifetimes as described in detail by Cunnold et al. (1982a). Industrial emission rates for CH_3CCl_3 which are required for estimation of lifetimes are obtained from various chemical industry sources. Methyl chloroform is widely used as an industrial vapor degreasing solvent particularly in the sheet-metal industry which supplies automobile manufacturers.

3. GLOBAL METHYL CHLOROFORM DATA

Daily-average CH_3CCl_3 mixing ratios and their daily standard deviations determined from the measurements at the 5 ALE sites in the period from July, 1978 through June, 1981 are shown in Figures 1-5. The monthly-average mixing ratios $\bar{X}$(pptv) and their standard deviations σ at each site in this period are reported in Table 1. In the figures, the times of calibration tank changes (and the calibration tank numbers) are indicated along the top of each plot. To obtain our current best estimates of the absolute concentration of CH_3CCl_3 in the atmosphere, all values reported in Figures 1-5 and Table 1 must be multiplied by the calibration factor $\zeta = 1.0 \pm .15$ (Rasmussen and Lovelock, 1982).

The variation in the CH_3CCl_3 mixing ratios χ(pptv) over seasonal and longer time scales is conveniently described at station i by the function

$$\ln\chi_i = a_i + b_i\left(\frac{t-18}{12}\right) + d_i\left(\frac{t-18}{12}\right)^2 + c_i\cos\left(\frac{2\pi t}{12}\right) + s_i\sin\left(\frac{2\pi t}{12}\right) \qquad (1)$$

where t is time measured in months with month 1 being July, 1978. The coefficients a_i, b_i, d_i, c_i, and s_i have been determined from the monthly-mean $\bar{X}$ and σ values given in Table 1 using the method described by Cunnold, et al. (1982a). Values of the latter coefficients for each of the 5 ALE stations are given in Table 2. An estimate of the global-average mixing ratio and trend of CH_3CCl_3 in the lower troposphere may be derived by suitably averaging the time series obtained in each latitude region. For this purpose as well as for all the other data processing reported in this paper, the Adrigole, Ireland and Cape Meares, Oregon data have been optimally

combined into a single time series. At Northern Hemisphere mid-latitudes we thus derive a_1 = 5.021, b_1 = 0.069, d_1 = -0.013, e_1 = 0.001, and s_1 = 0.009. Using the various time series, we deduce at the mid-point of the second year of the experiment (January 1,1980) that the annually averaged surface mixing ratio and trend are respectively: 152 pptv and 10.3 pptv/year at Adrigole/Cape Meares; 133 pptv and 9.3 pptv/year at Ragged Point; 106 pptv and 12.3 pptv/year at Point Matatula; and 103 pptv and 10.9 pptv/year at Cape Grim. Averaging these 4 values of mixing ratio and trend yields a global-average surface mixing ratio and trend of 123 pptv and 10.7 pptv (8.7%) per year respectively.

The locations of the 5 ALE stations were deliberately chosen to represent, as much as possible, the 4 major equal mass subdivisions of the global atmosphere. To the extent that this goal is accomplished, the globally-averaged trends quoted above are valid. In this respect, our principal concern must be with any major deviations from a monotonic gradient in CH_3CCl_3 concentrations with latitude. Available data (Rasmussen and Khalil, 1981) suggest that a small deviation does exist (mixing ratios at 70°N are 3-6% less than those at Cape Meares while mixing ratios at 30°S are about equal to those at Cape Grim). This suggests that our use of only Cape Meares and Adrigole (which shows similar mixing ratios) may lead us to overestimate slightly the average mixing ratio in the 30°N - 90°N semi-hemisphere. In contrast, our neglect of polluted air at Adrigole will cause us to slightly underestimate the mixing ratios in this semi-hemisphere. Present indications are that these two off-setting errors are of similar magnitude and are therefore not expected to have an important effect on our estimate of the global CH_3CCl_3 trend. These combined errors are also expected to lead to an uncertainty of at most 1% in the global CH_3CCl_3 content.

The coefficients c_1 and s_1 define the magnitude and phase of the annual cycle at each site. Maxima occur in late Spring at Adrigole, Ragged Point, and Point Matatula and in late Winter at Cape Meares and Cape Grim. It is apparent from Table 2 that these seasonal cycles are not very well defined by our 3-year data set but they are nevertheless much larger than, and possess phases different from those for $CFCl_3$ and CF_2Cl_2 (Cunnold et al., 1982a, b). Annual cycles are expected for CH_3CCl_3 due to the seasonal oscillations in atmospheric circulation particularly if, as observed, a significant meridional concentration gradient exists. Cycles are also expected due to the seasonal variation in CH_3CCl_3 destruction by OH but only if the CH_3CCl_3 destruction time $\leq$ the interhemispheric mixing time. Detailed interpretation of the observed cycles for CH_3CCl_3 in terms of the global circulation will appear elsewhere (Alyea et al., 1982).

In examining the data at Adrigole, Ireland (Figure 1), it is evident that this site shows higher σ values for CH_3CCl_3 relative to the two southern hemisphere sites and that identifiable pollution periods (evidenced by the small gaps in the data) are frequent. The large gap in the presented data from Nov. 24, 1978 until Jan. 4, 1979 was caused by obvious detector contamination in this period resulting in the data being discarded.

Greater atmospheric variability (and therefore larger σ's) at Adrigole than at the southern hemisphere sites is expected due to the relative proximity of Adrigole to the predominantly northern mid-latitude sources of CH_3CCl_3. However, the larger σ values may also be due to the fact that Adrigole uses a constant frequency detector while the two southern hemisphere stations use constant current detectors (Simmonds et al., 1982). This latter explanation is supported by a comparison of the σ values at

Samoa during the 6-month period when a constant frequency detector was temporarily used (Nov. 10, 1978 to May 8, 1979) with the σ values following this period when the constant current detector was reinstated. It is also supported by the similarity of σ values at Adrigole and Ragged Point where a constant frequency detector is also in use. It is not supported however by the often similar σ's at Adrigole and Cape Meares where a constant current detector is used. It is clear that both instrumental differences and true atmospheric variability are involved in explaining the station-to-station differences in standard deviations.

The standard deviations at Cape Meares, Oregon (Figure 2) are clearly anomalously high in the period from September, 1980 through February, 1981. There are no instrumental or calibration reasons to suspect the data in this period although it corresponds largely to the period of use of calibration tank number 114--the phenomenon may indicate presently unrecognized local sources for CH_3CCl_3 at this station. Other than this latter phenomenon, we have no reason to suspect any important effects of local pollution in the CH_3CCl_3 data at this site. The data gap from late January to mid-March, 1980 is due to problems encountered during the start-up of this station.

As already noted, the CH_3CCl_3 measurements at Ragged Point, Barbados (Figure 3) show similar standard deviations to those at Adrigole. A visual inspection also indicates an apparent oscillation in the observed mixing ratios with a 1-2 month period. Identifiable local pollution does occur at this site but it is isolated and infrequent and is evident largely in the last year of the CH_3CCl_3 data. The gap in data from late March through

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April, 1979 was due to a temporary inability to deliver chromatographic carrier gas tanks to the site. On May 1, 1979 a new constant frequency detector was installed with an obvious improvement in instrumental precision.

The daily standard deviations of the measurements at Point Matatula, Samoa (Figure 4) are about 1/2 of those at Barbados and the 1-2 month oscillations in the Barbadan data are not discernable in the Samoan data. As noted earlier, a temporary constant frequency detector was used in the period from Nov. 10, 1978 to May 8, 1979. There is no evidence for local CH_3CCl_3 pollution at this site. The absence of data for 3 weeks in January, 1979 was caused by a bee restricting the outside air intake. Gaps in the data from early October through early November, 1980 and from late January through late February, 1981 were due to instrumental damage caused by extremely poor voltage regulation in the power supply of American Samoa.

The Tasmanian CH_3CCl_3 data (Figure 5) generally shows the lowest σ's of any of the sites which, as noted earlier, we believe is due to a combination of the remoteness of this site from the major CH_3CCl_3 sources and to the use of the constant current detector. On November 4, 1978, the silicone column sample volume was changed from 5 to 7 ml resulting in an obvious increase in the precision of the measurements. Occasional periods of identifiable pollution do occur at Cape Grim (about 30 days per year) and these periods have been omitted from the data presented. The instrument was inoperative in the latter half of October, 1978. The data gap from Dec. 11, 1978 through Jan. 18, 1979 is due to identified contamination of an input valve.

3. GLOBAL BUDGET OF METHYL CHLOROFORM

As outlined by Cunnold et al. (1978), there are two principal methods for analyzing globally-distributed observations of a long-lived atmospheric trace species such as CH_3CCl_3 in terms of its sources and sinks. In one approach, the measured total global atmospheric content $c(t)$ of CH_3CCl_3 at time t is expressed in terms of its known release rate $R(t)$ and unknown lifetime τ through the equation

$$c(t) = \int_0^t R(t')e^{(t'-t)/\tau}dt'. \qquad (2)$$

In the other approach, the measured globally-averaged trend in CH_3CCl_3 mixing ratio $X(t)$ is expressed in terms of the known $R(t)$ and the unknown τ through the equation

$$\frac{1}{X}\frac{dX}{dt} = \frac{1}{c}\frac{dc}{dt} = \frac{R(t)}{\int_0^t R(t')e^{(t'-t)/\tau}dt'} - \frac{1}{\tau} \qquad (3)$$

The relative sensitivity of these two approaches to errors in the concentrations X or c and the release rates R leads one to generally favor the trend technique over the global content technique for accurately defining τ. In this section, we first review our knowledge of the global release rates of CH_3CCl_3 and their probable accuracy. We then analyze the ALE CH_3CCl_3 data using both of the above methods.

2.1 Methyl chloroform emissions

Neely and Plonka (1978) have presented global production and atmospheric release estimates for 1,1,1-trichloroethane computed by the Dow Chemical Company for the period 1951-1976. We also have an update of these estimates which provides release data for 1977-1979 (W.B. Neely and M. Farber, private communication). Independent of these Dow Chemical Company data, we also have obtained through one of our authors (E.C.L.) the global CH_3CCl_3 sales estimates for the period 1977-1981 computed by Imperial Chemical Industries, PLC. These latter estimates include the fraction of the total sales applicable to each of the four equal mass subdivisions of the global atmosphere. The available data are summarized in Tables 2 and 3.

The year-to-year fluctuations in the ratio of the annual production to the annual release discernable in the Dow Chemical Company estimates are evidently due to year-to-year changes in the inventory held by the manufacturers. For example, inventories were obviously building up in the middle 1970s evidently as a result of 1,1,1-trichloroethane replacing the solvent trichloroethylene as the use of the latter compound become increasingly regulated.

In order to relate the available data on annual production P(t), sales S(t), inventory I(t), and releases R(t), we make the reasonable assumption that a constant fraction f of the CH_3CCl_3 sales in each year is emitted to the atmosphere and that there is no important time lag between the sale and use of this compound. Thus, for the year t

$$R(t) = f\,S(t)$$

$$= f(P(t) - I(t) + I(t-1)) \qquad (4)$$

The fraction f is less than unity due to decomposition of CH_3CCl_3 during storage and use, to its use as an intermediate in production of other chemicals, and most important, to incineration or incarceration of concentrated organic solutions in which CH_3CCl_3 was used as the solvent. Using equation (4), the value of f appropriate to the Dow Chemical Company estimates is simply

$$f = \frac{\sum_{t=1951}^{t=1976} R(t)}{\left(\sum_{t=1951}^{t=1976} P(t)\right) - I(1976)} \qquad (5)$$

$$= 0.94$$

where we have assumed I(1976) = P(1976)/8 which is typical of inventories in the industry. This f value is consistent with an independent estimate by Imperial Chemical Industries, PLC implying only about 5% of CH_3CCl_3 sold is incarcerated or incinerated. Using (4) and (5), we have converted the S(t) values for 1977-1981 from Imperial Chemical Industries, PLC to R(t) values which can be compared to the R(t) values estimated by the Dow Chemical Company for 1977-1979 (see Table 4). The global R(t) estimates for 1977, 1978, and 1979 from Imperial Chemical Industries, PLC are respectively 1.0% higher, 6.1% lower, and 3.4% lower than the corresponding estimates for these 3 years by the Dow Chemical Company. The agreement between these

two essentially independent estimates is encouraging.

Based on these considerations we have adopted the Neely and Plonka (1978) release data for 1951-1976. We assume that the percentages applicable to each semi-hemisphere in this period vary linearly between 1951 and 1977. Values assumed for 1951 are 100% for 90°N-30°N and 0% for the other 3 semi-hemispheres. Values assumed for 1977 are those given in Table 4.

For the 1977-1979 period we adopt an average of the two global release estimates given in Table 4, since we have no reason to prefer one estimate from the other. The percentages applicable to each semi-hemisphere are assumed to be those estimated from Imperial Chemical Industries, PLC data during this period.

As far as can be gauged from the data in Tables 3 and 4 and from industry sources polled by one of our authors (B.C.L.), the large inventory fluctuations evident in the middle and late 1970s are not expected in the 1979-1981 period due to the new relative stability in supply versus demand for CH_3CCl_3. Thus any fractional changes in global production from 1979 to 1981 should have produced similar fractional changes in sales and releases. Data on production of CH_3CCl_3 in the U.S.A. are readily available (U.S. International Trade Commission, 1979, 1980, 1981). In particular, a comparison of the annual data for 1979 and 1980 indicates production of CH_3CCl_3 decreased by 3.36% from 1979 to 1980, and a comparison of the annual data for 1980 and the preliminary annual data for 1981 indicates production increased by 0.76% from 1980 to 1981. Due to the international character of the sheet metals industry, and thus of the use of CH_3CCl_3 in its primary

role as a degreaser, changes in production in the U.S.A. should be at least qualitatively indicative of world-wide trends. We have therefore assumed a 3.36% decrease from 1979 to 1980 and a 0.74% increase from 1980 to 1981 in the Dow Chemical Company estimates of global releases. With these 1980 and 1981 estimates and/or extrapolations in hand, we then adopt an average of the Imperial Chemical Industries, PLC and Dow Chemical Company global release values for the 1980-1981 period, with the percentages of release in each semi-hemisphere being those calculated from the Imperial Chemical Industries, PLC data alone.

A completely objective estimate of the probable errors in these adopted release values is not presently possible. However, we note that the number of different companies involved in CH_3CCl_3 production, and the number of different release scenarios associated with CH_3CCl_3 end-uses, are both significantly less than, for example, the corresponding numbers for the chlorofluorocarbons $CFCl_3$ and CF_2Cl_2. This is undoubtedly one of the major reasons behind the good agreement between the independent release estimates by Dow Chemical Company and Imperial Chemical Industries, PLC for 1977-1979. The fractional differences ϵ between these latter two estimates and their mean in the 5 years 1977-1981 have a standard deviation σ given by

$$\sigma = 100\sqrt{\frac{\sum_{n=1}^{n=10_2} \epsilon_n}{9}} \qquad (6)$$

$$= 1.\%$$

and we make the reasonable assumption that this latter σ value is a measure of the standard error in the release estimates adopted in this paper. That is the 95% confidence limits on our release estimates are $\pm 2 \times 1.8\% = \pm 3.7\%$.

One important caveat concerning the above release estimates should be emphasized. They neglect any possible production of CH_3CCl_3 in Eastern Europe, U.S.S.R., and the Peoples Republic of China. Such unknown production is expected to be small relative to the known production included in Tables 3 and 4, because of the unimportance of the automobile industry in these countries relative to the rest of the world. However, the possibility that we are systematically under-predicting CH_3CCl_3 releases by a small fraction should be kept in mind in interpreting our results. For example, recent measurements by Rasmussen et al., (1982) suggest the release of this chemical in the Peoples Republic of China.

2.2 Methyl Chloroform Lifetimes

The optimal estimation technique used in this paper to derive the atmospheric lifetime of CH_3CCl_3 from the $\bar{X}$, σ, and R values given in Tables 1-4 is fully described in Cunnold et al. (1982a). The technique involves the use of a 9-box model of the global atmosphere. Mean advective and eddy diffusive transports between the boxes are completely specified except that the amplitude of all the horizontal eddy diffusive transports are expressed in terms of an unknown dimensionless amplitude factor F of order unity. The lifetime τ_s of CH_3CCl_3 in the stratospheric box (90°S-90°N, 0-200 mb) is assumed to be 6 years based on stratospheric destruction of CH_3CCl_3 by OH and ultraviolet radiation computed in a three-dimensional global circulation model (Golombek, 1982).

The principal recognized sink for CH_3CCl_3 in the troposphere is the reaction

$$OH + CH_3CCl_3 \rightarrow H_2O + CH_2CCl_3 \qquad (7)$$

By comparison, the loss of CH_3CCl_3 by transfer to ocean water is negligible (Neely and Plonka, 1978). In our analysis of the data we wish to recognize the fact that the distribution of the principal tropospheric scavenger of CH_3CCl_3, namely OH, varies significantly with latitude and the fact that the chemical lifetimes and global transport times of CH_3CCl_3 may conceivably be comparable. Under these circumstances, the use of a globally-averaged lifetime would be inappropriate (Logan et al., 1981; Derwent and Eggleton, 1981). We have therefore allowed for the existence of different lifetimes τ_i in each of our 8 tropospheric boxes. The inverse lifetimes τ_i^{-1} are defined by

$$\tau_i^{-1} = k_i\,[OH]_i$$

$$= [5.4 \times 10^{-12}\exp(-1820/T_i)]\,A\,[OH]_i^{*} \quad (sec^{-1}) \qquad (9)$$

where k_i is the rate constant for the reaction of OH with CH_3CCl_3 in the ith box (Jeong and Kaufman, 1979; Kurylo et al. 1979), $[OH]_i$ and $[OH]_i^{*}$ are respectively the actual and assumed average concentrations of OH (molecule cm^{-3}) in the ith box, T_i is the average temperature (°K) of the ith box, and A is an unknown dimensionless and box-independent amplitude factor of order unity. The prediction of the globally-averaged tropospheric lifetime τ_t is therefore equivalent to the prediction of the factor A which relates our assumed OH concentrations to the actual ones. That is the relative OH concentrations in the 8 boxes are specified but the absolute OH concentrations are predicted.

For our assumed values for OH in each box, we have chosen the computed annual-average OH concentrations at 15 and 45 degree latitudes for land and sea surfaces given in Figure 27b of Logan et al. (1981). Annual rather than seasonal-average values are chosen since the box-to-box mixing times are generally shorter than the CH_3CCl_3 destruction times in each box and also because most of the CH_3CCl_3 destruction occurs in the tropics where the seasonal variations in OH are relatively small. There are of course several other model OH distributions which we could choose from the literature. However, the Logan et al. (1981) distributions appear typical and are extensively compared to other calculations in their paper. Using equation (9), these assumed OH concentrations yield the following values for $A\tau_i$: 18.6 yrs in the 90°N-30°N, 200-300 mb

box; 6.4 yrs in the 90°N-30°N, 500-1000 mb box; 6.2 yrs in the 30°N-0°, 200-500 mb box; 2.1 yrs in the 30°N-0°, 500-100 mb box; 5.9 yrs in the 0°-30°S, 200-500 mb box; 2.2 yrs in the 0°-30°S, 500-100 mb box; 14.9 yrs in the 30°S-90°S, 200-500 mb box; and 5.8 yrs in the 30°S-90°S, 500-1000 mb box.

The analysis of the CH_3CCl_3 data to determine the value of A (or equivalently the tropospheric lifetime) utilizes a box-model transport factor, F, equal to 1.6 which is principally determined by the more precisely defined latitudinal distributions of $CFCl_3$ and CF_2Cl_2 (Cunnold, et al., 1982a and b); this value of F results in fact in an underprediction of the latitudinal gradient of CH_3CCl_3 which will be discussed later. Using this latter transport factor, the R(t) values given in Tables 3 and 4, and applying the estimation technique to each time series individually, we obtain the atmospheric lifetime estimates given in Table 5. Averaging the reciprocal lifetime estimates from the four time series with equal weight gives an atmospheric lifetime of methyl chloroform of $10.5^{+6.2}_{-2.8}$ years where the uncertainty limits correspond to the standard error of the four series mean. This may be translated into a tropospheric lifetime (and thus a value for A) using the expression which is valid for our box model

$$\frac{A+r}{\tau} = \frac{A}{\tau_t} + \frac{r}{\tau_s} \qquad (9)$$

where τ, τ_s, and τ_t are the atmospheric, stratospheric (6 years), and tropospheric lifetimes respectively and r is the ratio of the stratospheric mixing ratio to the average mixing ratio in the upper troposphere. Using a troposphere to stratosphere transfer time (t_s) of four years (as used for $CFCl_3$

and CF_2Cl_2 by Cunnold et al. (1982a, b)) we obtain r = 0.47 on January 1, 1980. This may be compared with a value of about 0.58 obtained in the three-dimensional model simulation of the methyl chloroform distribution by Golombeck (1982) (which would correspond to a t_s value of approximately three years). Using (9) with r = 0.47 gives a tropospheric lifetime of methyl chloroform of $11.5 \begin{smallmatrix}+9.6\\-3.5\end{smallmatrix}$ years and a value of A = 0.37 ± 0.17 (using r = 0.58 yields τ_t and A values differing by only about 2% from these).

It is apparent that the ALE measurements yield an A value less than unity. An A value equal to unity corresponds to a tropospheric lifetime in the box model of approximately 4.3 years (and using (9) an atmospheric lifetime of 4.5 years). Values of A less than unity thus correspond to lifetimes greater than 4.3 years which are significantly longer than the global atmospheric transport time. When A < 1 lifetime estimates should not therefore, be strongly dependent on the assumed latitudinal distribution of OH. In fact, our computations show that assuming a uniform distribution of OH in the troposphere produces a change in the lifetime estimate by only approximately 0.1%. In other words, while CH_3CCl_3 measurements provide a useful measure of the globally-averaged tropospheric OH concentration they are not useful for determining the latitudinal distribution of this radical.

The optimal lifetime estimate (as opposed to the 4-station-average estimate given above) is obtained by weighting each monthly observation by

$$\sigma^{-2} = \left(\frac{\sigma_m^2}{n_m} + \sigma_0^2 \right)^{-1} \qquad (10)$$

where σ_m is the standard deviation of the measurements during month m, n_m is the number of measurements made in month m divided by 12 (to allow for the typical observed three-day correlation between individual measurements), and σ_0^2 is the variance of the residuals of the monthly-mean observations relative to the fitted empirical model (equation (1)) increased, however, to reflect the month-to-month autocorrelation of the residuals (see Table 2). The optimal estimate of the atmospheric lifetime is $13.4^{+7.3}_{-3.8}$ years and may be approximately obtained by weighting the individual station estimates by the weights given in Table 5. This optimal estimate is obviously strongly influenced by the two southern hemisphere estimates of lifetime which are substantially longer than those for the northern hemisphere.

To provide further insight into these results, we have plotted in Figure 6 the month-by-month residuals $\ln(\chi_m/\chi_c)$ for each station where the mixing ratios χ_m and χ_c are respectively those measured by ALE and those calculated in the 9-box model (with τ=10.5 years and F=1.6). It is apparent that the observed mixing ratios at the two southern hemisphere stations (and thus the latitudinal gradient) are underpredicted in the model. There is a slight downward temporal trend in the residuals at Adrigole/Cape Meares and Ragged Point; a slight upward trend at Cape Grim; and a pronounced upward trend at Point Matatula. This means that the underprediction of the latitudinal gradient is generally decreasing with time and that, as already noted, the derived τ values at Adrigole/Cape Meares and Ragged Point are slightly less than 10.5 years, while those at Cape Grim and Point Matatula are respectively slightly greater and much greater than 10.5 years. Neglect of the first few months of data at each station could be justified

based on general start-up problems. This would tend to decrease the temporal trends in the residuals at all stations except Point Matatula and thus bring the τ values derived from these stations into closer agreement with the average τ value (10.5 years).

The optimal estimate of τ(15.4 years) is suspicious because this estimate gives greatest weight to Point Matatula which, from the residuals in Figure 6, is behaving quite differently from the other 3 stations. Moreover, recently-obtained CH_3CCl_3 data for the period July-December, 1981 suggest that the Point Matatula lifetime estimate based on the July, 1978 - June, 1981 period is anomalously long. The optimal lifetime is further suspect when we compare the lifetime estimates obtained by optimally combining and by averaging the individual station estimates for several time periods as shown in Table 6. Here it is to be noted that in contrast to the results for $CFCl_3$ and CF_2Cl_2 (Cunnold, et al., 1982a, b), the standard error of the estimate of the mean does not decay as $N^{-3/2}$, where N is the number of years of observation, which would be the case for random errors. Apparently the optimal estimate is not adequately accounting for the differences between individual station estimates and also one or more sites is giving a steadily biased estimate of the lifetime over the three year period. Also in contrast to the results for $CFCl_3$ and CF_2Cl_2, the optimal estimate appears to be converging more slowly than the estimate obtained by averaging. For these reasons we reject the optimally-combined estimate of lifetime for CH_3CCl_3 and recommend the 4-station-average lifetime estimate of $10.5\ ^{+6.2}_{-2.8}$ years as the current best estimate by the trend method.

This latter estimate of lifetime is independent of the absolute calibration factor ξ for the CH_3CCl_3 mixing ratios. The quoted error bars do not, however, include uncertainties in the trend in global release. No attempt has been made to thoroughly assess these uncertainties. If the difference between the two estimates of release given in Table 4 in the period 1977-1981 (suggesting 1σ errors of only 1.8%) were to be regarded as an estimate of the total release uncertainty, the effect on the lifetime estimate would be small and the uncertainty in the lifetime would be dominated by the measurement uncertainties already discussed.

It is apparent that the trend technique applied to the ALE data is yielding τ estimates similar to the largest estimates by previous workers as quoted in the introduction. We should therefore address the question of whether the CH_3CCl_3 lifetimes derived using the trend technique are consistent with the release history R(t) and present global content of this species c(t) as expressed by equation (2). The ALE CH_3CCl_3 data at each station when combined with runs of our 9-box model enable us to estimate a c(t) value for January 1, 1980 of 2580×10^6 kgm. Using the emission data in Tables 3 and 4 we then estimate $\tau = 9.8$ years.

To assess errors in this latter τ estimate we first note that our deduced random error of $\pm 1.8\%$ in R(t) is much less than the errors in c(t) so we will specifically consider τ uncertainties due to c(t) uncertainties only. Our assessment of c(t) is deduced, in essence, from the global-average lower tropospheric CH_3CCl_3 mixing ratio $\bar{\bar{\chi}}$ (obtained from ALE measurements) and from the ratio r of the global-average stratospheric to upper tropospheric mixing ratio (obtained from models). Uncertainties in $\bar{\bar{\chi}}$ include a standard error of 12% in the absolute calibration factor ξ (Rasmussen and Lovelock, 1982) and an error ~1% resulting from equating

Cape Meares and Adrigole measurements with their semi-hemispheric average. Uncertainty in r is ~22% based on the difference between the r values computed in our 9-box model and in the Golombek (1982) 3-dimensional model.

The uncertainty in $\overline{\chi}$ is converted into an uncertainty in τ using $\partial(\ln\overline{\chi})/\partial(1/\tau)$ = - 4.4 years (derived from the 9-box model) giving $\Delta(1/\tau)$ = .033 year^{-1}. The uncertainty in r uses $\partial r/\partial(1/\tau)$ = -25.9 years (also derived from the 9-box model) to give $\Delta(1/\tau)$ = 0.004 year^{-1}. Combining these two uncertainties in 1/τ gives an atmospheric lifetime estimate by the global content technique of $\tau = 9.6\ ^{+4.5}_{-2.3}$ years.

It is apparent that lifetimes τ computed using equation (2) are consistent with those computed by the trend method. For example, the trend lifetime which we derived of 10.2 years when combined with the emission history of CH_3CCl_3 yields a value of σ(t) only 2.7% greater than the σ(t) value inferred from ALE observations. This discrepancy obviously lies well within the error bars on the observationally derived σ(t) value. Using equation (4) with r = 0.47 the τ value determined by the global content technique corresponds to A = 0.40 ± 0.15 and $\tau_t = 10.6\ ^{+6.5}_{-2.9}$ years.

As noted earlier, our 9-box model (with transport factor F = 1.6 and lifetime τ = 10.3 years) does not predict as large a latitudinal gradient for CH_3CCl_3 as that observed by ALE. This discrepancy can of course be removed by appropriately decreasing the rates of meridional mixing in the model--in particular it is largely removed by taking F=1. However, this latter F value would then result in an over-prediction by the model of the latitudinal gradients for the chlorofluoromethanes $CFCl_3$ and CF_2Cl_2 (Cunnold et al., 1982a, b). The discrepancy can alternatively be removed by decreasing τ so that it becomes more comparable to the interhemispheric

mixing time--in particular by taking $\tau \sim 5$ years there is reasonable agreement between the model and observations (except that the model now over-predicts the Adriatic to Ragged Point gradient by ~40 and underpredicts the Ragged Point to Cape Grim gradient by ~60). However, this latter τ value is outside even the 2σ (95% confidence) limits on the τ values predicted by both the trend and global content methods (i.e. it would result in a very significant underprediction by the model of the CH_3CCl_3 trends and absolute mixing ratios).

In the absence of the simultaneous ALE observations of CH_3CCl_3, $CFCl_3$ and CF_2Cl_2 we would conclude from the CH_3CCl_3 data alone that $F \sim 1$ and $\tau \sim 10$ years. It is therefore apparent that we are unable to simultaneously explain with the same model the ALE observations of these three halocarbons. The resolution of this problem is not yet apparent. One possibility is that we are presently underestimating southern hemispheric releases of $CFCl_3$ and CF_2Cl_2 and therefore that the value of $F = 1.5$ derived from these compounds is erroneously high. Another possibility is that the presently available ALE measurements for CH_3CCl_3 are inadequate and in particular are providing erroneously high estimates of either the temporal trends or latitudinal gradient. A third possibility is suggested by the differences between CH_3CCl_3 and $CFCl_3$ and CF_2Cl_2 releases (namely CH_3CCl_3 releases are less spatially diffuse than $CFCl_3$ and CF_2Cl_2 releases, and about 30% of CH_3CCl_3 released to date was released in the last 2 years compared to about 15% for $CFCl_3$ and CF_2Cl_2). These differences may necessitate a higher resolution model for CH_3CCl_3 than for $CFCl_3$ and CF_2Cl_2. A fourth possibility is that the rate of increase in release of CH_3CCl_3 in the last few years is being underestimated causing us to underestimate the latitudinal gradient.

Finally, there may be real year-to-year variations in interhemispheric mixing which are not present in our simple model.

4. CONCLUSIONS

Averaging the inverse trend lifetime of 0.095 ± 0.035 $year^{-1}$ and the inverse global-content lifetime of 0.102 ± 0.032 $year^{-1}$ calculated for CH_3CCl_3 from the ALE data we obtain $\tau = 10.2 \, ^{+5.2}_{-2.6}$ years. Using equation (9), this latter τ value provides an estimate of $\tau_t = 11.0 \, ^{+7.8}_{-3.2}$ years which corresponds to $A = 0.39 \pm 0.16$. Since $A = 1$ in our 9-box model corresponds to a global tropospheric average OH concentration $[OH] \sim 1.2 \times 10^6$ molecule cm^{-3}, then the CH_3CCl_3 ALE data implies $[OH] \sim 1.2 \times 10^6 A = (5 \pm 2) \times 10^5$ molecule cm^{-3}.

In the Logan et al. (1981) two-dimensional model (whose OH concentrations are used to define our standard model) $A \sim 1 \, ^{+1.0}_{-0.5}$ and $[OH] \sim (1.2 \, ^{+1.2}_{-0.6}) \times 10^6$ molecule cm^{-3}. The two-dimensional diagnostic model of Chameides and Tan (1981) has $[OH] \sim (4.2 \, ^{+3.8}_{-2.0}) \times 10^5$ molecule cm^{-3} while the two-dimensional model of Volz et al. (1981) implies $[OH] \sim (6.5 \, ^{+3}_{-2}) \times 10^5$ molecule cm^{-3} based on an analysis of ^{14}CO measurements. The small differences between the ALE-derived result and the results from the latter two models are not statistically significant but it is apparent that the ALE results imply tropospheric OH concentrations ~2.5 times less than those computed by Logan et al. (1981). Since the latter model is carefully constrained by using observed concentrations of N_2O, O_3, CO, CH_4, NO, NO_2, and HNO_3 and also attempts to include all the important known OH production and loss processes, the disagreement with the ALE results may conceivably be due to presently unrecognized sources or sinks for tropospheric OH.

For the reasons discussed in detail in section 3, we have rejected the CH_3CCl_3 lifetime of 15.4 years deduced from ALE using the optimal trend

method and the lifetime of 5 years required to simultaneously fit the ALE latitudinal gradients of CH_3CCl_3, CF_2Cl_2, and $CFCl_3$. If we included these rejected estimates with the two we consider valid (4-station average trend lifetime = 10.5 years, global content lifetime = 9.8 years) we would obtain an average lifetime of 8.7 years compared to our preferred value of 10.2 years.

Our model results are in qualitative agreement with the model results of Derwent and Eggleton (1981). They found a reasonable fit to northern hemispheric CH_3CCl_3 trend observations using τ = 5 years but this lifetime was far too short to explain the then available southern hemispheric observations. For comparison, if we ignored in our model the two southern hemisphere ALE stations we would deduce a 2-station-average trend lifetime of 6.6 years. The southern hemispheric CH_3CCl_3 trends are significantly greater than those in the northern hemisphere and imply globally-averaged lifetimes significantly greater than those derived from northern hemisphere trends alone.

The ALE program has provided the most extensive measurements of the global concentrations and trends for CH_3CCl_3 and the most accurate determination of its atmospheric lifetime yet obtained. Continued measurements of this species at the ALE sites should result in a significant improvement in our knowledge of its lifetime and thus of global-average OH concentrations. In particular, it is important to establish whether the significant differences between trends in the two hemispheres persist as further years of ALE data are obtained. Also, the need for improvement in the absolute calibration of CH_3CCl_3 concentrations in the atmosphere in order to improve the accuracy of the τ values derived using the global content method is readily apparent.

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Table 1

Monthly-averaged CH_3CCl_3 mixing ratios $\bar{X}$ (pptv) and their standard deviations σ (pptv) determined from measurements at the five ALE sites over the period July, 1978 through June, 1981. Values tabulated assume an absolute calibration factor $\xi = 1$. The number N of measurements made each month is also tabulated.

MONTH	Adrigole (52°N, 10°W)			Cape Meares (45°N, 124°W)			Ragged Point (13°N, 59°W)			Point Matatula (14°S, 171°W)			Cape Grim (41°S, 145°E)		
	$\bar{X}$	σ	N	$\bar{X}$	σ	N	$\bar{X}$	σ	N	$\bar{X}$	σ	N	$\bar{X}$	σ	N
7-78	140.1	5.7	224				124.5	7.2	144	88.9	3.6	61	86.0	6.3	52
8-78	137.2	4.7	185				124.4	7.8	200	90.1	4.2	125	83.3	3.2	124
9-78	132.3	4.9	235				117.8	10.3	168	90.5	3.6	126	85.6	3.6	74
10-78	134.2	4.8	151				118.2	10.2	111	92.8	3.6	108	88.5	2.8	44
11-78	134.6	4.1	92				115.9	8.9	125	93.2	5.2	97	93.6	1.4	57
12-78	---	---	---				124.1	8.4	129	93.7	6.4	57	92.7	1.3	38
1-79	139.3	5.7	74				125.2	9.3	114	97.5	4.1	18	91.4	1.5	52
2-79	140.9	3.9	25				124.7	8.7	112	94.8	4.5	95	91.4	1.4	92
3-79	140.3	6.2	68				126.1	8.6	95	95.7	3.7	117	93.9	2.0	109
4-79	144.2	6.1	62				---	---	---	95.3	4.2	120	95.6	1.2	106
5-79	146.5	5.7	81				127.4	4.1	80	97.4	2.5	122	95.8	1.7	107
6-79	147.1	6.4	60				124.9	5.8	40	98.1	0.9	114	97.6	2.3	104
7-79	143.9	7.0	136				128.5	8.3	88	99.6	1.4	118	96.6	1.8	89
8-79	144.7	6.2	104				132.1	5.2	117	101.5	2.1	111	98.4	1.5	112
9-79	146.1	6.4	94				123.7	9.3	134	101.6	2.4	102	99.7	1.6	101
10-79	150.4	5.1	53				123.6	7.4	127	103.8	2.2	115	101.0	1.1	94
[illegible]-79	149.4	7.2	72				128.5	7.3	90	106.4	2.1	113	101.9	1.4	110
[illegible]-79	153.1	7.0	69				131.5	5.1	130	98.9	5.8	102	101.3	0.9	81
1-80	152.3	8.0	58	159.6	6.0	71	134.8	6.2	133	105.0	3.0	100	100.7	1.1	94
2-80	153.8	6.8	106	---	---	---	135.6	6.5	105	107.8	3.2	122	101.2	1.4	72
3-80	158.3	7.1	89	154.9	2.4	20	140.6	4.8	104	108.4	3.3	103	103.0	1.4	114
4-80	162.6	7.5	103	158.0	3.0	78	137.6	3.9	79	108.9	3.9	116	102.5	1.6	44
5-80	165.1	7.4	60	157.9	2.3	93	138.8	4.7	137	110.3	2.3	115	107.4	2.2	76
6-80	163.2	8.3	115	155.1	3.0	114	142.3	4.3	147	111.5	1.5	94	108.5	2.2	83
7-80	163.4	6.3	111	151.0	3.6	85	141.1	5.7	129	113.1	1.0	117	109.5	1.8	93
8-80	158.7	5.9	111	151.9	2.[illegible]	81	139.1	4.3	59	114.5	1.3	117	110.9	1.4	92
9-80	156.0	5.2	104	156.7	[illegible]	103	137.0	8.3	126	115.1	2.0	103	112.4	1.0	69
10-80	159.3	5.5	81	165.1	8.2	11	137.4	7.9	126	115.6	1.3	17	113.5	1.3	78
11-80	161.2	4.8	75	162.6	4.8	[illegible]	143.3	5.8	117	117.8	2.3	63	113.2	1.8	96
12-80	161.5	3.0	66	160.2	5.8	[illegible]	144.3	7.8	118	120.1	3.7	100	111.8	0.8	85
1-81	160.6	7.3	118	161.8	5.2	[illegible]	143.5	5.5	138	120.9	4.0	42	111.7	0.9	54
2-81	161.7	5.2	60	166.3	9.8	107	146.0	5.2	119	-----	----	---	112.1	0.9	44
3-81	162.7	6.1	96	160.7	3.6	120	140.7	4.7	100	122.2	2.0	30	114.0	1.3	86
4-81	164.9	4.1	46	161.1	2.9	106	146.8	6.6	104	120.3	2.4	135	113.1	0.9	76
5-81	168.8	5.0	59	162.3	3.6	104	148.9	4.5	123	119.[illegible]	2.[illegible]	123	114.7	1.5	86
6-81	169.1	5.9	79	163.2	2.8	108	146.9	4.2	110	121.8	1.9	113	118.2	1.4	60

Table 2

Coefficients in the empirical function (equation (1) in the text) describing the long term variation of the natural logarithm of the CH_3CCl_3 mixing ratios (with calibration factor $\xi = 1$) at the 5 ALE sites. The coefficients for Cape Meares are computed from 18 months of data (January, 1980 to June, 1981). The coefficients for all other stations refer to the 36 month period from July, 1978 to June, 1981. The quoted error bars for the coefficients include the effects of any non-white distribution of residuals. There is insufficient data at Cape Meares to adequately define values for d_2. Values of the variance σ_o^2 of the residuals of the monthly-mean observations relative to the empirical function for each station are also tabulated.

i	Station	a_i	b_i	d_i	c_i	s_i	σ_o^2
1	Adrigole	5.026 ± 0.007	0.076 ± 0.005	-0.012 ± 0.007	0.017 ± 0.007	-0.008 ± 0.007	3.61×10^{-4}
2	Cape Meares	5.038 ± 0.005	0.037 ± 0.010	————	-0.015 ± 0.006	-0.011 ± 0.007	2.62×10^{-4}
3	Rugged Point	4.989 ± 0.007	0.070 ± 0.006	-0.001 ± 0.008	0.011 ± 0.007	-0.012 ± 0.008	4.94×10^{-4}
4	Point Matatula	4.656 ± 0.005	0.116 ± 0.004	-0.004 ± 0.005	-0.006 ± 0.005	0.005 ± 0.005	2.18×10^{-4}
5	Cape Grim	4.626 ± 0.005	0.108 ± 0.005	-0.012 ± 0.006	0.000 ± 0.006	0.010 ± 0.006	2.51×10^{-4}

Table 3

Estimates of global production and atmospheric releases for CH_3CCl_3 for the period 1951-1976. Units are 10^9 gm yr^{-1} (after Neely and Plonka (1978)).

Year	Production	Releases	Year	Production	Releases
1951	0.1	0.1	1964	64.3	56.6
1952	0.2	0.2	1965	82.4	72.9
1953	1.0	1.0	1966	116.0	108.7
1954	2.9	2.7	1967	145.4	130.5
1955	8.4	8.0	1968	158.1	145.0
1956	13.8	12.4	1969	167.6	148.1
1957	20.6	19.6	1970	181.2	154.5
1958	21.8	20.7	1971	191.2	166.7
1959	31.8	30.3	1972	266.8	230.1
1960	38.0	36.1	1973	349.7	3[illegible].9
1961	39.9	38.0	1974	389.1	362.4
1962	59.3	56.2	1975	373.7	364.2
1963	52.0	50.7	1976	437.1	415.4

Table 4

Estimates of global and semi-hemispheric sales and atmospheric releases of CH_3CCl_3 for the period 1977-1981. Units are 10^9 gm yr^{-1} for the global estimates, and percentages of the appropriate global estimates for the semi-hemispheric data.

			Global	90°N-30°N	30°N-0°	0°-30°S	30°S-90°S
1977	Sales†		483.6	96.67%	1.36%	0.47%	1.50%
	Releases	ICI♦	454.6	96.67%	1.36%	0.47%	1.50%
		Dow♦	443.9	---	---	---	---
1978	Sales†		497.5	96.38%	1.41%	0.55%	1.66%
	Releases	ICI♦	467.7	96.38%	1.41%	0.55%	1.66%
		Dow♦	498.3	---	---	---	---
1979	Sales†		535.5	96.36%	1.40%	0.56%	1.68%
	Releases	ICI♦	503.4	96.36%	1.40%	0.56%	1.68%
		Dow♦	521.0	---	---	---	---
1980	Sales†		544.2	95.96%	1.65%	0.60%	1.79%
	Releases	ICI♦	511.5	95.96%	1.65%	0.60%	1.79%
		Dow♦	503.5	---	---	---	---
1981	Sales†		544.2	95.96%	1.65%	0.60%	1.79%
	Releases	ICI♦	511.5	95.96%	1.65%	0.60%	1.79%
		Dow♦	507.3	---	---	---	---

† Imperial Chemical Industries, PLC estimates. Data for South African sales have been divided equally between the two southern semi-hemispheres.

♦ Computed in this paper using equations (4) and (5).

♦ W.B. Neely and M. Farber, Dow Chemical Co., private communication.

♦ Estimated in this paper by extrapolation (see text).

Table 5

Methyl chloroform atmospheric lifetime estimates and their standard deviations σ derived from the trend at each ALE site.

Site	Reciprocal Lifetime ($year^{-1}$) $\pm 1\sigma$	Lifetime (years) $\pm 1\sigma$	Approx. weight given to station in optimal code
Adrigole, Ireland/ Cape Meares, Oregon	.143 ± .024	$7.0^{+1.3}_{-1.0}$	.2
Ragged Point, Barbados	.162 ± .029	$6.2^{+1.3}_{-1.0}$	.1
Pt. Matatula, Amer. Samoa	.009 ± .019	$111.0^{+\infty}_{-75}$	.4
Cape Grim, Tasmania	.065 ± .021	$15.4^{+7.3}_{-3.8}$	.3

Table 6

Reciprocal atmospheric lifetime estimates ($years^{-1}$) and their standard deviations σ for methyl chloroform as a function of time obtained by averaging and by optimally combining the lifetime estimates at the ALE sites.

Time Period (Month/year)	Optimal Combination $\pm 1\sigma$ ($year^{-1}$)	Average $\pm 1\sigma$ ($year^{-1}$)
7/78 - 6/79	.246 ± .059	.131 ± .067
7/80 - 6/81	.124 ± .051	.132 ± .030
7/78 - 6/80	.086 ± .021	.094 ± .027
7/79 - 6/81	.044 ± .019	.083 ± .033
7/78 - 6/81	.070 ± .011	.095 ± .035

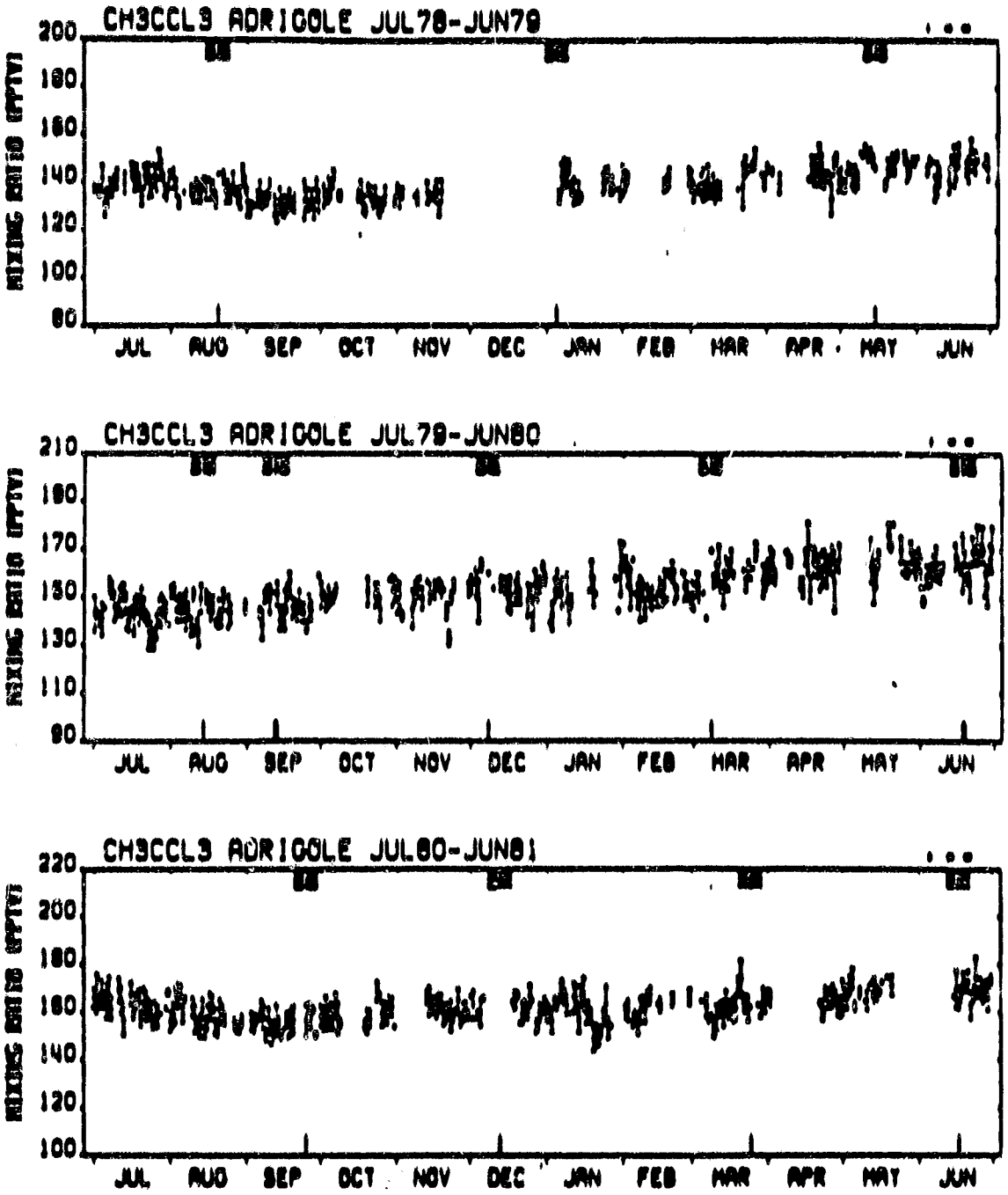

Figure 1. Daily-averaged CH_3CCl_3 mixing ratios (pptv) and their standard deviations (pptv) determined at Adrigole, Ireland (52°N, 10°W) during the period July, 1978 through June, 1981. Measured values presented here and in Figures 2-6 assume an absolute calibration factor $\xi = 1$.

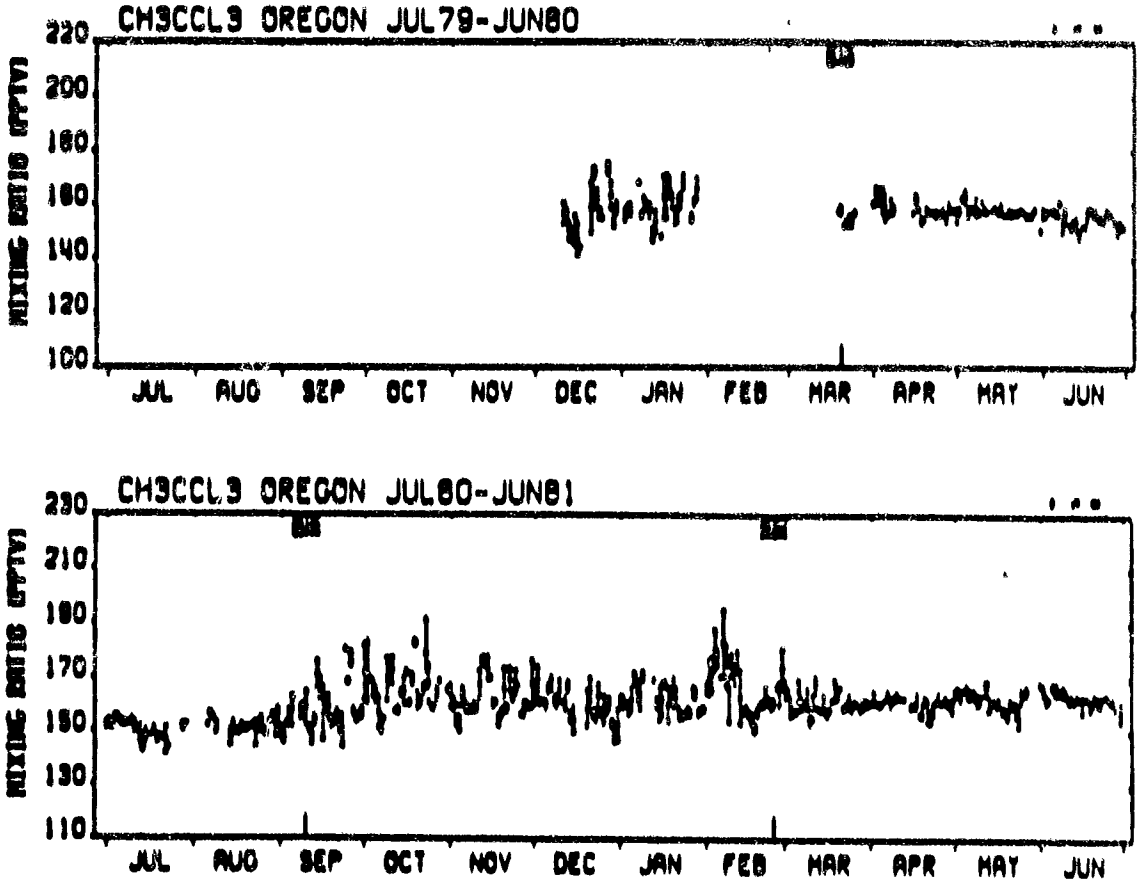

Figure 2. As in Figure 1 but for Cape Meares, Oregon (45°N, 124°W) for the period January, 1980 through June, 1981.

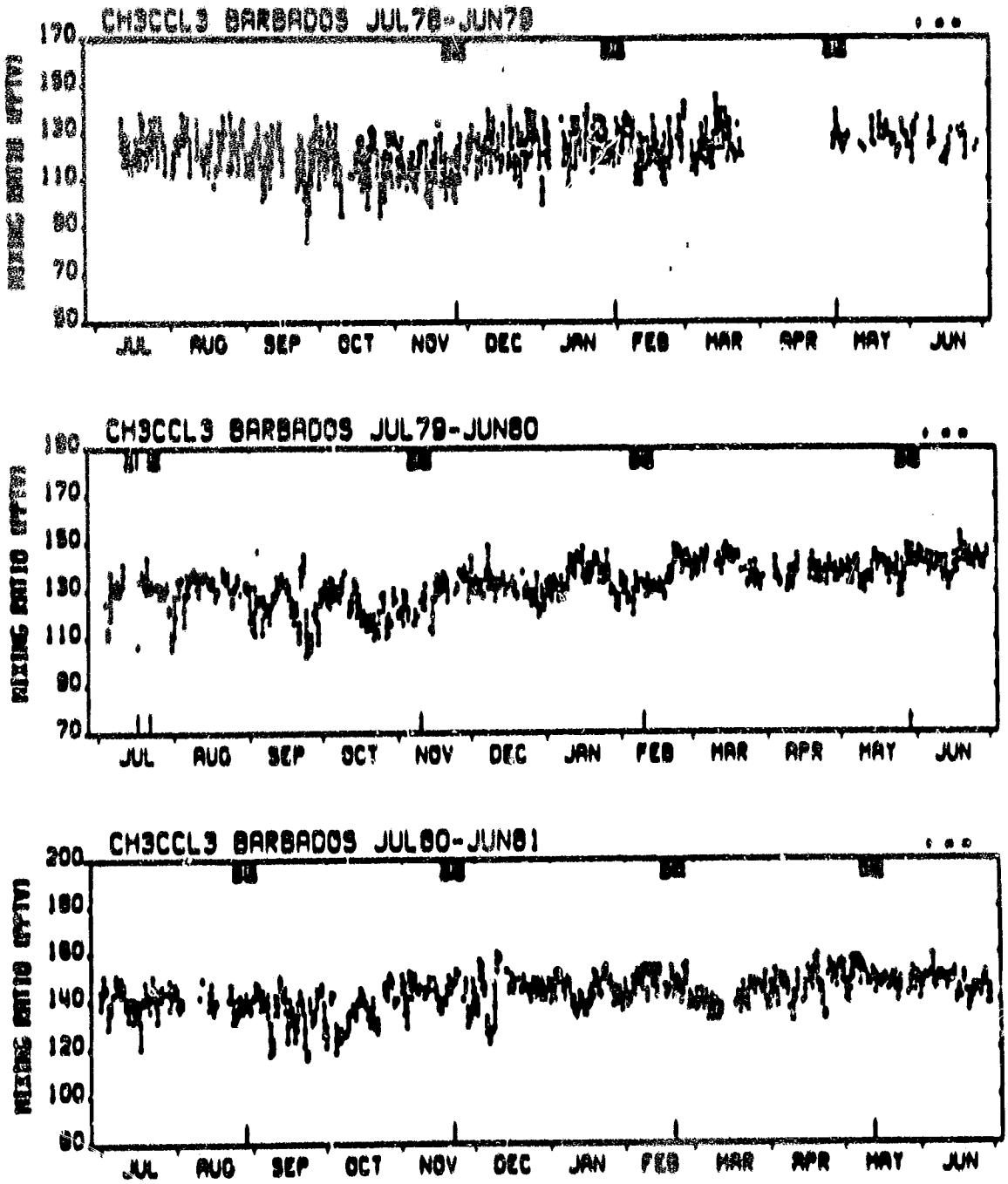

Figure 3. As in Figure 1 but for Ragged Point, Barbados (13°N, 59°W).

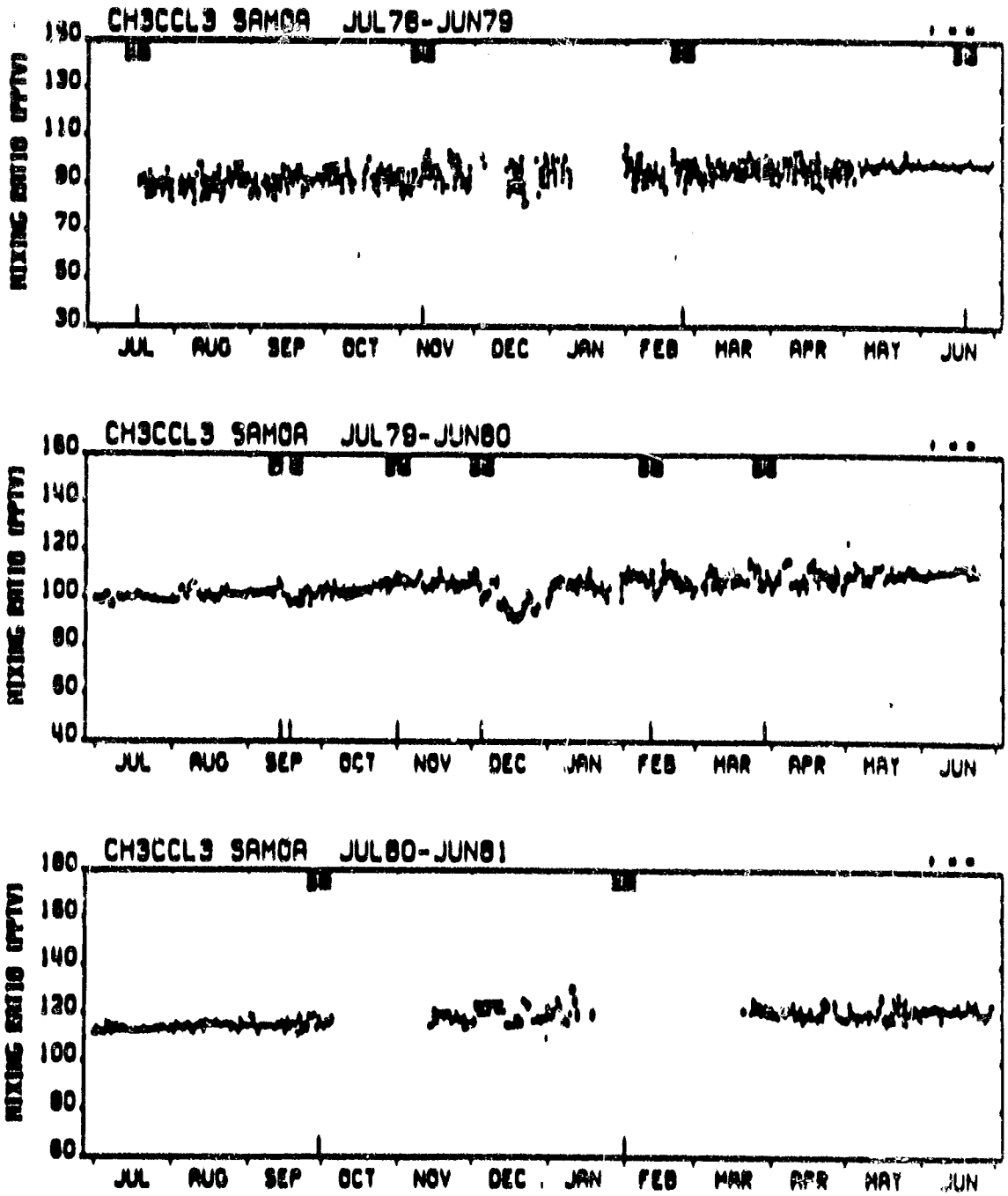

Figure 4. As in Figure 1 but for Point Matatula, American Samoa (14°S, 171°W).

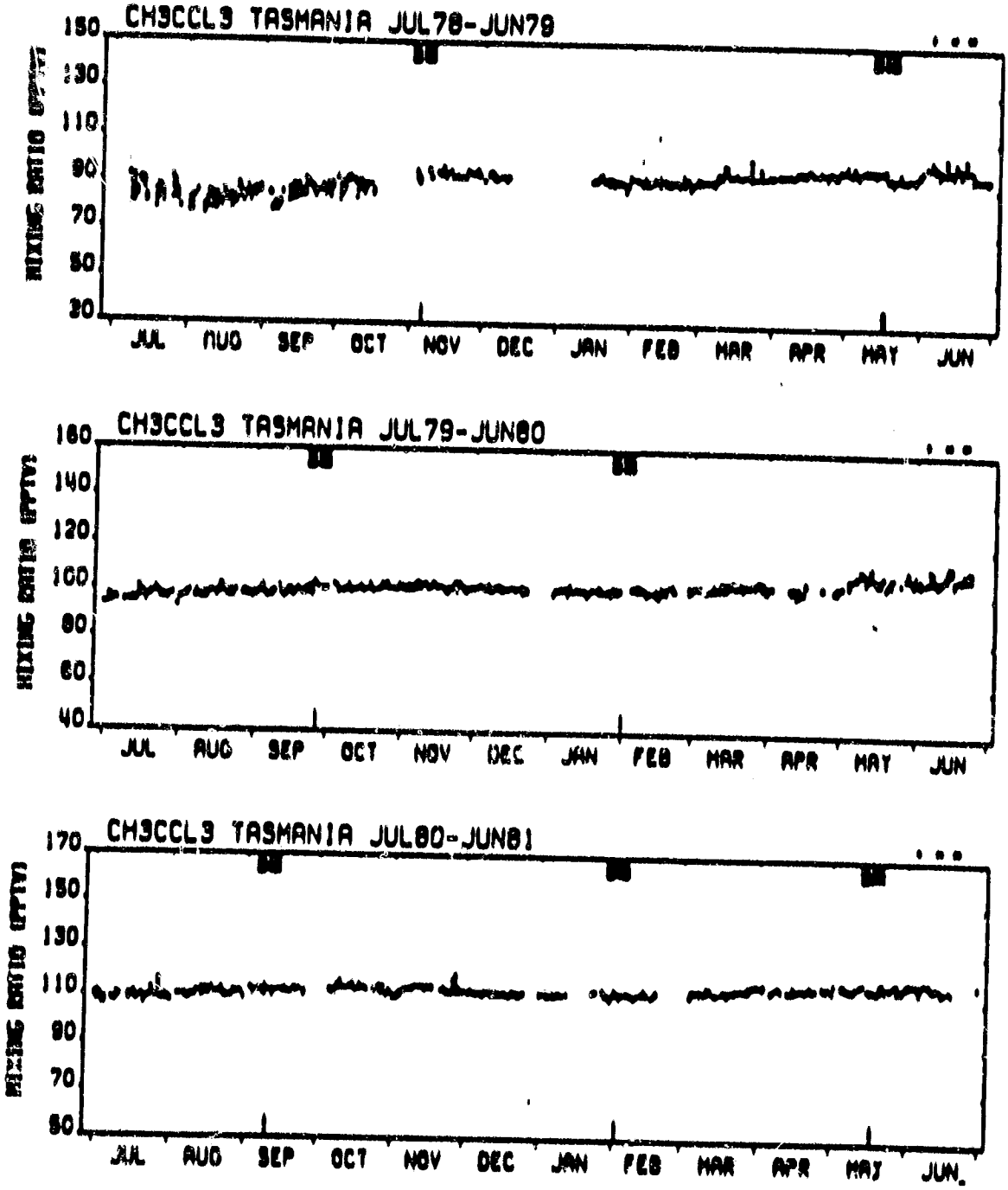

Figure 5. As in Figure 1 but for Cape Grim, Tasmania (41°S, 145°E).

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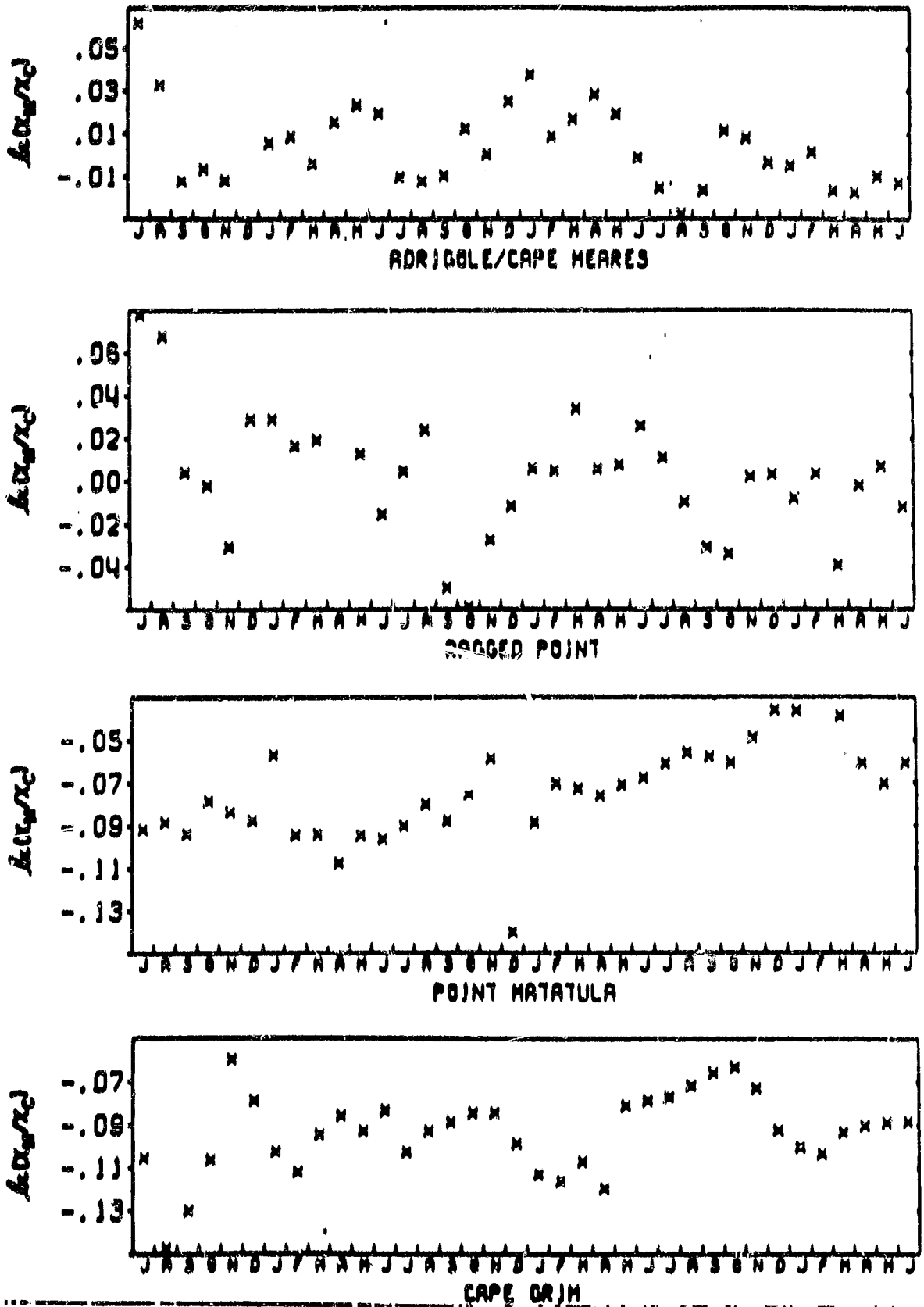

Figure 6. Values for methyl chloroform of the natural logarithm of the ratio of the monthly-mean measured (X_m) and calculated (X_c) mixing ratios. Calculated mixing ratios are 12-month running mean values obtained from the 9-box model with F = 1.6 and τ = 10.5 years.

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METHYLCHLOROFORM AND OTHER CHLORINATED ORGANIC SOLVENTS; A STATUS REPORT

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METHYLCHLOROFORM AND OTHER CHLORINATED ORGANIC SOLVENTS:

A STATUS REPORT

by

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(NOT FOR PUBLICATION)

1. OH Depletion Problem.

Although OH is extremely reactive, it is difficult to alter its global concentration. It is true that trichloroethylene ($CHCl{=}CCl_2$) reacts rapidly with OH as shown in Table 1, but its global emissions would have to be many orders of magnitude higher than they are before it can affect OH. In Table 1 the parameters defined by Eqn. (1) are calculated for those atmospheric gases which have some potential for affecting the global OH concentrations.

$$R_x = \frac{K_x\,[x]}{K_{CO}\,[CO]} = \frac{\tau_{(OH)x}}{\tau_{(OH)CO}} \qquad (1)$$

This ratio is a measure of the effectiveness of gas x, relative to CO, in removing OH under steady state conditions.

TABLE 1

Species x	K_x $\frac{cm^3}{molec\text{-}sec}$	[x] ppb	R_x (250°K)
CO	1.4×10^{-13}	150	1
CH_4	3×10^{-15}	1500	0.3
NO_2	5×10^{-12}	~1	0.3
N_2	2.4×10^{-15}	500	0.1
C_5H_8 (Isoprene)	$5\text{-}6 \times 10^{-11}$	~0.5	1.5 - 2
C_2HCl_3	2.8×10^{-12}	0.1	0.02
		0.5	0.08
		1.0	0.17
C_2Cl_4	9×10^{-14}	0.1	0.0005
		0.5	0.003
		1.0	0.005
CH_2Cl_2	0.2×10^{-14}	0.1	0.0005
		0.5	0.002
		1.0	0.005

Lifetimes: $\tau(C_2HCl_3)$ = 6 days; τ(PCE) = τ(methylene chloride) = 6 months. Table 1 is from Khalil (1979). Reaction rate constants are from Graedel (1978); NASA (1981). T = 250°K is the density weighted average temperature in the earth's atmosphere.

The reaction of trichloroethylene (TCE) is 20 times faster than CO, but the atmospheric concentration is about 3 orders of magnitude less. It would take approximately 10 times greater than present emissions to make TCE reduce OH levels by about 10%. Depending on how much effect C_6H_6 has on tropospheric OH concentrations, TCE is even less likely to affect OH. The reactivities of the other solvents such as perchloroethylene and dichloromethane (methylene chloride) are so much less that their effects on OH are 30 to 40 times less than TCE.

In the EPA studies concern for OH depletion has not been registered for methylchloroform (Weinstein, 1981). Calculations by eqn. (1) would result in $R = 2 \times 10^{-4}$ at a concentration of CH_3CCl_3 of 0.5 ppbv. It is expected that CH_3CCl_3 concentrations will never exceed 0.5 ppbv, and are not likely to reach near that level over the next 30 years unless current production and release are increased drastically (see Table 2).

2. The Greenhouse Effect.

The fluorocarbons 11 and 12 as well as methylchloroform and F-113 are capable of leading to a global warming by the greenhouse effect. At current concentrations F-11 and F-12 are thought to have so far caused a global warming of about 0.08°K at concentrations of about 0.5 ppb (F-11 + F-12, Lacis et al., 1981). In comparison current global concentrations of F-113 are around 20 ppt, F-22 around 50 ppt, CH_3CCl_3 around 120 ppt. The greenhouse effect due to all these gases is therefore negligible at present. In the future, however, their contributions may be important because they will, in most cases, be additive. Furthermore, because there are so many trace gases increasing due to human activities that even though each will make an insignificant contribution to the greenhouse effect, taken together they could be quite important.

On the other hand, it is noteworthy that because the future greenhouse effect may come from small contributions by a large number of gases, restricting one or another gas will not cause much reduction in the global warming. Furthermore, the concentrations of these gases have to increase many fold before their effects would even become significant relative to the major effects expected from increasing CO_2.

It is unlikely that CH_3CCl_3 concentrations will ever exceed 0.5 ppbv as shown in Table 2 below (Khalil, 1979), so its greenhouse effect would be $\lesssim$ 0.1°K based on comparisons with the calculations of Lacis et al. (1981). Thus, CH_3CCl_3 is likely to be least important among the gases expected to lead to global warming in the future (e.g., CO_2, CH_4, N_2O, F-11, F-12).

Table 2. Expected Tropospheric Concentrations of CH_3CCl_3

Time	ζ_{nT} (pptv)	ζ_{sT} (pptv)
(a) Source Constant at 1978 Emissions.		
1/1979	130	100
1989	195	160
1999	213	177
(b) Source Continues to Rise at 8%/Yr.		
1/1979	130	100
1989	306	236
1999	683	530
(c) Source Rises at 8%/Yr, then Becomes Constant at Twice 1978 Emissions.		
1/1979	130	100
1989	306	236
1999	400	350
Later	~ 430	~ 380

Numbers based on τ = 8.5 yrs

ζ_{nT}, ζ_{sT} are the northern and southern hemisphere mixing ratios.

3. Methane and ozone depletion.

The increase of CH_4 may indeed prevent the depletion of the stratospheric ozone layer from the fluorocarbon , CCl_4, and CH_3CCl_3. There is preliminary evidence that the atmosphere contained much less CH_4 in the past, perhaps about half of today's levels. Although this result has far-reaching implications, further speculation would not be productive until some of the on-going experimental and theoretical work is concluded.

4. CH_3CCl_3 and stratospheric O_3.

There seems to be no doubt that CH_3CCl_3 is not as effective in destroying stratospheric ozone as the fluorocarbons 11 and 12 or some of the rarer fluorocarbons such as F-113. This feature is due primarily to the reactivity of CH_3CCl_3 with OH because of which large amounts of it are removed from the troposphere before it can reach the stratosphere and destroy ozone. The resulting lifetime of about 8 years also prevents large atmospheric accumulations of CH_3CCl_3 unlike F-11 and F-12. In summary, then, if the fluorocarbons-ozone theory is correct CH_3CCl_3 will lead to ozone depletion, but the effect is never likely to be as much as can be expected from the fluorocarbons 11 and 12.

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THE ATMOSPHERIC LIFETIME OF METHYL CHLOROFORM (CH_3CCl_3) PREPARED BY DEPT OF ENVIR SCIENCE OR GRADUATE CTR

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THE ATMOSPHERIC LIFETIME OF METHYLCHLOROFORM (CH_3CCl_3)

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THE ATMOSPHERIC LIFETIME OF METHYLCHLOROFORM (CH_3CCl_3)

M. A. K. Khalil and R. A. Rasmussen

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ABSTRACT

Global mass balance calculations based on results of recent laboratory experiments show that the atmospheric lifetime of CH_3CCl_3 is around 6 years. Based on this relatively short lifetime, the continued global release of CH_3CCl_3 at present levels is not expected to significantly affect the stratospheric ozone layer or to lead to a perceptible global warming. A trend method for relating lifetime to the same atmospheric data suggests a somewhat longer lifetime of about 8-10 years. Continued global measurements and an investigation of the sensitivities of models is necessary to firmly establish the lifetime of CH_3CCl_3.

1. Introduction

It has been suggested that the continuing accumulation of methyl chloroform (CH_3CCl_3) in the atmosphere may ultimately lead to some depletion of the stratospheric ozone layer and a slight warming of the earth. Such global scale effects of anthropogenic trace gases are in most cases controlled by the atmospheric lifetimes of these gases, and in particular, the existence of tropospheric sinks. Since both ozone depletion and global warming depend on the tropospheric burden of trace gas, a shorter lifetime allows for greater emissions before affecting the environment through these two mechanisms. A shorter lifetime also provides an opportunity to quickly control the global environmental effects should they reach perceptible or significant magnitudes. Therefore, a part of the controversy on the environmental significance of continuing or increasing releases of CH_3CCl_3 rests on estimates of its atmospheric lifetime.

It is accepted that reaction with trospospheric OH radicals provides a dominant pathway for removing CH_3CCl_3 from the atmosphere; however, because of uncertainties in our knowledge of global OH levels and the absolute concentrations of CH_3CCl_3, it has not been possible to unambiguously distinguish between a global lifetime of around 5 years and one of around 10 years. For CH_3CCl_3 this uncertainty is of considerable importance. At current levels of emissions, the role of CH_3CCl_3 in adversely affecting the environment may be negligible if the lifetime is around 5 years, but may be of concern if the lifetime is around 10 years.

In this report, we address the new developments in our laboratory which suggest that the global lifetime of CH_3CCl_3 is around 6 years rather than the 10 or 11 years as recently estimated by Prinn, et al. (1982). The

main reason why the lower lifetime is currently supported by Rasmussen's data between 1975 and 1982 is that a recalibration experiment showed the absolute concentration of CH_3CCl_3 to be only 80% of the original estimate. On the other hand, a somewhat longer lifetime (~8 years) is more consistent with the same data set if one relates the lifetime to the rate of change of CH_3CCl_3 concentrations ((1/c)(dc/dt)) rather than the absolute concentrations. Calculations of lifetime based on the rate of change of concentrations are not expected to be affected by errors in absolute concentration measurements. The reasons for this apparent inconsistency are currently under study.

In the rest of this report we provide the results of the research leading to the current estimates of the lifetime of CH_3CCl_3.

2. Absolute concentrations.

A static dilution technique was employed in 1974 and 1975 to determine the absolute concentration of CH_3CCl_3 in the primary standards used for global measurements over the past seven years. A standard prepared by the Ideal Gas Products Co. containing about 10 ppm of CH_3CCl_3 with a ±2% accuracy was used for the recalibration experiment.

The sample from Ideal Gas Products Co. was diluted with zero air. The amount of dilution was precisely controlled and measured with a Kurz mass flow meter. High pressure dilute samples were created and the calculated concentrations in these primary calibration tanks were used to establish the absolute concentrations.

Five analyses of an older primary standard (Ø133) revealed the following concentrations, based on the new calibration standard: 130.3 (pptv), 123.9, 127.0, 133.4, 122.3, yielding an average value of 127.4 pptv (±4.6 pptv = 1σ). The previously assigned value of CH_3CCl_3 concentration in this tank was 158.8 pptv. Thus we believe the previous measurements should be multiplied by 0.8 to reflect the correct absolute concentration.

We believe that the new absolute calibration is more accurate than the previous one obtained in 1975 because of the new, more precise dilution techniques used, inert high-pressure containers for standards, and the improved accuracy of commercially available standards. Considering these factors, the old calibration standard was quite accurate, being only 20% higher than the presently assigned value.

The lower absolute concentration of CH_3CCl_3 in the atmosphere leads to an estimate of a shorter lifetime than previously calculated.

3. Spatial and temporal distributions.

Figure 1 consists of the two longest time series of CH_3CCl_3 concentrations, at Pullman, Washington, and Cape Meares, Oregon (~45°N) in the northern hemisphere, and at the South Pole (90°S) and Cape Grim, Tasmania (42°S) in the southern hemisphere. These data have been corrected to agree with the new absolute calibration value.

Methylchloroform measurements have also been obtained from five other stations spanning the globe. These measurements, however, have not been made for as long a time as at the locations shown in Figure 1. In Figure 2 the locations of all the stations are shown by latitude. The rate of increase of CH_3CCl_3 in the atmosphere was faster in previous years compared to the past couple of years.

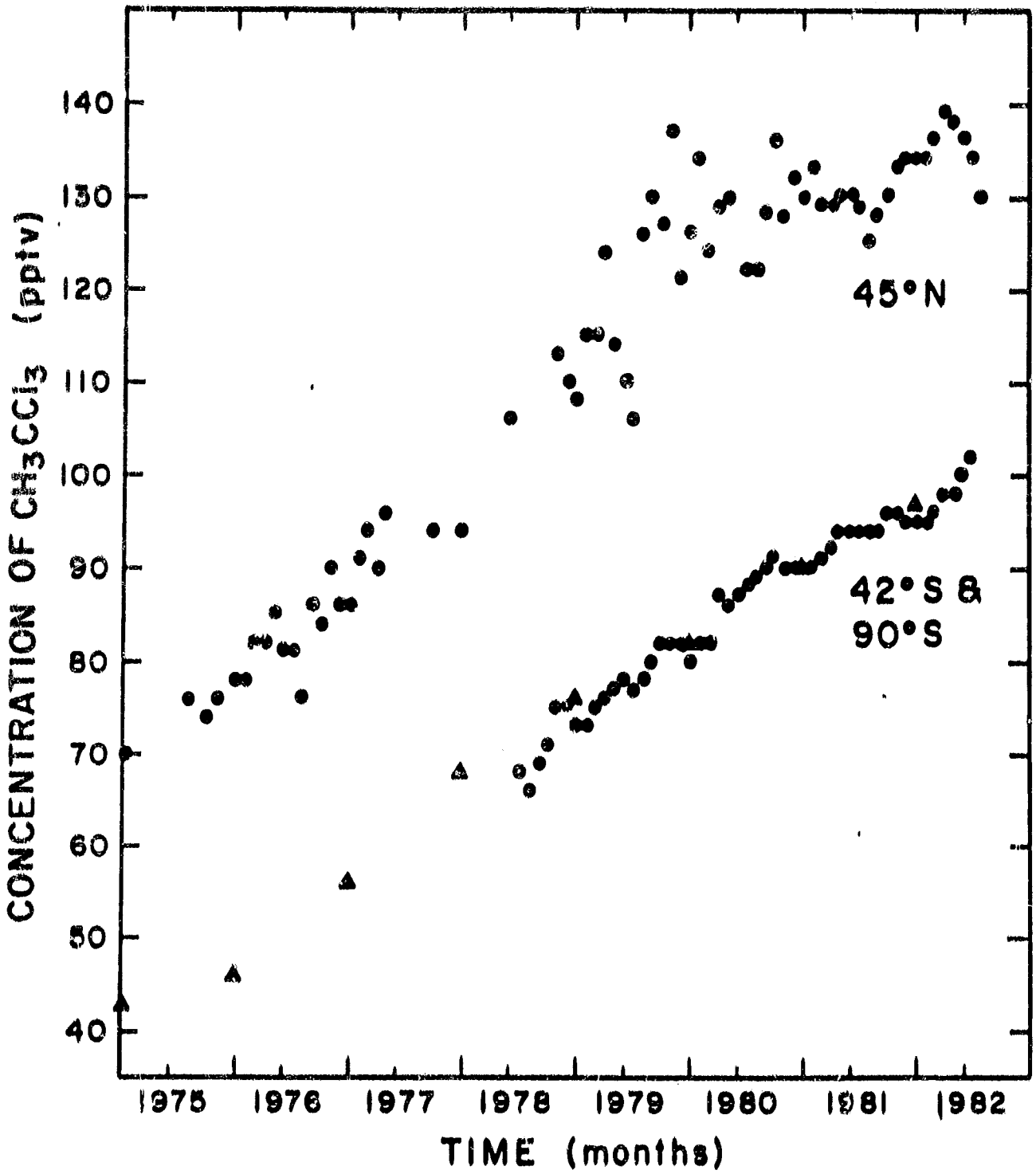

FIGURE 1. CH_3CCl_3 concentrations at 45°N latitude (Washington and Oregon) and at 42°S latitude (Tasmania) and at 90°S, South Pole (triangles).

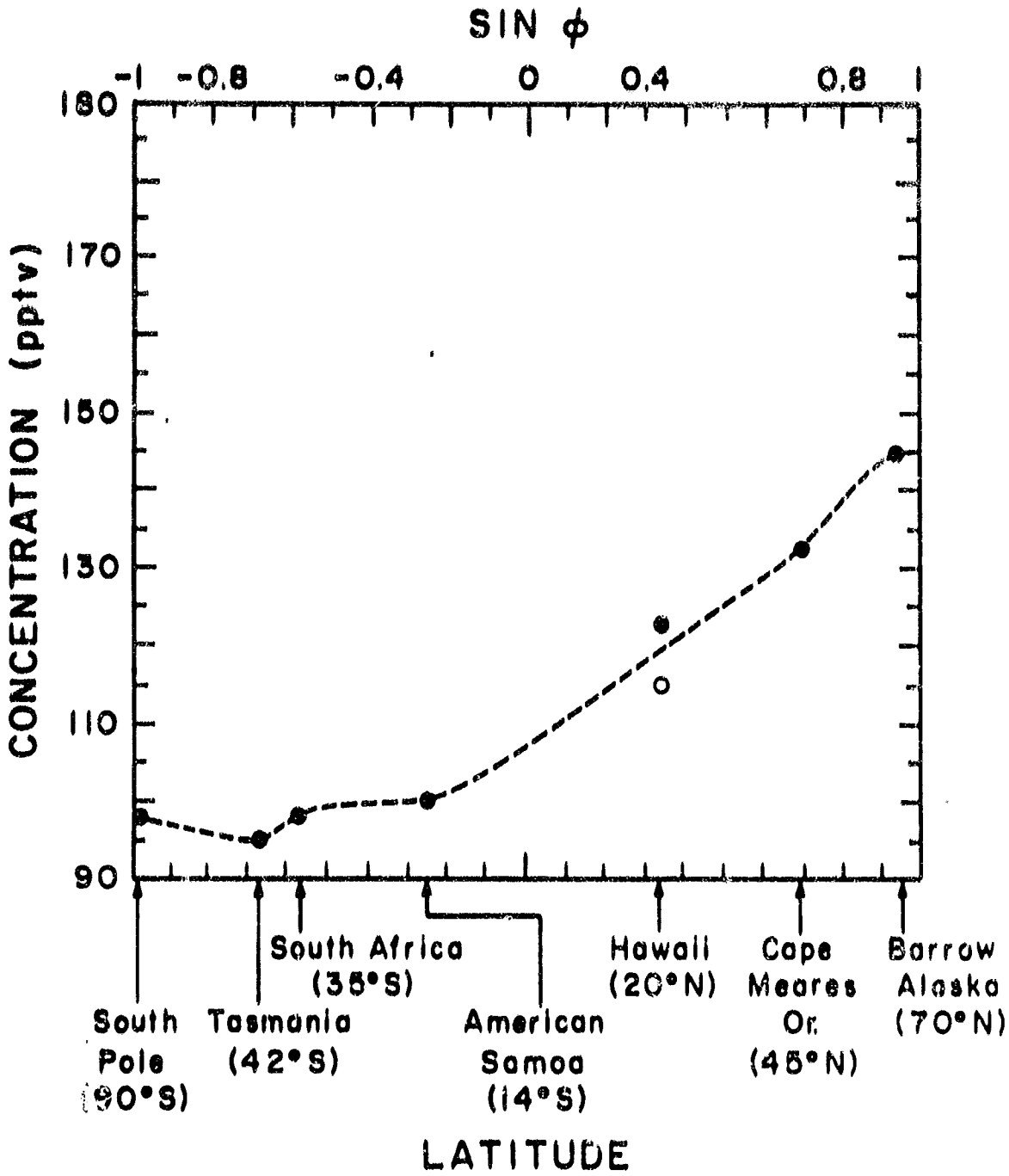

FIGURE 2. Locations of sampling sites and the latitudinal distribution of CH_3CCl_3.

4. The validity of flask samples.

Since January 1979 continuous measurements of CH_3CCl_3 have been obtained from Tasmania, Samoa, and Cape Meares (also a part of the atmospheric lifetime experiment, ALE, network). At all other times and places the data were obtained by analyzing air collected in specially designed and prepared stainless steel flasks. These "grab" samples are collected over short time periods and a few times every month. Thus, atmospheric variability may introduce large uncertainties in the averaged results obtained by flask sampling (Rasmussen & Khalil, 1981).

For the specific case of methylchloroform we found that flask samples produce the same quality of average concentration data and trends as the continuous measurements. This conclusion is based on the experiment conducted at Samoa from mid 1979 to the present. In Figure 3 the monthly average CH_3CCl_3 concentrations are shown, revealing the close agreement between flask sampling (open circles) and continuous measurement (dark circles) results. Because of its location, near the equator, concentrations of anthropogenic trace gases are more variable at Samoa than at other sites. Thus, the results obtained at Samoa may be extended to the other sites as well.

Table 1 was constructed to show the agreement between flask sampling measurements. On average a -0.3 pptv difference was found between concentrations in flask samples and concentrations obtained by continuous measurements. This small difference was not statistically significant. Similarly, the trends, deduced from the two data sets, were the same.

These results suggest that CH_3CCl_3 measurements obtained from the flask sampling network are highly accurate and reliable. Flask sampling provides the extensive global scale measurements necessary to estimate the atmospheric lifetime of CH_3CCl_3. Continuous measurements for a similar global network would be prohibitively expensive.

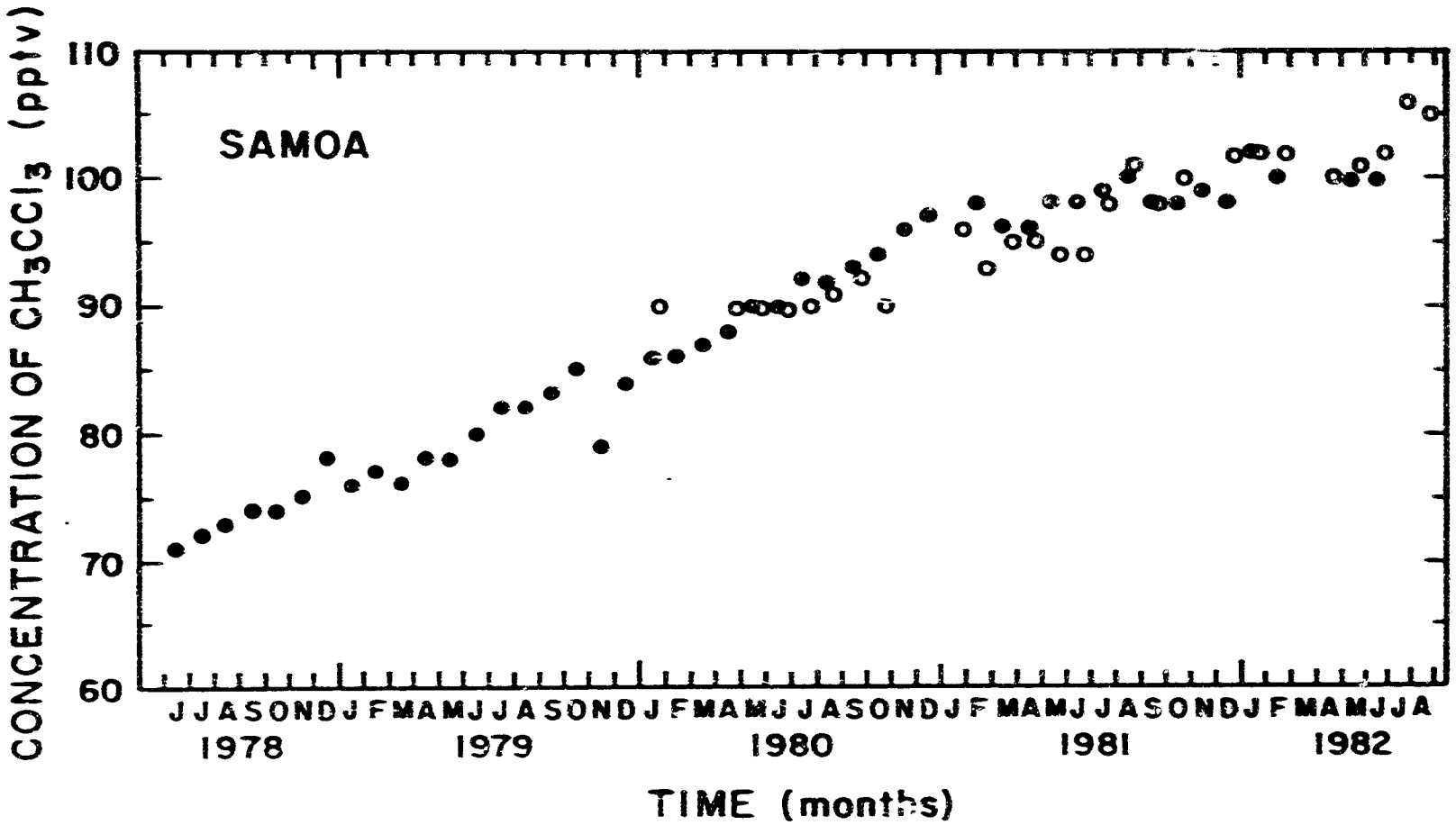

FIGURE 3. CH_3CCl_3 concentrations by continuous measurements (o: open circles) and flask sampling (•: closed circles) (Samoa, 14°S).

TABLE 1. Comparison of CH_3CCl_3 Concentrations from Flask Samples and Continuous Measurements

Time		Δ (pptv)
1980	J	--
	F	+4
	M	--
	A	--
	M	+2
	J	0
	J	0
	A	-2
	S	-1
	O	-1
	N	-4
	D	--
1981	J	--
	F	--
	M	-5
	A	-1
	M	-1
	J	-4
	J	-4
	A	-1
	S	+1
	O	0
	N	+2
	D	--
1982	J	+4
	F	0
	M	+2
	A	--
	M	--
	J	+1
	J	+2

Average Difference

$\bar{\Delta} = -0.3 \pm 0.9$ pptv

$s_\Delta = 2.49$

$s_{\bar{\Delta}} = 0.53$

$n = 22$

$t = 0.6$

Rate of Increase Trends

	Flask	Continuous	
b	0.54	0.53	pptv/mo
a	87.1	87.2	pptv
r	0.93	0.93	
n	26	33	

5. <u>Concentration differences in and above the boundary layer</u>.

It has been found previously (CAMETAO) that certain gases are more abundant in the tropical boundary layer compared to above the boundary layer (Rasmussen et al., 1980; Rasmussen & Khalil, 1982a). Measurements of trace gases made at ground level can therefore lead to an over-estimate of the global burden if the reduced concentrations in the free troposphere are not taken into account.

In Figure 4 we show the results of our boundary layer experiment. Lower concentrations were observed at Mauna Loa Observatory (above the boundary layer) compared to Cape Kumukahi (sea level). In Table 2 the results shown in Figure 4 are contrasted with the results of our previous studies, which have been corrected for the new calibration constant.

Based on the evidence available we have assumed that these differences of concentrations in and above the boundary layer exist throughout the tropics.

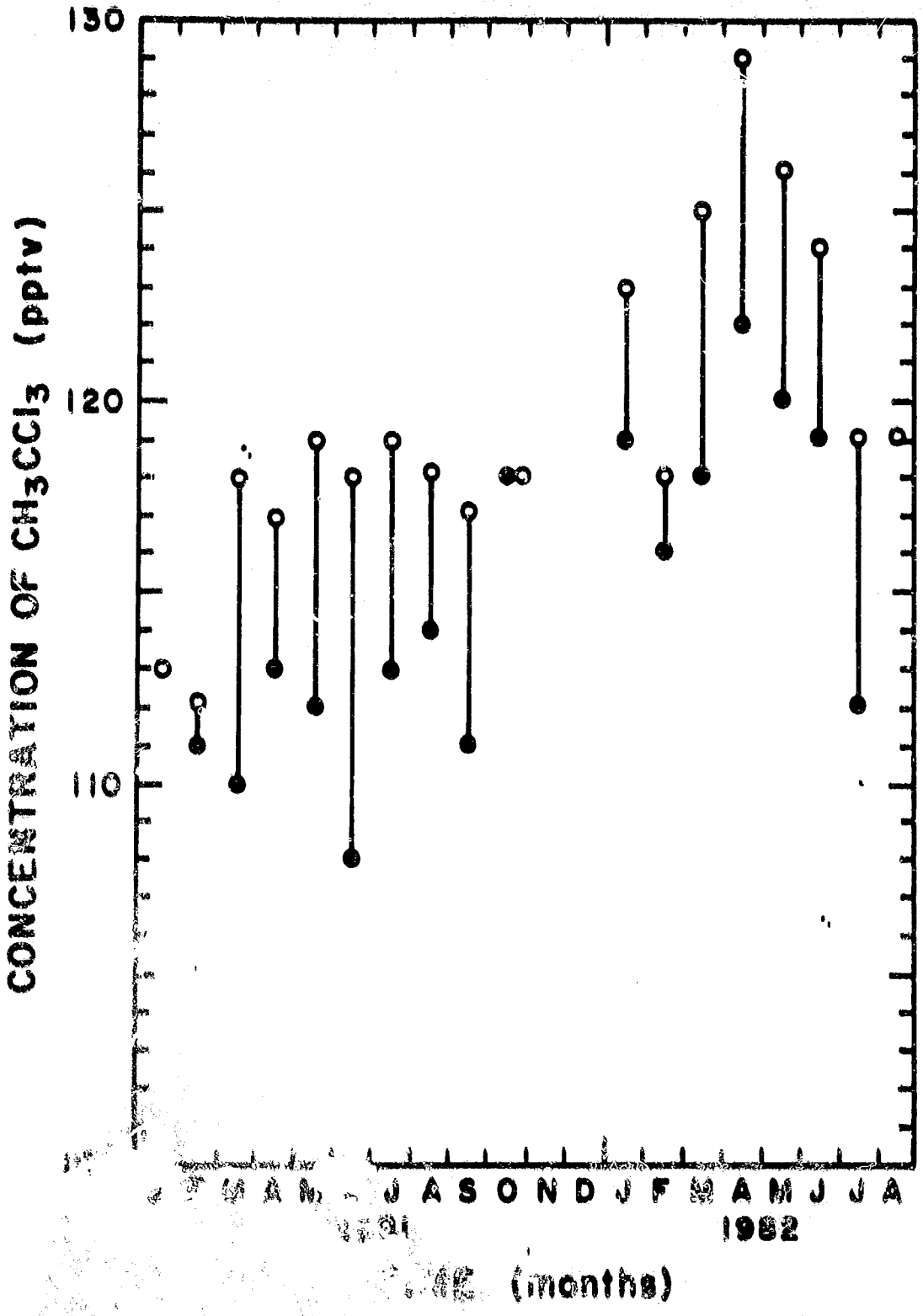

Fig. [illegible] Trends of [illegible] in (O: open circles) and above (●: [illegible]) the tropical boundary layer (Hawaii [illegible]).

TABLE 2. Concentration Difference In and Above the Boundary Layer

Time		Δ (pptv)
1981	J	--
	F	1
	M	8
	A	4
	M	7
	J	10
	J	7
	A	6
	S	6
	O	0
	N	--
	D	--
1982	J	4
	F	2
	M	7
	A	7
	M	6
	J	5
	J	7

Average Δ

$\bar{\Delta}$ = 5 ± 1 pptv

s_Δ = 2.7

n = 16

t = 7.9

Summary

	Δ	
This work	5.3 ± 1.1	Hawaii
Rasmussen & Khalil		
Chesapeake	5.2 ± 5.2	Tropics
Rasmussen & Khalil		
PACHOPH	8.8 ± 2.1	Hawaii

Δ corrected for the new absolute concentration scale.

6. <u>Lifetime estimates</u>.

The global burdens were estimated by using the network sites to obtain average concentrations in four equal mass regions of the atmosphere. These regions were "n" (north) from 30°N latitude to 90°N, "nt" (approximately, northern tropics) from 0° to 30°N, "st" (s for south) from 0° to 30°S, and "s" from 30°S to 90°S.

$$C_n = \tfrac{1}{2}[C(\text{Cape Meares}) + C(\text{Barrow})]$$

$$C_{nt} = 0.2C(\text{Cape Kumukahi}) + 0.8C(\text{Mauna Loa}) \qquad (1)$$

$$C_{st} = 0.96C(\text{Samoa})$$

$$C_s = \tfrac{1}{3}[C(\text{South Pole}) + C(\text{Cape Grim}) + C(\text{South Africa})]$$

$$\bar{C} = \tfrac{1}{4}[C_n + C_{nt} + C_{st} + C_s] \qquad (2)$$

The equations for C_{nt} and C_{st} reflect the approximate weightings for the air above the boundary layer and in the boundary layer. The global burden is

$$\bar{C}_B = (N_T + \alpha N_S)\,\bar{C} \qquad (3)$$

where $\bar{C}_B$ is in number of molecules of CH_3CCl_3 which may be converted to grams upon multiplication by M_w/N_o where M_w is the molecular weight of CH_3CCl_3 and N_o is Avogadro's number. In eqn. (3) N_T and N_S are the numbers of molecules of air in the troposphere and stratosphere respectively, $\bar{C}$ is in pptv ($\times 10^{-12}$) as in eqn. (2), and α reflects the lower concentration of CH_3CCl_3 in the stratosphere ($\alpha = 0.2$, Khalil, 1979).

The mass balance relates the known emissions (S) and the global burden (C_B) to the unknown lifetime by

$$dC_B/dt = S - (1/\tau)C_B \qquad (4)$$

The emissions were taken from Neely & Plonka (1978) and the more recent figures provided by Farber and Neely (see also Prinn et al., 1982). The eqn. (4) was solved numerically with the yearly emissions.

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Figure 5 shows the results of the lifetime calculations by eqn. (4) and the global concentration C_B/N_∞ ($N_\infty = N_T + N_S$).

Since it has been argued in the past (Cunnold et al., 1978) that lifetimes determined by global burdens are sensitive to inaccuracies in obtaining the absolute concentration, a "trend" method has been proposed whereby one matches the observed relative rate of increase (1/C) dC/dt to the value of the same quantity expected on the basis of known emissions and the unknown lifetime. We estimated the expected value of (1/C)dC/dt over the past four years by the following equation:

$$(1/C)\ dC/dt = S(t)\left[\int_0^t e^{(\nu-\eta)t}\ S(\nu)d\nu\right]^{-1} - \eta \qquad (5)$$

$$\eta = 1/\tau$$

Thus, the relative rate of increase (1/C)dC/dt is related to the inverse lifetime η ($= 1/\tau$). Using the same release estimates as before, we obtained the results shown in Figure 6. The observed average rate of increase of CH_3CCl_3 during the same four years is also marked on Figure 6, along with 90% confidence limits. The most suitable lifetime by this method is about 8 years (±2 years).

The technique we have used here is a much simplified version of the optimal estimation methods used by ALE. It is provided to show that the lifetime estimated from the data is still dependent on the method of calculation and thus to demonstrate the need for evaluating the special sensitivities of the trend method.

The results of the ALE program (Prinn et al., 1982) also suggest that the lifetime estimated by the trend method is much longer than the corrected lifetime based on the global burden and the new absolute calibration.

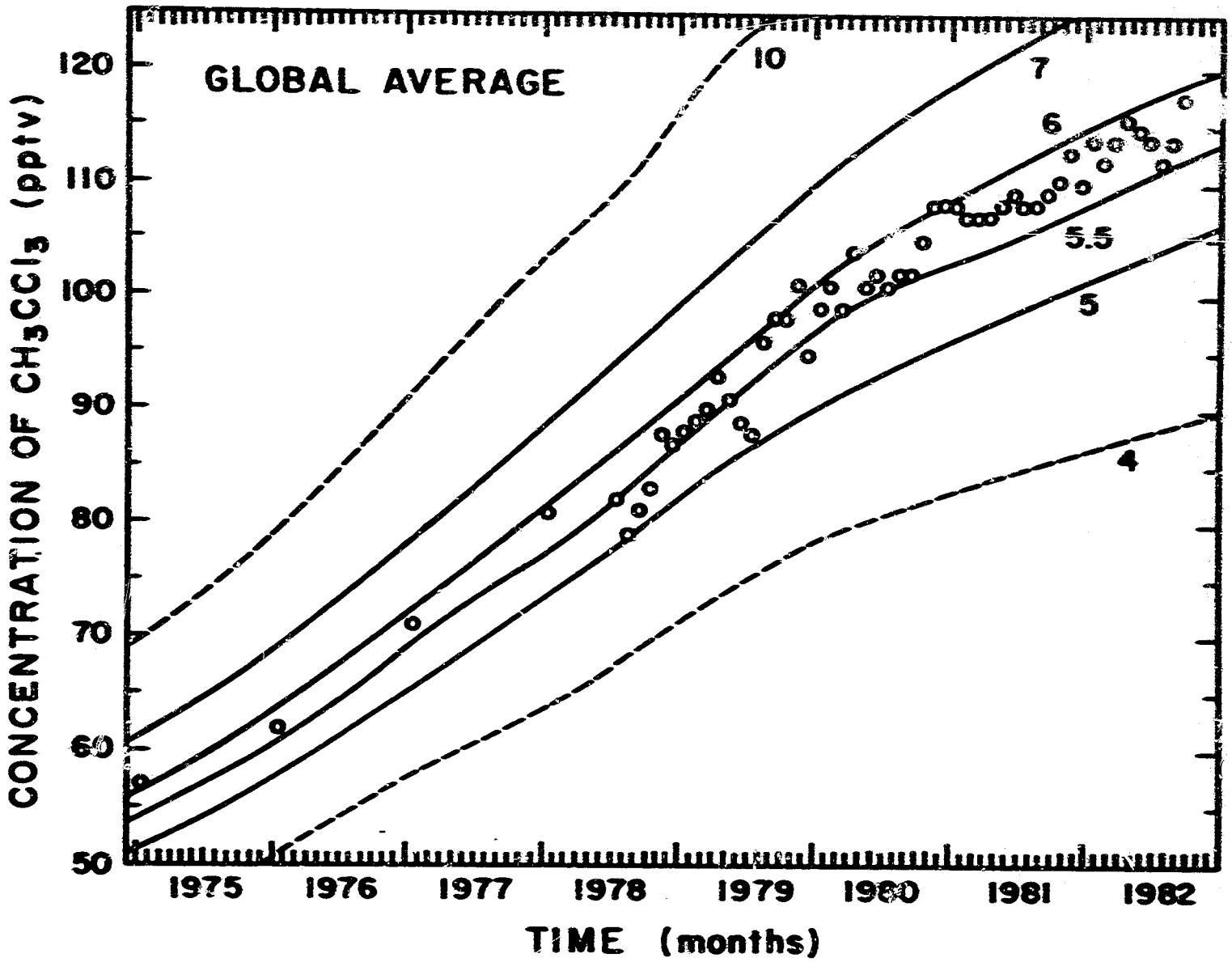

FIGURE 5. Globally averaged time series of CH_3CCl_3 concentrations and mass balance calculations.

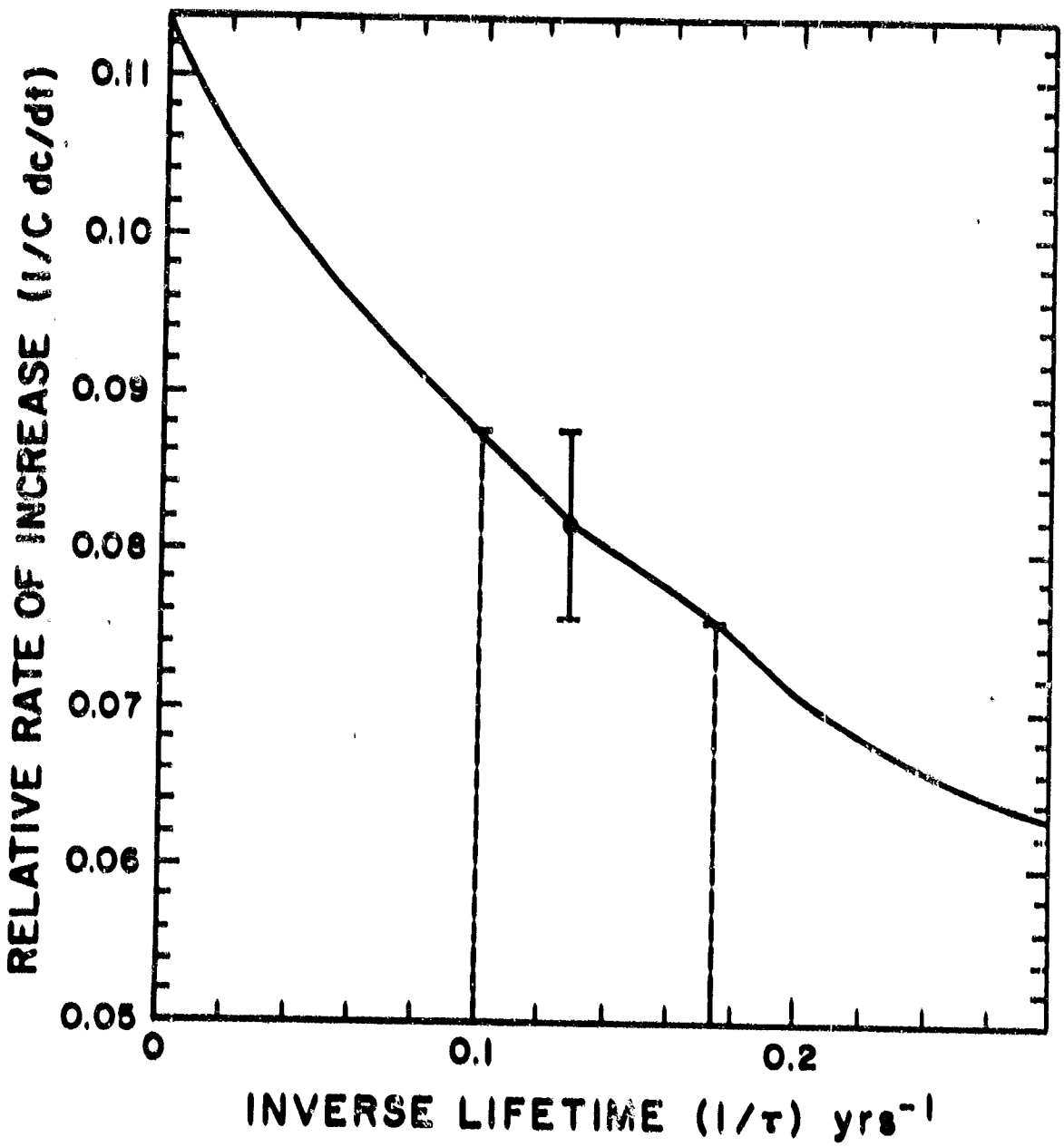

FIGURE 6. Relationship between the relative rate of increase of CH_3CCl_3 and the lifetime (1978-1982). The solid circle (●) is the observed rate of increase, and the vertical bars represent 90% confidence limits. This corresponds to an average lifetime of about 8 years.

These calculations are summarised in Table 3. The environmental importance of CH_3CCl_3 depends on whether the lifetime is 5-6 years as shown by the global burden or 10 years as suggested by the ALE calculation. Figure 7 shows, for instance, the rapidity with which the CH_3CCl_3 concentrations can be controlled if the lifetime is short, should the need for such control ever arise.

TABLE 3. Summary of Lifetime Calculations (1982)

	Years		
	τ	τ_L, τ_U	
Global average mass balance	5.5	4.5- 6.5	This work (1/1975-8/1982)
Trend analysis	7.7	5.8-10.0	This work (6/1978-8/1982)
ALE trend	10.5	7.0-16.7	(1/1979-1/1982)
ALE mass balance	9.8	7.4-14.4	(1/1979-1/1982)

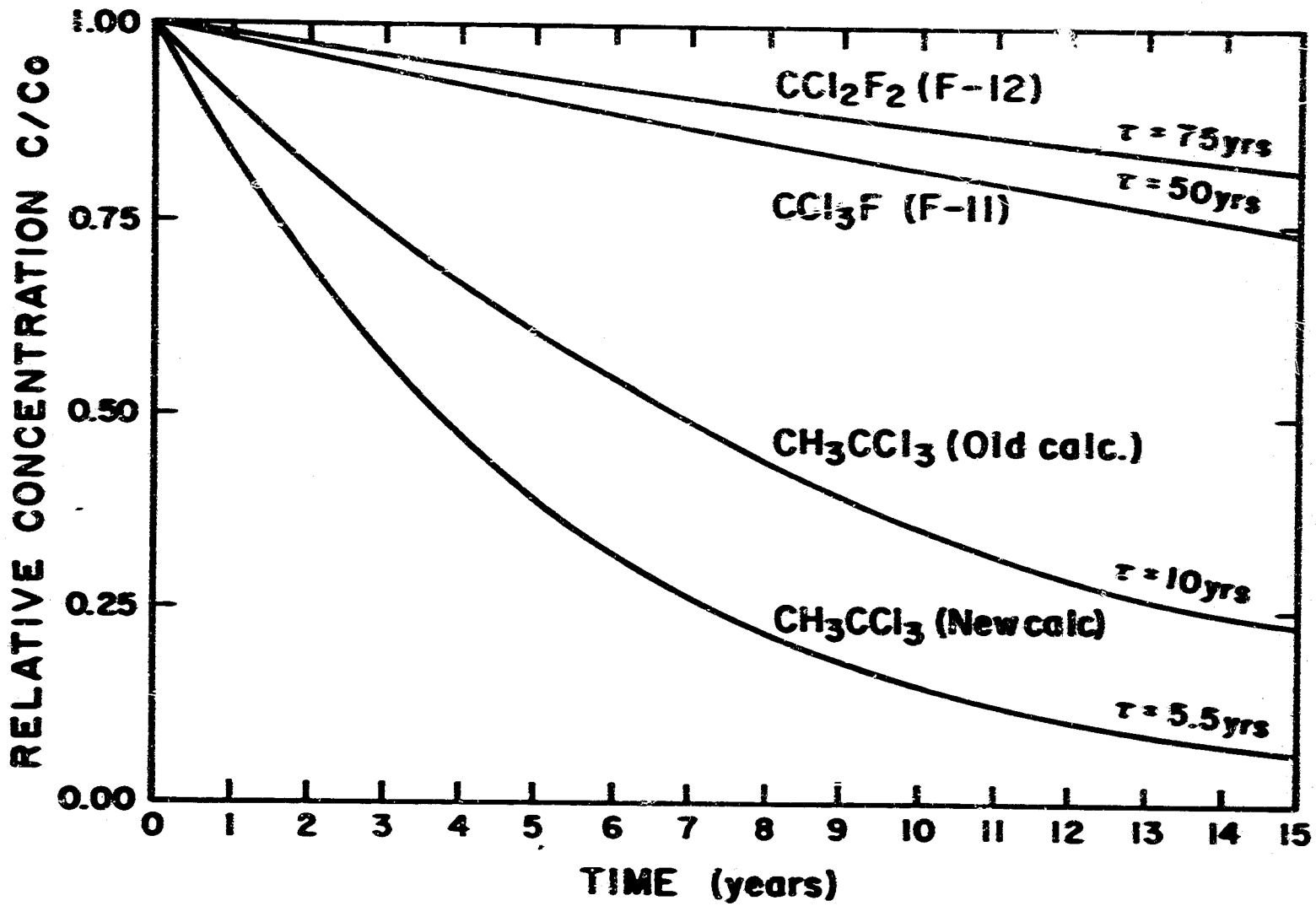

FIGURE 7. Effect of short lifetime on the removal of gases from the atmosphere assuming emissions are stopped.

7. <u>Estimated ultimate tropospheric distribution.</u>

Assuming emissions continue at a constant rate equal to the current yearly emissions of about 0.54 Tg/yr (1 Tg = 10^{12} gm), the ultimate concentration of CH_3CCl_3 can be estimated based on a five-year lifetime.

A one-dimensional steady state model was formulated as follows:

$$\frac{1}{R^2} \frac{d}{d\mu} \left[K(\mu)(1 - \mu^2) \frac{dC}{d\mu}\right] + S - \eta C = 0 \qquad (6)$$

$\mu = \sin \phi$

ϕ = latitude; R = radius of the earth

The sources (S), transport parameter (K), and lifetime τ (= $1/\eta$) are shown in Figure 8 as functions of $\sin \phi$. The solution of eqn. (6) for tropospheric concentrations is shown (τ = 5 yrs) in Figure 9.

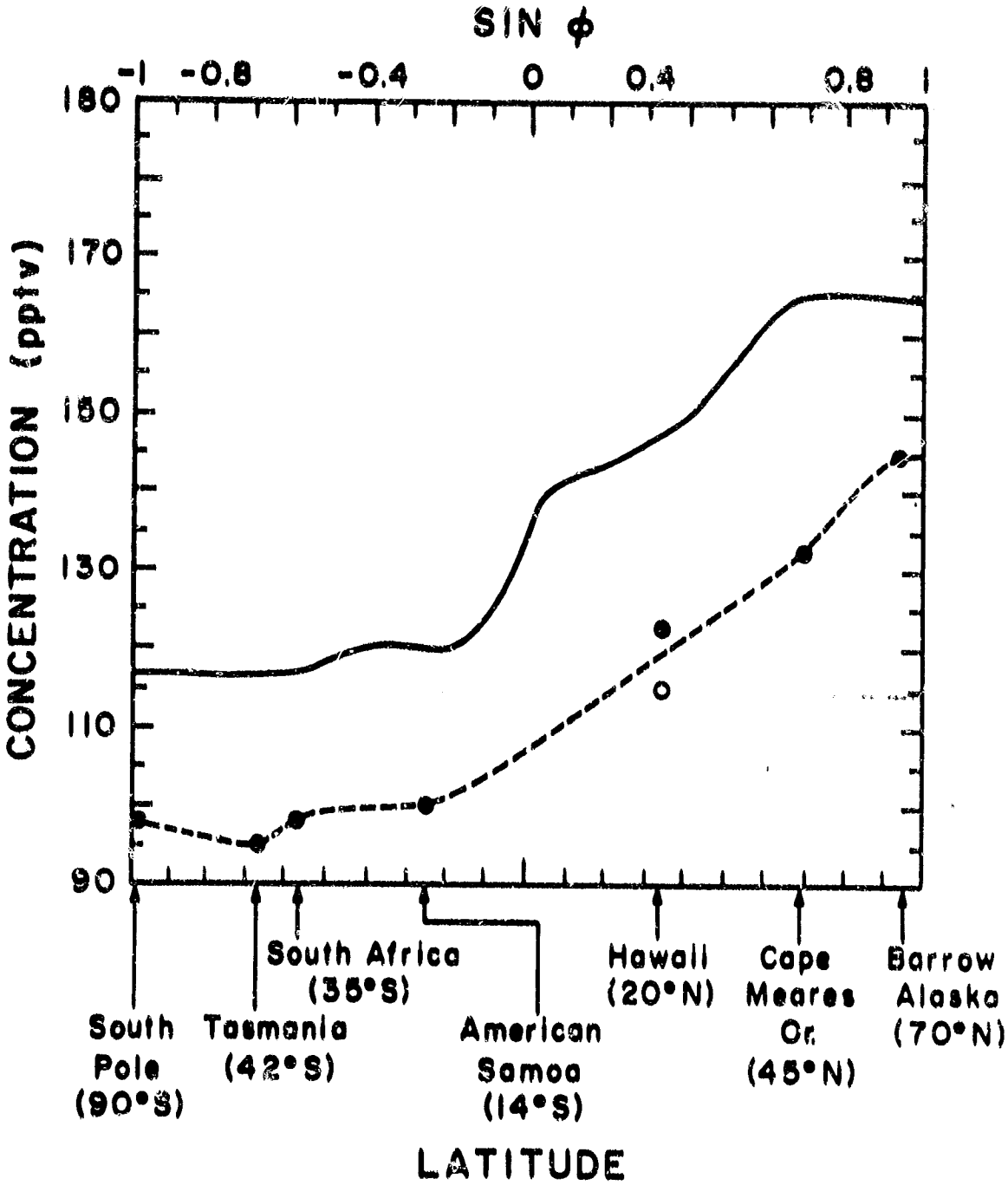

FIGURE 9. Ultimate expected concentration distribution of CH_3CCl_3.

8. Proposed research.

In view of the results obtained, the following research is proposed for the next two years:

(1) Continued measurements of the global concentrations: The rate of increase of CH_3CCl_3 in the atmosphere is slowing down as shown in Figures 1 and 5. In this case it is a reflection of the possibly short (≈5 yr) lifetime. Whenever changes are taking place, careful documentation is required to establish their consequences.

(2) Theoretical studies of sensitivities of the global mass balance model and the trend method. It appears that the new calibration constant suggests a short lifetime for CH_3CCl_3 of about 5 or 6 years. On the other hand, the trend method yields a lifetime of about 8 years (our work) to 10.5 years (ALE paper). This contradiction has to be resolved before the shorter lifetime of CH_3CCl_3 is accepted. Since the trend method is unaffected by absolute accuracy, this discrepancy will otherwise be assumed to arise from inaccurate emissions data, and the longer lifetime will be considered more acceptable.

(3) Uncertainty analysis for the lifetime of CH_3CCl_3.

(4) Statistical analyses of the reliability of data.

(5) Publications on the lifetime and global time series of CH_3CCl_3.

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Methylchloroform (CH_3CCl_3):

Accumulation in the Earth's Atmosphere

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ABSTRACT

Observations of methylchloroform concentrations have been made over five years, at remote locations (45°N and 90°S). The average global concentration of CH_3CCl_3 has been increasing at 12% per year. The difference between the northern and southern hemisphere concentrations has changed over the years. These features can be explained by including cyclic terms in the function describing past global industrial emissions of methylchloroform.

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Methylchloroform (CH_3CCl_3) is a trace gas in the earth's atmosphere, believed to be entirely man-made (1). The current concentrations exceed 100 ppt everywhere in the troposphere and have resulted from ever increasing industrial production, use and consequent direct emissions into the atmosphere (2). Current data suggest that the atmospheric lifetime of CH_3CCl_3 is relatively long and between 7 and 11 years (3). These lifetimes and the rapidly increasing global emissions have ignited new interest in the possible adverse effects of CH_3CCl_3 on the future global environment. Its main dangers are similar (though smaller in magnitude per molecule emitted) to the much publicized effects of continuing anthropogenic releases of CCl_3F (F-11) and CCl_2F_2 (F-12), namely the depletion of the stratospheric ozone layer by chlorine atom catalized destruction of O_3 (4), and the enhancement of the earth's greenhouse effect. It is, therefore, desirable to have a consistent and reliable data base on the atmospheric burden of CH_3CCl_3 over several years and an accurate estimate of global emissions. With this time series of data, the sources, sinks, lifetimes and distribution of CH_3CCl_3 can be determined, which can then be used to more accurately estimate the possible future ecological effects of continuing emissions of CH_3CCl_3.

Here we will report a self-consistent set of data (5) obtained over the last five years. These data indicate that the global burden of CH_3CCl_3 has been rising at an average rate of a little over 12% per year, since January 1978. There is one further observation implicit in those data. Consider the ratio of the amount of CH_3CCl_3 in the troposphere of the northern hemisphere

to the amount in the southern troposphere. This ratio, R, has been declining over the years, but has now started to rise again. In this report we offer simple explanations of these two observations.

A global budget analysis is a useful theoretical tool in establishing lifetimes of trace gases and in determining the agreement between observed concentrations and those expected on the basis of emissions estimates. Essentially, the budget is a relationship (or a set of relationships) between the sources, sinks and ambient concentrations. It is generally assumed that the global emissions of CH_3CCl_3 have been increasing exponentially -- a conclusion based on the yearly estimates of industrial production and use (2, 6). Thus the source function (release in lbs/yr at year t), denoted S(t), may be written as $S(t) = a \exp(bt)$. Over the last 15 years the average rate of increase in the global emissions has been b = 0.15 - 0.16 (15% - 16% per yr)(6,7). Simple budget analyses would predict that the rise in the global atmospheric burden should also be about 15% - 16% per yr, which is larger than our data indicate. Furthermore, by taking smaller scale spatial averages in the mass conservation or budget equations, the ratio R (north to south burden) is predicted to be almost constant over the last five years -- again at odds with our data. Upon a closer examination of the emissions data we observed that the emissions function deviated considerably from a simple exponential (8). Furthermore, it was remarkable that these deviations were cyclic. In any case, the observed growth rate and the rather significant changes of the north-south ratio of concentrations (R) are both explained by the cyclic fluctuations of the source function. Without incorporating these deviations

of the source, from the average exponential behaviour, neither of these observations can be explained (9). It should be noted that both the observations discussed above are not very sensitive to absolute accuracy of measurement, since both are based on ratios of measured concentrations.

The remainder of the report is devoted to quantifying the statements made thus far: The time series of observations is shown in Table 1, which also includes the N/S ratio R_0 (10).

The source function: Figure 1a shows the emissions estimates from 1961-1978 (ln S(t), where S(t) is in millions of lbs per yr) as a function of time -- thus the least squares straight line corresponds to $S = a \exp(bt)$. We chose the years 1963-1978 for further analysis. Most of the emissions that account for current burdens have come from these years (11). Let us assume for the sake of discussion that the emissions function in Figure 1a is the true source function. Clearly a model function: $S_0 = a' \exp(bt)$ can be constructed as usual, but this doesn't describe the true source function adequately. By considering the residuals (difference between true and model source functions) one can isolate two cycles in the emissions history of CH_3CCl_3 and write the source functions as:

$$S = a' \exp(bt)[1 + \Delta_1 + \Delta_2] \qquad 1$$

$$\Delta_1 = \alpha \cos(\omega t + \xi) \qquad 2$$

$$\Delta_2 = [\alpha_0 + \alpha_1 \cos(\tilde{\omega} t + \tilde{\xi})]\, H(t - T) \qquad 3$$

Fig. 1b illustrates the first residual $\tilde{\Delta}_1$ (12) ($\ln S - (a + bt) = \tilde{\Delta}_1$; S is the true emissions function and Δ_1 is a model function describing $\tilde{\Delta}_1$). The cyclic nature of the residual Δ_1 is apparent. Fig. 1c shows the analogous

second residual $\tilde{\Delta}_2 = \ln S - (a + bt) - \Delta_1$ and it is described by Δ_2 in eqn. 3 where $H(t - T) = 0$ if $t < T$; $H(t - T) = 1$ if $t \geq T$; T is the year 1972 (13). The parameters a', b, α, ω, ξ, a_0, a_1, $\tilde{\omega}$ and $\tilde{\xi}$ have the values 121.2 pptv/yr, 0.133/yr, 0.22, 0.94 rad/yr, 1.91 rad, -0.01, 0.12, $\pi/2$ rad/yr and 4.3 rad respectively. Note that all these variables are completely determined by the emissions estimates.

Global rate of increase: The global mass balance eqn. is written as:

$$d\xi/dt = S(t) - \eta\xi \qquad 4$$

where ξ is the mean global mixing ratio and η the reciprocal of the lifetime. The only undetermined and free parameter is η. When eqns (1-3) are inserted into eqn. 4, the resulting eqn. can be solved exactly, and gives:

$$\xi = a_0 e^{-\eta t} + a_1 e^{bt} + H(t - T)\, e^{-\eta t} \int_0^t A e^{bt}\, \Delta_2(t)dt \qquad 5$$

$$a_0 = \left[\xi_0 - \frac{a'}{b+\eta} - \frac{\omega\alpha a}{\omega^2 + (b+\eta)^2}\, f(\xi)\right] \text{ and } a_1 = \left[\frac{\omega\alpha a'}{\omega^2 + (b+\eta)^2}\, f(\xi + \omega t) + \frac{a}{b+\eta}\right] \qquad 6$$

$$f(x) = \sin x + \frac{b+\eta}{\omega} \cos x \qquad 7$$

The last (third) term in eqn. 5 is also exactly solvable by standard techniques, but the solution is not included here because it is complicated and small in magnitude (3). Fig. 2a shows the natural log of global averages from 1/1975 -1/1979, the predicted concentrations assuming $S = a' \exp(bt)$ for the source function, and the predictions when the source fluctuations are added on (eqns.

1-3)(14). The growth rates ($\sim (1/\xi)\, d\xi/dt$) from Fig. 2a are: 0.12/yr (observed); 0.15+/yr (based on 16 years constant exponential growth of source-$a \cdot \exp(bt)$) and 0.1[illegible]/yr (exponential source with Δ_1 & Δ_2 cycles). Inclusion of a more accurate description of the source function (eq. 1) brings theory and observations in very close agreement.

The ratio R_o: To calculate R_o, eqn. 4 was extended to smaller spatial scales, each covering about one-fourth of the atmosphere:

$$d\underline{\xi}/dt = \underline{S}(t) - \underline{\Pi} \cdot \underline{\xi} \qquad 8$$

There are four boxes, separated by latitudes. (Box 1: $0 < \phi \leq \pi/3$ rad. Box 2: $-\pi/3 < \phi \leq 0$. Box 3: $\pi/3 < \phi \leq \pi/2$. Box 4: $-\pi/2 < \phi \leq -\pi/3$). Therefore ξ_3 is the mean mixing ratio in high northern latitudes where the U.S. Pacific Northwest site is located; and ξ_4 is the mixing ratio given by the measurements at the South Pole (10). All one needs to do is solve eqn. 8 and R_o will be theoretically predicted by: $R_o = \xi_3/\xi_4$. Once again such a formulation (eqn. 8) is exactly solvable in closed form for $S = S_1 + S_2 + S_3 + S_4$ given either by eqn. 1 or $S = a \exp(bt)$. The final equations for R_o are very complicated for either the average exponential source or the source of eqn. 1. When only the Δ_1 cycle is considered, R_o takes the simpler form

$$R_o = \bar{R}_o \frac{1 + a_o \sin(\omega t + \phi) + a_1 \cos(\omega t + \phi)}{1 + b_o \sin(\omega t + \phi) + b_1 \cos(\omega t + \phi)} \qquad 9$$

where $\bar{R}_o$, a_o, b_o, a_1, b_1 are constants determined by the constants used to describe the source. The reader will notice that eqn. 9 is of the type capable

of describing the observed R_0. For a steady exponential source a_0, b_0, a_1, b_1 $\rightarrow 0$ and $R_0 = \bar{R}_0$ (a constant). The complete equations for R_0 (with the Δ_2-cycle and eqns. for a_0, b_0, a_1, b_1) will not be discussed here (3). Fig. 2b shows the results of the calculations. If $a' \exp(bt)$ is adopted for the source function, the predicted value of R_0 ($= \bar{R}_0$) is almost constant at around 1.5. Incorporating the fluctuations reveals changes in R_0 which match observations (13). The two theoretical curves reflect slightly different transport times between boxes 1 and 3. It is especially noteworthy that the rises and falls of the source fluctuations occur at just the right times to match the rise and fall of the observed values of R_0. The excess of CH_3CCl_3 in the northern hemisphere compared to the southern hemisphere was probably greater in the early years of measurements (Jan. 1975) than in subsequent years (particularly early 1978). This theory (eqn. 8) also reproduces the observed concentrations at both sites for all the years studied, if the Δ_1 and Δ_2 cycles are included in the source function.

We have discussed a time series of data on CH_3CCl_3 concentrations at remote locations in the northern (~45°N) and southern (90°S) hemispheres. The industrial emissions of CH_3CCl_3 have been increasing year after year, but we have also shown that superimposed on the steady exponential rise are cyclic fluctuations. This more detailed model of the emissions function leads to predictions of the increasing global burdens of CH_3CCl_3 and changing north-south ratio, R_0, which are in coincidence with observations. Such an accurate balance, between expected and observed behaviour of an atmospheric trace gas, is rare.

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5. The term self-consistent means that the data were collected by the same techniques, at the same locations and at the same time each year. The GC/EC analytical techniques were used throughout and carefully prepared standards were maintained throughout the course of the study.

6. J. S. Chang and J. E. Penner, Atmos. Environ. 12, 1867 (1978).

7. In the last five years the increase has been around 8% per year.

8. The simple exponential function for the source is determined by considering $\ln S(t) = a' + bt$, where a' and b are found by linear least squares methods.

9. It is possible to dismiss these two discrepancies between observations and mass balance with a simple exponential source, as due to inaccuracies and imprecisions in the measurements. More detailed analysis of the data suggests such an explanation to be unlikely because of the size of the discrepancies. It is also possible to relegate the effects to atmospheric variability. It is, however, not possible to make a quantitative case for such an explanation with currently available data.

10. R is the ratio of the northern hemisphere burden to the southern hemisphere burden. R_0 is the ratio of measured concentrations at high northern latitudes to high southern latitudes. In general R and R_0 are not equal in magnitude and $R_0 > R$. More extensive latitudinal concentration data on CH_3CCl_3 and other trace gases suggest that there is a simple model latitudinal profile so that R and R_0 are closely related and contain the same information. The model profile is: $\xi(\phi) = \alpha$ when $-\pi/2 < \phi < -\phi_0$, $\frac{1}{2}(\alpha + \beta) + \frac{1}{2}[(\beta - \alpha)/\phi_0]\phi$ when $-\phi_0 < \phi < \phi_0$ and β when $\phi_0 < \phi < \pi/2$ $\xi(\phi)$ is the mixing ratio at latitude ϕ (α, β and ϕ_0 are constants). Thus the relationship between R and R_0 can be shown to be: $R_0 = \{R(1 - \frac{\gamma}{2\phi_0}) - \frac{\gamma}{2\phi_0}\}/\{1 - \frac{\gamma}{2\phi_0}(1 - R)\}$ where $\gamma = (1 - \cos\phi_0)$; ϕ_0 is found to be between 30° and 40°. The concentrations reported are the mean values obtained from a large number of measurements made during January of each year.

11. The emissions prior to 1963 are also included in the theoretical calculations, but their effects are small.

12. There are several more or less equivalent ways of considering the residuals which constitute the more detailed structure of the source function. We have simply chosen one method. If S is written as: $\ln S = a + bt + \Delta_1$, then $S = a' \exp(bt) \exp(\Delta_1)$. When $|\Delta_1|$ is sufficiently small, $S \approx a' \exp(bt)[1 + \Delta_1(t)]$. Alternatively one may simply define Δ_1 by $\Delta_1 = S(\text{true}) - a' \exp(bt)]/[a' \exp(bt)]$. The final results in this study are not significantly affected by this choise.

13. Eqn. 1 is accurate enough for our study. The Δ_1 cycle has a much greater effect on observable concentrations since its amplitude is more than twice

as large as that of the Δ_2 cycle. Furthermore, the Δ_1 cycle has a lower frequency which also makes it more effective. A rough measure of the accuracy of each model function can be made by the mean deviation: $\delta = (1/N) \Sigma_{i=1}^{N} | S(\text{true}, t_i) - S(\text{model}, t_i)|$. If we adopt the simple exponential model, $\delta = 12\%$ (if the Δ_1 & Δ_2 cycles are just ignored). Adopting the model of eqn. 1 with only the Δ_1-cycle gives $\delta = 4\%$ (the mean error between the true and model functions is only 4%). If we adopt eqn. 1 with both the Δ_1 & Δ_2 cycles, $\delta = 1.2\%$.

14. If one wishes to ignore the cycles and adopt $S = a \exp(bt)$ for the source, then the resulting eqns. for the concentration can be found from eqns. 5-7 by setting $\Delta_i = 0$ & $\alpha = 0$. In order to keep the discussion simple, we have adopted this simple global method for discussion in this report. More detailed theoretical analyses have also borne out the closer agreement with observations when the Δ_1 & Δ_2 cycles are included. The parameter η is adjusted to get the best agreement for both the exponential source and fluctuating source theories and correspond to $1/\eta = 12.8$ yrs and 11.8 yrs respectively. These are not true lifetimes because proper adjustments for stratospheric burdens have not been made. The global average is taken as the mean of the values at the two sites, each year. This mean is implied by the profile discussed in note (10). The mean deviations between predicted and observed concentrations are 4% for the exponential source and 1.6% for the fluctuating source. These averages are not very meaningful in absolute terms, and should be used only for the comparison of the two theories.

15. When the slopes of the logs of observed CH_3CCl_3 concentrations at the two sites were compared by a t-test, it was found that $b_n - b_s < 0$ at the 0.01 level of significance. This indicates that R_o has been declining. In eqn. 9 Ω is a 4x4 matrix made up of lifetimes in the various boxes and the transport times. $\underline{S}(t)$ is a 1x4 vector -- the sources were taken to be 80% in latitudes above 30°N, 10% in each of the boxes around the equator.

TABLE 1

CH_3CCl_3 CONCENTRATIONS AT REMOTE NORTHERN AND SOUTHERN HEMISPHERE LOCATIONS

(~ +45°, U. S. Pacific Northwest and -90°, South Pole).

Year		Jan. 1975	Jan. 1976	Jan. 1977	Jan. 1978	Jan. 1979	Jan.* 1980
CH_3CCl_3 Concentration (pptv)	PNW	90	98	107	117	135	157
	SP	54	57	70	85	95	103
R_o		1.67	1.72	1.53	1.38	1.42	1.52

*Preliminary data

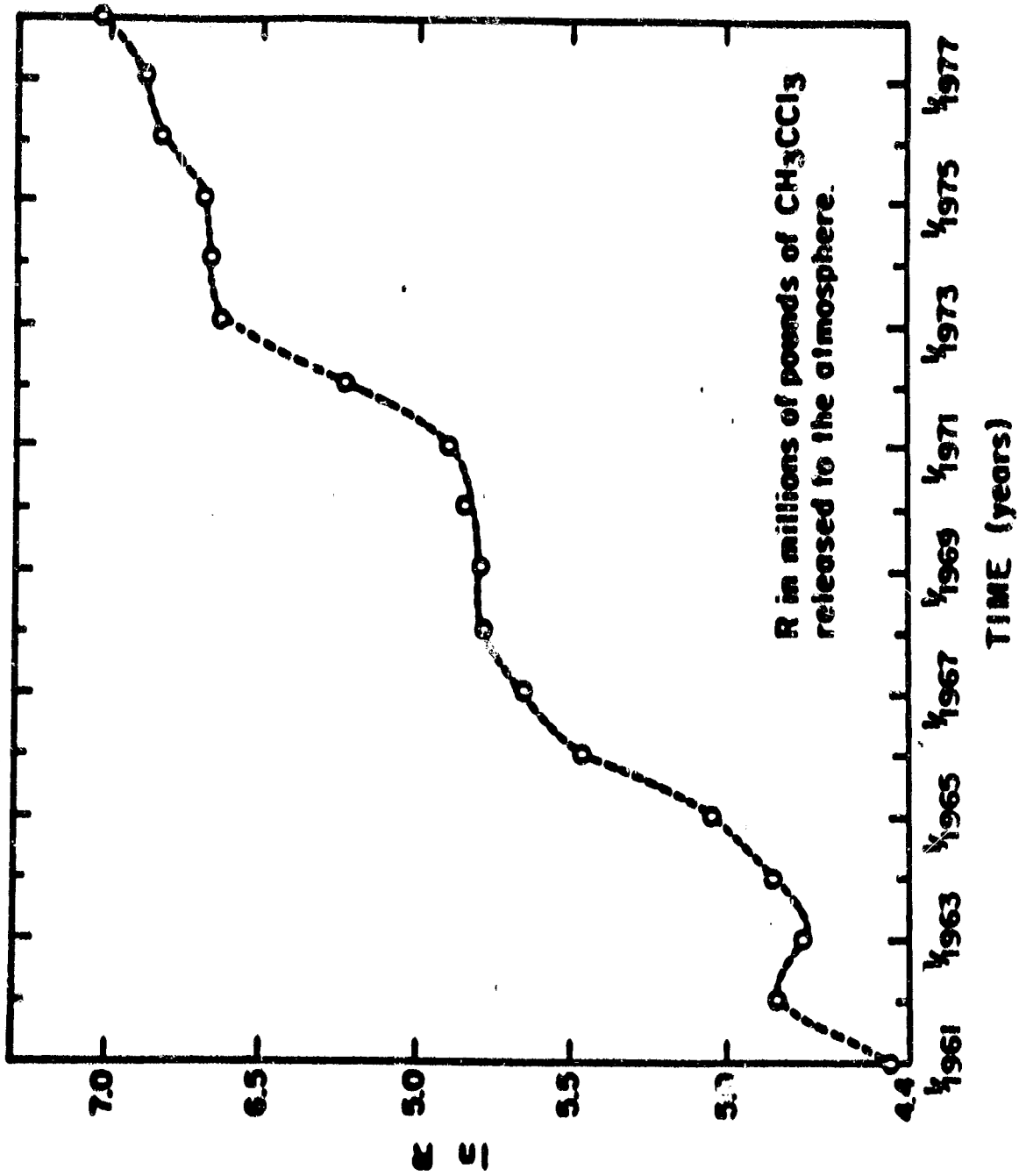

Figure (1d): Time variation of global CH_3CCl_3 emissions (1961-1978).

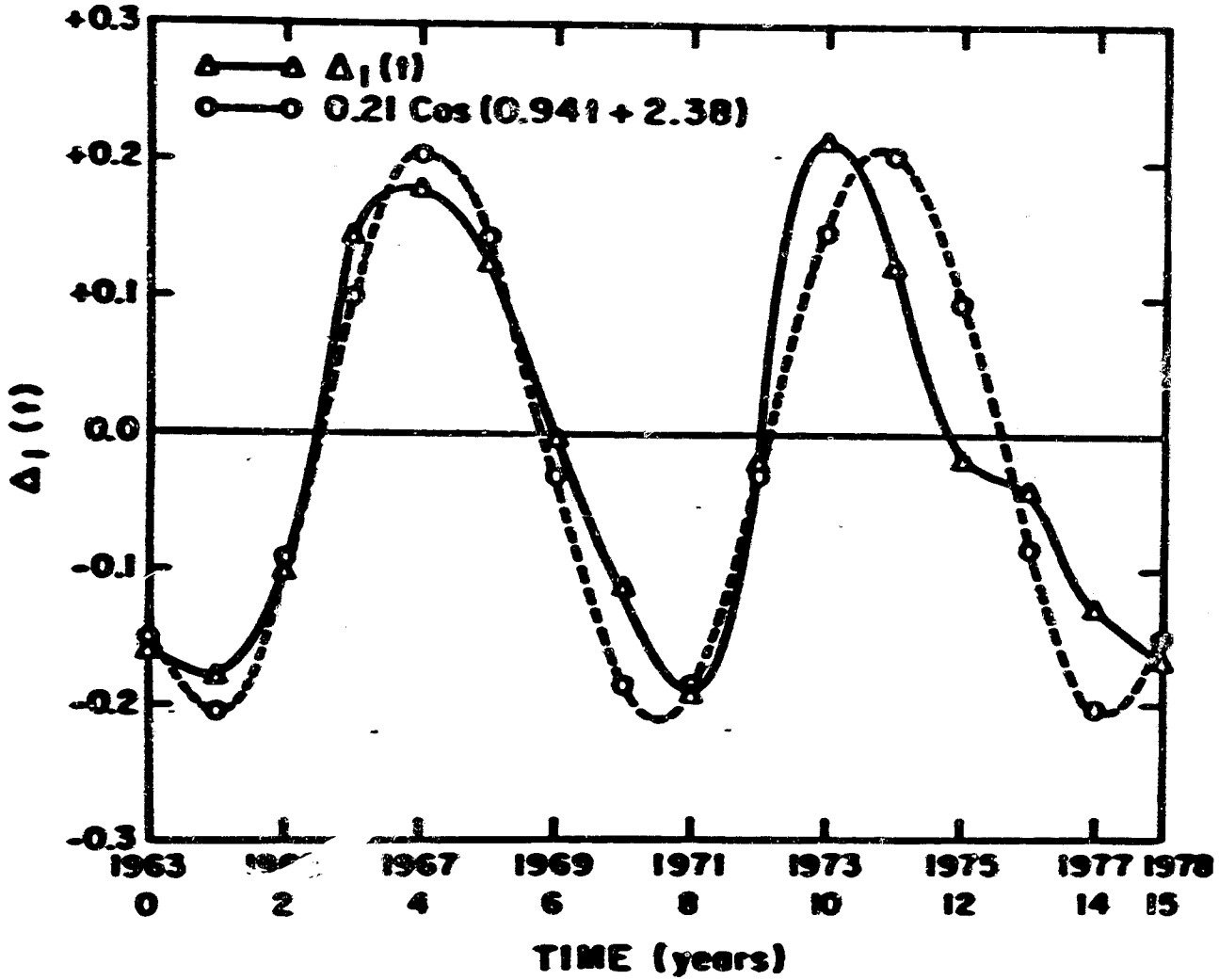

Figure (1b): The Δ_1 cycle in the global emissions of methylchloroform.

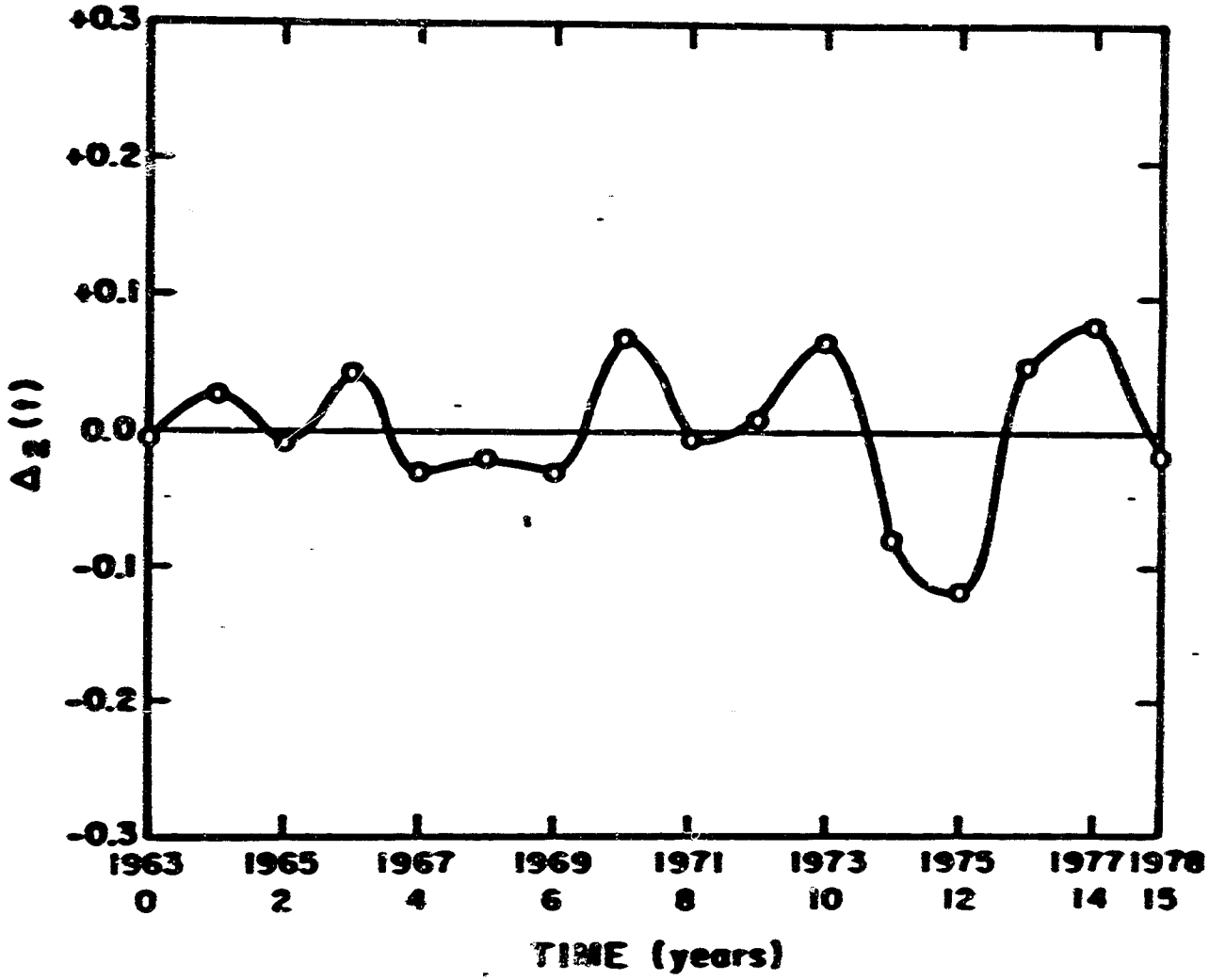

Figure (1c): The Δ_2 cycle in the global emissions of methylchloroform.

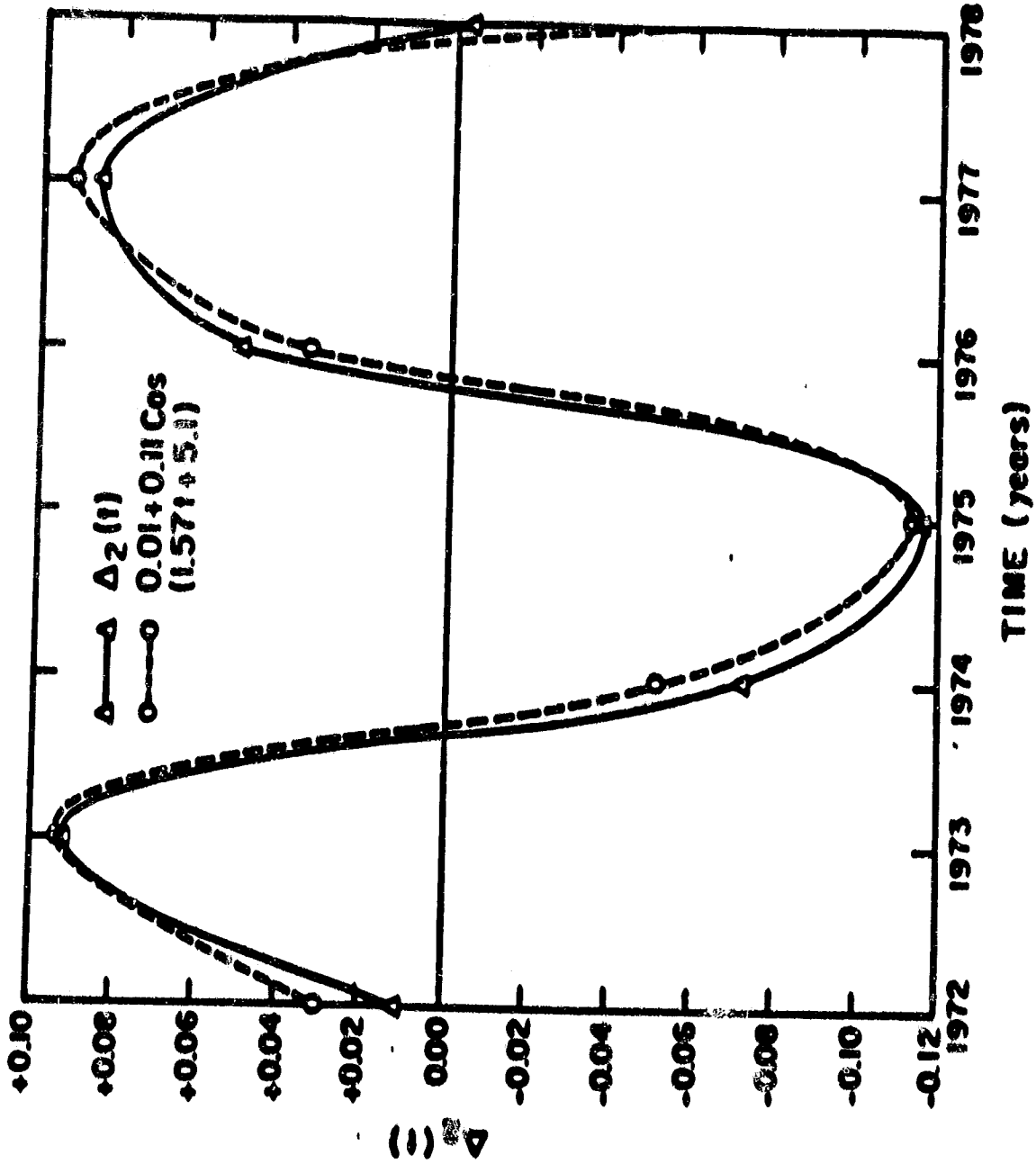

Figure (id): A model for the Δ_2 cycle in the global emissions of CH_3CCl_3.

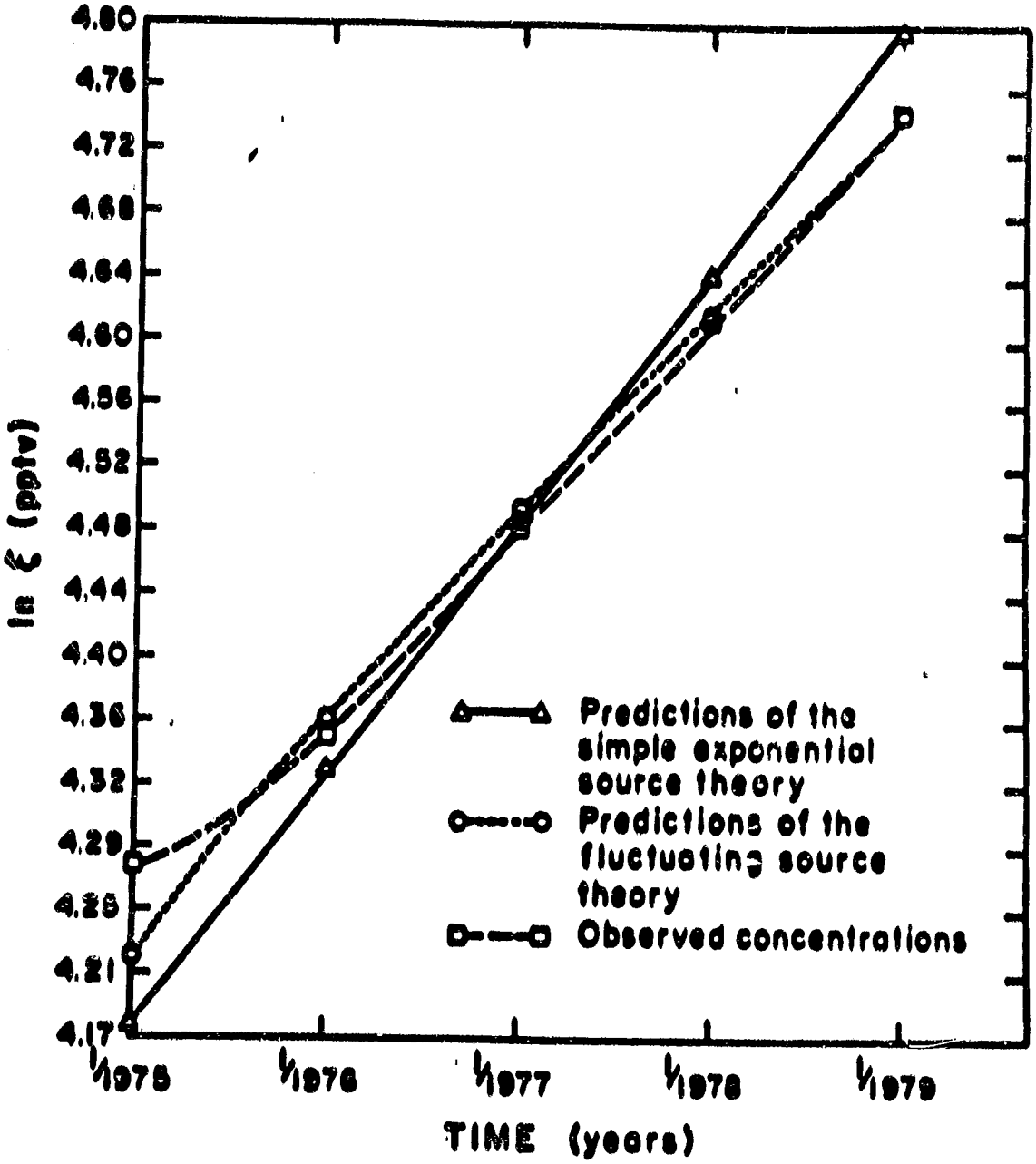

Figure (6a): A comparison of observed concentrations of CH_3CCl_3 with two theories.

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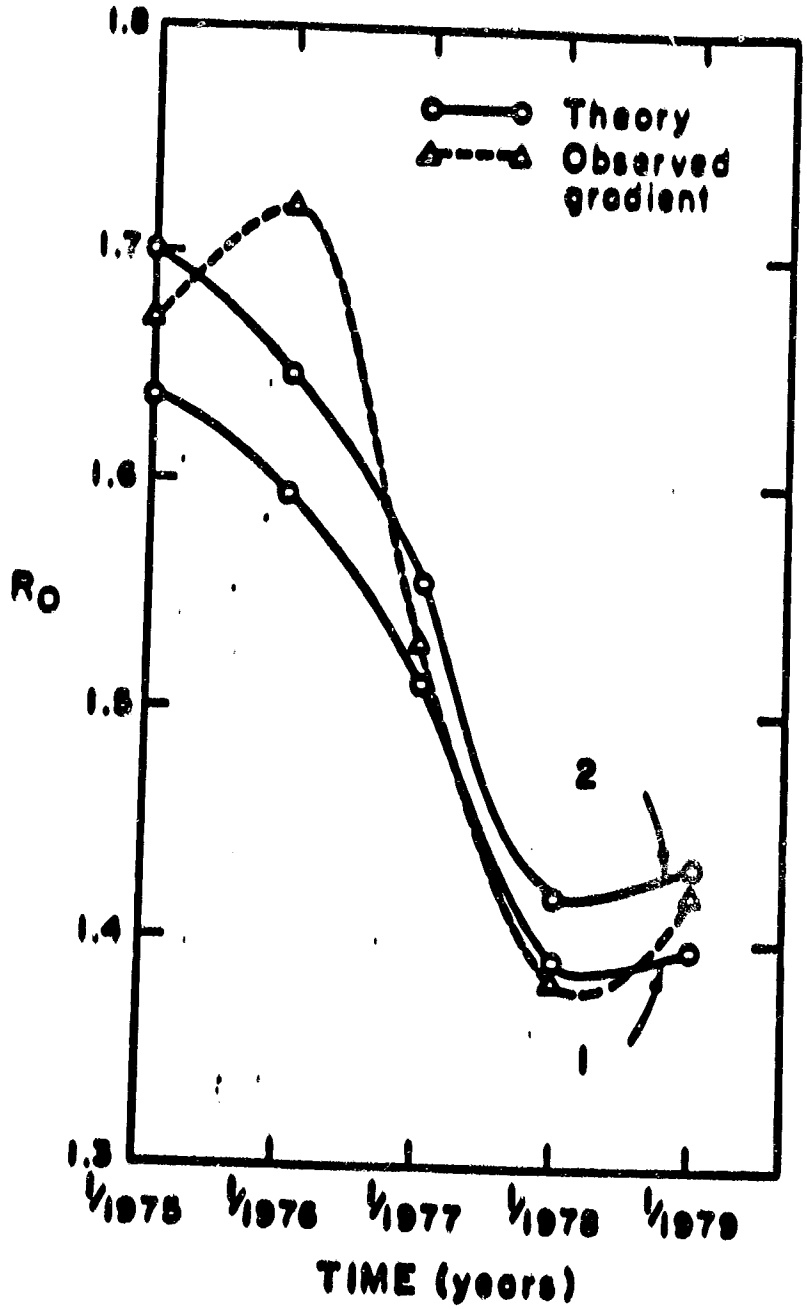

Figure (2b): The observed methylchloroform gradient and the four box theory with the Δ_1 and Δ_2 cycles.

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IN VIVO MUTAGENICITY STUDIES WITH TRICHLOROETHYLENE AND OTHER SOLVENTS (PRELIMINARY RESULTS) PREPARED BY LABORATORIO DI GENETICA DELL'UNIVERSITÀ DEGLI STUDI

Chemical Name (300 per name) 25	CAS No. (10) 26
1,1,1-TRICHLOROETHANE	71-55-6

A.K. 5/31/83

D-630

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IN VIVO MUTAGENICITY STUDIES WITH TRICHLOROETHYLENE AND OTHER SOLVENTS (PRELIMINARY RESULTS).

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1. INTRODUCTION

During 1976 a report was published by the National Cancer Institute (1), referring on the results obtained on a long-term carcinogenicity study developed on TCE. In these experiments TCE was administered by gavage, 5 days a week, for a period of 78 weeks to B6C3F1 mice and to Mendel Osborne rats (both females and males were treated for the two species). The treatments were at the maximum tolerated dose (MTD): this was for rats of 1300 mg/kg and for mice of 2000 mg/kg (males) and 1400 mg/kg (females); a second dose was also given (the half of the MTD). During treatments, the doses for both species were reduced.

The final data of these experiments have concluded that TCE did not produce tumours in rats at the MTD (1300 mg/kg); but it produced hepatocellular carcinoma in both male and female mice with a statistical significant difference from the control; the incidence of tumours was higher in males compared to females.

In 1977, HENSCHLER et al. (2) questioned the results obtained by the NCI experiment, on the basis that the carcinogenic effect reported by the NCI could have been due, largely, to the types and amounts of epoxides present in TCE sample used for long-term study, namely epichlorohydrin and 1,2-epoxybutane. Moreover, these Authors analyzed a sample of TCE similar to that employed by the NCI and

they observed the presence of 0.42% of epoxides employed as stabilisers. Mutagenic analyses developed by the same Authors, by using TA100 strain of Salmonella in the Ames test, demonstrated that epichlorohydrine and 1,2-epoxybutane were strong mutagens for Salmonella, whereas trichloroethylene of pure grade was not mutagenic.

On the basis of HEINSCHLER'S criticism (2) and of other Authors (3) we have investigated the mutagenicity of different types of TCE (technical and pure grade) containing different types of stabilisers, (including epichlorohydrine): the mutagenic experiments have been performed in vivo, in the host mediated assay, on NMRI mice, by treating the animals by gavage (similarly to the procedure adopted by NCI on the same strains of mice); other solvents, such as epichlorohydrine, trichloroethane and cyclohexanone have also evaluated in the same study.

The aim of the present study was the possibility to verify by a direct methodology the criticism developed by HEINSCHER (1), in order to promote further studies on trichloroethylene for a more accurate evaluation of its potential mutagenic as well carcinogenic risk.

2. BIOLOGICAL MATERIAL AND GENETIC END POINT

Yeast cell gene-mutation test in *Schizosaccharomyces pombe* is based on the treatment of a haploid double mutant strain - P_1 strain - of the genotype *ade6-60/ade 10-108/h⁻*: it allows the evaluation of the frequency of forward gene-mutations induced in five different genetic loci located on the three chromosomes of this yeast.

The strain employed consists of purple colonies, and the induced mutants are represented by white colonies: they are of the genotype *ade6-60/ade X*. The second "ade" mutation may have occurred in one of the following 5 genetic loci, namely *ade1*, *ade3*, *ade4*, *ade7*, *ade8*.

Forward mutations induced by chemicals in each one of these 5 loci have been shown to consist of base-pair substitution as well of insertion/deletion base-pairs; seventhy chemicals of different molecular nature have been so far tested in this mutational assay. (see 7).

3. HOST MEDIATED ASSAY

Intraperitoneal assay. The animals (mice or rats) are starved overnight before the experiment. The yeast cell suspension is inoculated into the peritoneal cavity of mice (25-30 gr of body weight) by injection (1.5 ml of suspension containing 2.10^9 cells/ml). The chemical is administered by gavage (0.5 ml per animal per treatment). After different incubation times, the animals are killed by cervical dislocation, the peritoneal cavity is open and cells are recovered by a pipette and by washing the peritoneal cavity with 1 ml of sterile distilled water. The cell suspension is counted on the microscope and appropriately diluted according to the assay: a dilution to 1.5×10^3 cells/ml is prepared and 0.2 ml of this suspension is spread on a yeast extract agar plate.

4. ANALYSIS OF THE RESULTS

The induction of genetic effect is evaluated by regression analysis, according to equation

$$y = a + bx$$

where (y) is the induced frequency of genetic effect to be evaluated, and (x) is the dose of the mutagen.

The regression coefficient (b) is the slope of the linear relationship observed and represent the amount by which the induced frequency (y) increases for a unit increase of the dose (x); the coefficient (a) represents the frequency of genetic effect produced at a dose x = 0.

In the present cases, the correlation factor (r) has been calculated for an evaluation of the statistical significance of the data.

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5. TREATMENT WITH A CHEMICAL IN VIVO

5.1. Yeast cell suspension

One fresh deep-red yeast colony grown on YEA is resuspended in a 50 ml YEL broth and allowed to grow for 36 hours at 30°C on a shaker. After this incubation time yeast cells are washed and collected by centrifugation (3 min. at 3300 x g). Cell titer is adjusted at 4×10^8 cell/ml in YELD and 1 ml of such a suspension is inoculated in a sterile test tube (approx 30 ml volume).

1 ml of S-9 mix, if metabolic activation is required, is added to each test tube, otherwise 1 ml of phosphate buffer is added.

5.2. Treatment procedure

The test substance is added in a final volume of 0.1 ml to the cell suspension.

Routinely the compound is tested with the following doses: 100, 30, 10, 1, 0.3, 0.1, 0.03 mMolar.

The cells suspensions are allowed to grow for 16 hours in a shaking water bath at 32°C. At the end of the treatment the cell are washed twice, counted at the microscope and are plated for evaluation of the presence of eventually induced mutants.

Only a sample of treated suspensions, according to the following criteria, are plated: 1. the control, 2. the highest dose treated suspension which is grown up the control, 3. a suspension which is weakly inhibited, 4. a suspension which is intermediately inhibited (see the example).

5.3. Plating procedure

0.1 ml of cells suspension containing approximatively 2-3 x 10^3 cell are inoculated in 3 ml soft agar (45°C) and poured onto a YEA petri dish (100 mm diameter). Usually 10 petri dishes per dose are plated.

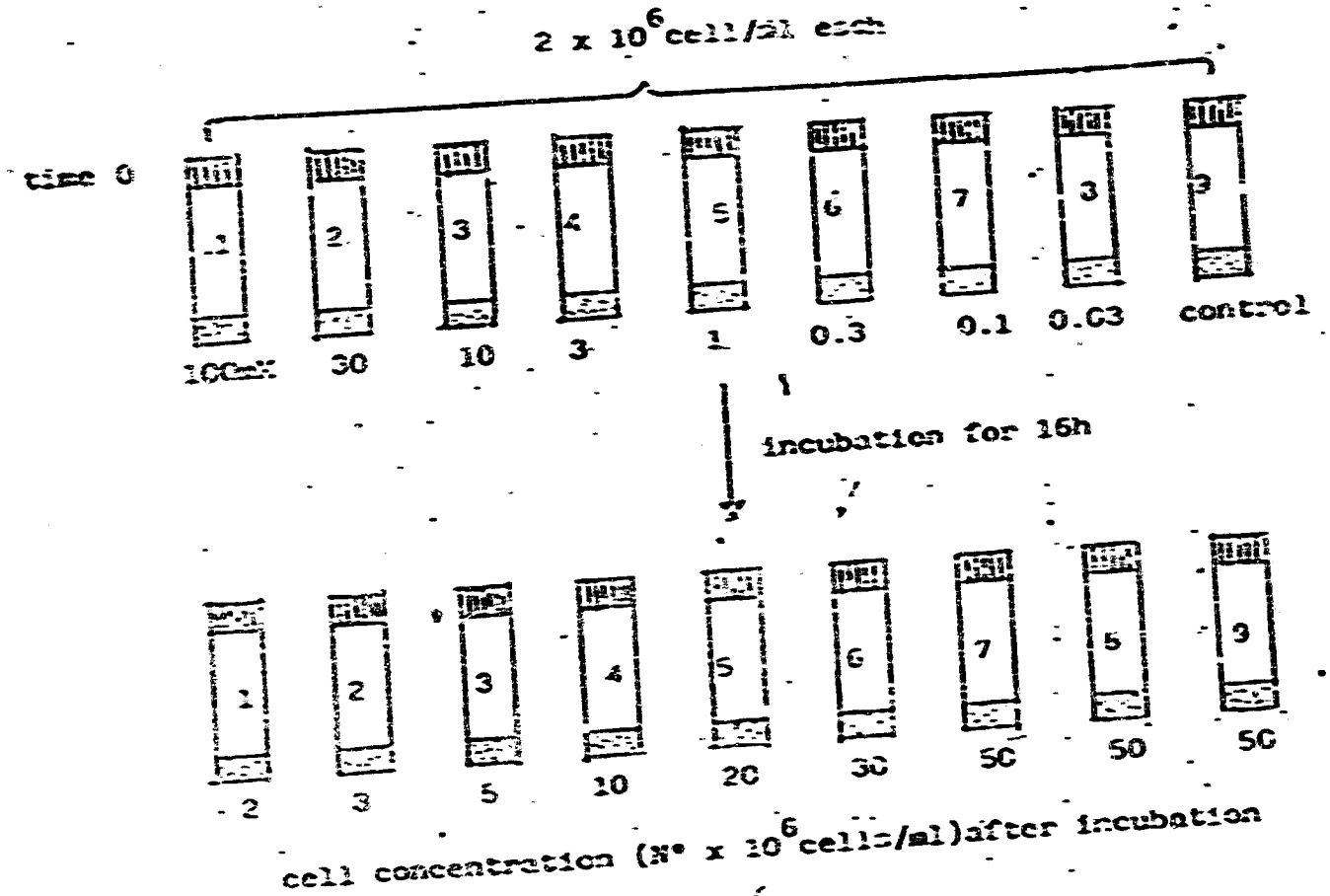
3 x 0.1 ml of the same cell suspension diluted 1 x 10^{-1} are plated with the same procedure for the population evaluation. For this the colony are allowed to grow for 5 days at 32°C; then 1-2 days at +4°C are requested to increase the pod'pigmentation of the colony.

5.4. Scoring of the Mutants

All the plated petri dishes are scored for white complete ore sectored mutant colony among the red ones.

Survival and mutants induction are scored on the same plates for each treatment series: in this case all colonies which have survived the chemical treatments are scored.

5.5. Example



For the plating are chosen tube n. 9,7,6,3

5.6. Materials

a. YEA (per liter)= glucose 30 gr, yeast extract 5 gr, Agar 15 g

b. YEL (per liter)= glucose 20 gr, yeast extract 5 gr, adenine 75 mgr

c. YELD (per liter)= glucose 40 gr, yeast extract 10 g. adenine 150 mgr

d. S-9 mix (per 10 ml)= 3 ml S-9, NADP 30 mgr, Glucose-6-P 60 mgr Glucose 6-P-Dehidrogenase 200 µl, $MgCl_2$ 400 µl from a 500 mM solution. Phosphate buffer pH 7.4 0.1 M 0.04 ml.

e. Soft agar (per liter Agar 2 gr).

f. Phosphate buffer = 0.1 M pH 7.4

METABOLIC ACTIVATION SYSTEM FOR IN VITRO EXPERIMENTS

A post-mitochondrial fraction of the liver homogenate (S-9) is used as an activation system. The procedure for its preparation is the following.

A liver is obtained from 3 rats, which have been treated five days before with i.p. injection of Aroclor 1254 at a dose of 500 mg/kg. The livers are weighed, minced, suspended in a buffer, and homogenized on ice. The homogenate is centrifuged twice (at 900 x g for 10 min. at 4°C.; at 9,000 x g for 20 min. at 4°C.). The supernatant (S-9) is decanted and it represents the post-mitochondrial fraction to be employed during the treatment.

To the S-9 preparation (0.1 ml) the following cofactors are added:

NADP	mg	3.0/ml
Glucose-6-P	"	6.0/ml
Glucose-6-P-Dehydh.	µl	20/ml
$MgCl_2$	"	40/ml

7. CHEMICAL COMPOUNDS TESTED ON *Schizosaccharomyces pombe* WITH DIFFERENT METHODOLOGIES "in vitro" AND "in vivo".

With the forward mutation system of *Saccharomyces pombe* (wild type and a more sensitive derivative strain, P_1) a certain number of chemical compounds of different nature (solid, liquid, gas) have been tested for the evaluation of their mutagenic potential. A schematic summary of the results so far obtained are reported in the following list. The quantitative data have been reported in several scientific paper since 1964; compounds 43-50 have been assayed in the Laboratoire de Génétique, University of Liege (Belgium), under the leadership of prof. J. HOUTSCHEN.

Several different methodologies have been applied in the mutation studies, including *in vitro* assays with and without metabolic activation, and *in vivo* assays, in the host mediated assay; with this latter procedure yeast cells have been inoculated into the animal via intraperitoneal, via intrasanguineous and via intragastric.

Besides the listed compounds, 20 other chemicals whose chemical formula is not yet known to us have been tested; their analysis is part of the "International Programme for the evaluation of short-term tests for Carcinogenicity" sponsored by MRC of England, ICI, and NIEHS of USA (Mutation Res. 64, 203-205, 1978).

CHEMICAL COMPOUNDS TESTED ON THE FORWARD MUTATION SYSTEM OF THE YEAST Schizosaccharomyces pombe.

1. N-METHYL-N-NITROSO URETHANE	M		
2. N-ETHYL-N-NITROSO URETHANE	M.		
3. URETHANE	inactive		
4. N-METHYL URETHANE	inactive		
5. N-ETHYL URETHANE	inactive		
6. METHYLMETHANE SULFONATE	M		
7. ISOPROPYL METHANE SULFONATE	M		
8. ETHYLMETHANE SULFONATE	M		
9. ETHYLENEIMINE	M		
10. DIETHYL SULFATE	M		
11. DI-EPOXYBUTANE	M		
12. N-NITROSO-N-METHYL-N-NITROGUANIDINE	M		
13. HYDROXYLAMINE	M		
14. NITROUS ACID	M		
15. CAFFEINE	inactive		
16. VINYL CHLORIDE	M	ma	hma
17. CHLOROETHYLENE OXIDE	M		
18. CHLORO ACETALDEHYDE	inactive	ma	hma
19. CHLORO ETHANOL	inactive	ma	
20. STYRENE	(M)		hma
21. STYRENE OXIDE	M		hma
22. CHROMATE	M		
23. MERCURY CHLORIDE	M		

24. DIMETHYL NITROSO AMINE	M	ma	hma
25. TRICHLORO ETHYLENE	inactive	ma	hma
26. EPOXY-1,1,2-TRICLOROETHANE	M		
27. 1,4-DICHLORO BUTENE-2	M		
28. 1,4-DICHLORO BUTENE-2,3-EPOXIDE	M		
29. 2,4-DIAMINO ANISOLE	M	ma	
30. CARMINIC ACID	inactive	ma	hma
31. CYCLOPHOSPHAMIDE	M	"	hma
32. MIYOMYCIN C	M		
33. DIMETHYLSULFOXIDE	inactive	ma	
34. METHANOL	inactive	ma	
35. ETHYLENE GLYCOL	inactive	ma	
36. 2-METHOXY ETHANOL	inactive	ma	
37. 2-PROPANONE	inactive	ma	
38. HYCANTONE	M		
39. PRAZIQUANTEL	inactive	ma	hma
40. DIFLUOROCHLORO METHANE	inactive	ma	hma
41. TRIIODIO-ISO FTALDIAMIDE	inactive	ma	hma
42. ICR-170	M		
43. PARAXON	M	ma	(-)
44. DICHLORVOS	M	ma	(-)
45. TRICHLORFON	M	ma	(-)
46. FENITLTRATHION	M		
47. ETHYLAZINPHOS	M		

48. METHYLAZINPHOS	M		
49. METHYL PARATHION	M		
50. ETHYL PARATHION	inactive		
51. DIMETHOATE	M		
52. METHYL BROMOPHOS	M		
53. ETHYL BROMOPHOS	inactive		
54. MALATHION	inactive		
55. TRIMETHYL-PHOSPHATE	M		
56. TRIETHYL-PHOSPHATE	M		
57. AMRAZINE	M	ma	hma
58. EPICHLORHYDRINE	M		hma
59. METHYLUREA	inactive		hma
60. NITROUS ACID + METHYLUREA	M		hma
61. AMINOPYRINE	inactive		hma
62. NITROUS ACID + AMINOPYRINE	M		hma
63. DIMETHYLAMINE	inactive		hma
64. NITROUS ACID + DIMETHYLAMINE	M		hma
65. 1,1,1 TRICHLOROETHANE	inactive		hma
66. 2-[p-(1-OXO-2-ISOINDOLINYL)-PHENYL] BUTYRIC ACID			
67. 3-METHYL-PIRAZIN-2-CARBOXILIC-4-OXIDE ACID			
68. UV LIGHT	M		
69. X RAYS	M		
70. SPONTANEOUS	M	ma	hma
71. CYCLOHEXANONE	inactive		hma

+ 20 other compounds

M = mutagenic ma = in vitro: metabolic activation

hma = in vivo: host mediated assay

6. RESULTS

In the following tables and figs. the results so far obtained in the several performed experiments are reported; the composition of chemical's samples employed in the mutagenic analysis is also included.

TABLE 1

CONTAMINANTS OF A TECHNICAL GRADE SAMPLE OF TRICHLOROETHYLENE MONTEDISON EMPLOYED IN MUTAGENICITY TEST

Compound	% w/w
TRICHLOROETHYLENE	99
1,2-EPOXYBUTANE	0.10
ETHYLACETATE	0.04
DICHLOROHYDRIN	0.09
N-METHYL PYRROLE	0.02
DI-ISOBUTYLENE	0.03

TABLE 2.

MUTAGENICITY OF TCE TECHNICAL GRADE ON Drosophila BY MEANS OF THE HOST MEDIATED ASSAY ON BDF1 HYBRID MICE (16 HOURS OF INCUBATION)

Treatment	Dose mg/kg	Animal n°	Forward n°	Mutants M.F.x10^{-4}	M ± S.E.
NONE	-	1	5/56400	0.88	
"	-	2	6/72100	0.83	0.84±0.08
"	-	3	8/72040	1.10	
TCE	500	1	12/6660	1.80	
"	"	2	12/108240	1.11	1.33±0.25
"	"	3	7/39380	1.77	
"	"	4	6/90300	0.66	
TCE	1,000	1	5/58680	0.85	
"	"	2	5/60210	0.80	1.32±0.19
"	"	3	10/76230	1.09	
"	"	4	6/41200	1.46	
TCE	2,000	1	1/20200	0.50	
"	"	2	8/39700	2.09	1.61±0.42
"	"	3	12/83330	1.44	
"	"	4	3/16700	1.80	
MMS	50	1	15/28700	5.22	4.16±0.54
"	"	2	21/64300	3.06	
"	"	3	18/52700	3.41	

Regression analysis (x=mg/kg; y=F.M.x10^{-4})

$y = 1.0370 + 0.0008096x \quad r = 0.86396^{**}$

TABLE 2

MUTAGENICITY OF TCE TECHNICAL GRADE ON *S.typhimurium* BY MEANS OF THE HOST MEDIATED ASSAY ON B6C3F1 HYBRID MICE (16 HOURS OF INCUBATION)

Treatment	Dose mg/kg	Animal n°	Forward n°	Mutants M.F.x10^{-4}	M ± S.E.
NONE	-	1	5/50400	0.00	
"	-	2	6/72100	0.83	0.04±0.08
"	-	3	8/72540	1.10	
TCE	500	1	12/6080	1.80	
"	"	2	12/108240	1.11	1.33±0.25
"	"	3	7/39380	1.77	
"	"	4	6/90700	0.66	
TCE	1,000	1	5/50680	0.85	
"	"	2	5/60210	0.80	1.32±0.19
"	"	3	16/76230	2.09	
"	"	4	6/41200	1.46	
TCE	2,000	1	1/20200	0.50	
"	"	2	8/39700	2.09	1.61±0.[illegible]
"	"	3	12/83330	1.44	
"	"	4	3/15700	1.00	
MMS	50	1	15/28700	5.22	4.16±0.[illegible]
"	"	2	21/54300	3.86	
"	"	3	18/52700	3.41	

Regression analysis (x=mg/kg; y=F.M.x10^{-4})

$y = 1.0370 + 0.0002092x \quad r = 0.86390^{**}$

TABLE 3

CONTAMINANTS OF A PURE GRADE SAMPLE OF TRICHLOROETHYLENE MONTEDISON EMPLOYED IN MUTAGENICITY TESTS

Compound	% w/w
TRICHLOROETHYLENE	99.00
CLOROFORM	10 ppm
CARBON TETRACHLORIDE	17 "
1,1,2-TRICHLOROETHANE	21 "
1,1,2,2-TETRACHLOROETHANE	14 "
OTHER CONTAMINANTS	16 "

p-Tert. BUTHYLCATECHOL used as a stabilizer.

TABLE 4

MUTAGENICITY OF A PURE GRADE SAMPLE OF TCE ON S.pombe BY MEANS OF THE HOST MEDIATED ASSAY ON B6C3F1 HYBRID MICE

Treatment	Dose mg/kg	Incubation hours	Animal n°	Forward mutants n°	M.F.x10-4	M±S.E
NONE (*)	"	3	1	3/46530	0.60	
"	-	"	2	1/39716	0.25	0.80±0.39
"	-	"	3	5/32140	1.55	
NONE (*)	-	6	1	3/39318	0.76	
"	-	"	2	2/37600	0.53	0.74±0.13
"	-	"	3	3/30435	0.99	
NONE (*)	-	16	1	8/18450	2.10	
"	-	"	2	6/29017	2.00	1.85±0.60
"	-	"	3	1/39716	0.25	
TCE	1,000	16	1	6/55200	1.08	
"	"	"	2	7/36655	1.90	1.59±0.22
"	"	"	3	3/14900	2.00	
"	"	"	4	3/22045	1.36	
TCE	3,000	3	1	4/67600	0.60	
"	"	"	2	2/34020	0.59	0.84±0.20
"	"	"	3	3/24500	1.23	
TCE	3,000	6	1	1/22750	0.29	
"	"	"	2	1/34506	0.28	0.44±0.16
"	"	"	3	3/33060	0.75	
TCE	2,000	16	1	4/27200	1.47	
"	"	"	2	3/31010	0.95	1.36±0.21
"	"	"	3	5/29930	1.67	[illegible]

continua

DMHA	100	16	1	102/40102	20.70	
"	"	"	2	45/23544	19.20	18.73±3.24
"	"	"	3	47/46291	10.30	

(*) AVERAGE CONTROL 1.055 ± 0.22

<u>Regression analysis</u> (x = mg/kg y = P.M. x 10^{-4})

y = 1.5177 - 0.00004608x r = 0.368 (NS)

TCE PURE GRADE SAMPLE

TRICHLOETHYLENE	99.88	%
CHLOROFORM	10	ppm
CARBON TETRACHLORIDE	17	"
1,1,2-TRICHLOROETHANE	21	"
1,1,2,2-TETRACHLOROETHANE	14	"
OTHER CONTAMINANTS	16	"

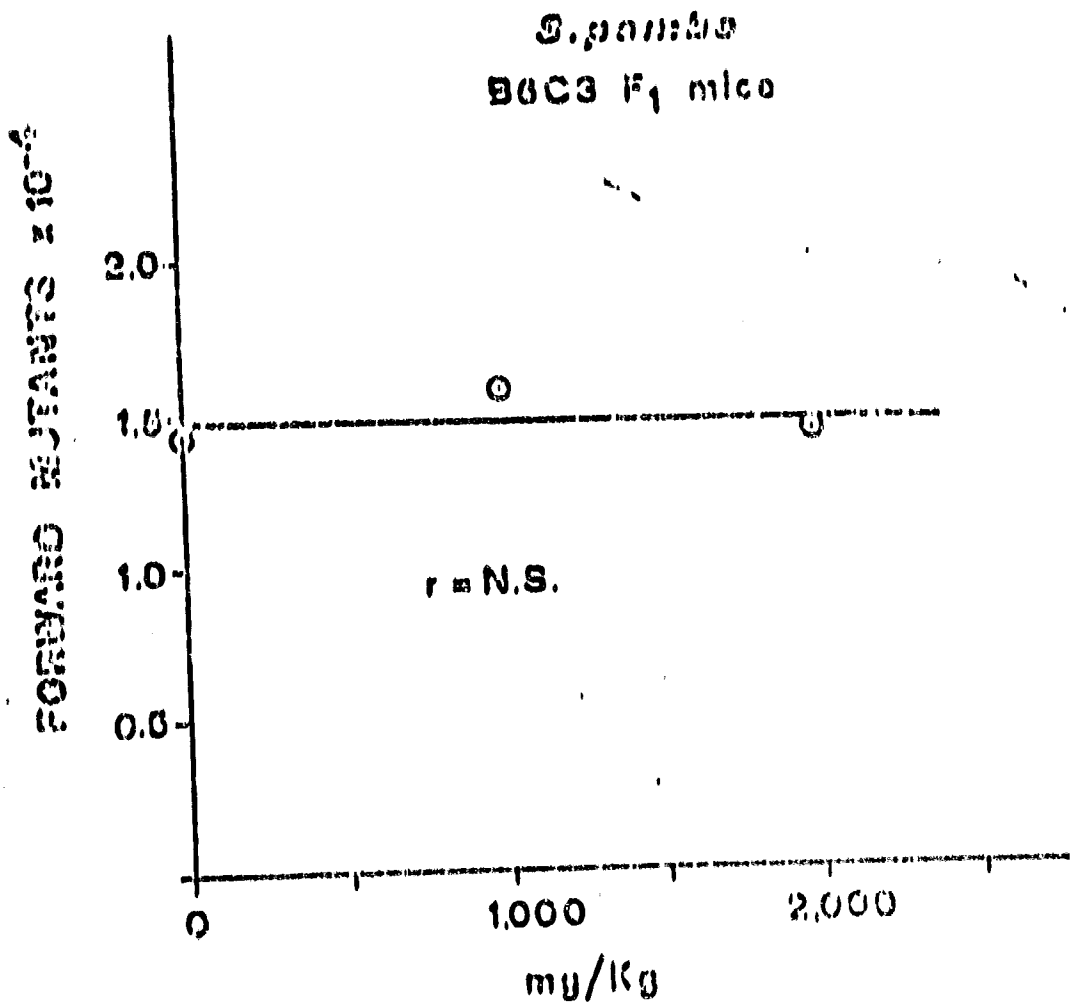


FIG. 2

TCE PURE GRADE SAMPLE

TRICHLOROETHYLENE	99.98	%
CHLOROFORM	10	ppm
CARBON TETRACHLORIDE	17	"
1,1,2,-TRICHLOROETHANE	21	"
1,1,2,2-TETRACHLOROETHANE	14	"
OTHER CONTAMINANTS	16	"

S. pombe

BDC3 F1 mice

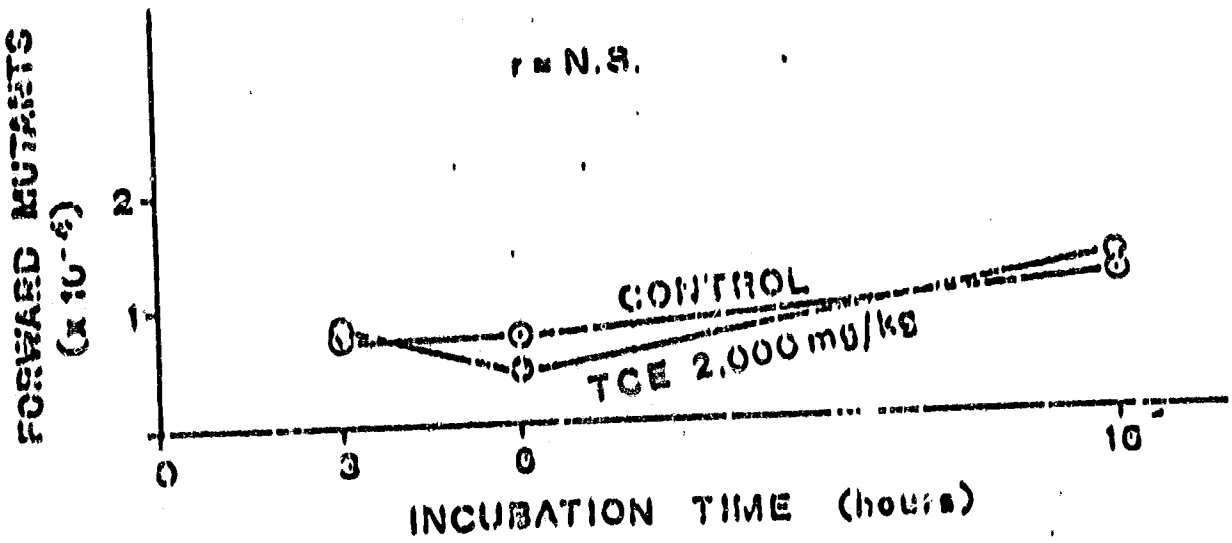


FIG. 3

TABLE 5

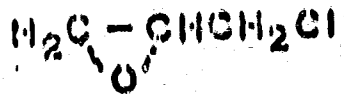
MUTAGENICITY OF EPICHLORONYDRIN ON *S.pombe* BY MEANS OF AN *in vitro* ASSAY (16 HOURS OF INCUBATION).

Treatment	Dose mM	Survival %	Forward mutants n°	M.F.x10^{-4}
NONE	-	100	3/16461	1.82
EPC	0.25	88.9	8/17328	4.62
"	0.50	119.0	14/15156	9.24
"	1.00	58.4	17/7160	23.72
"	2.00	12.0	5/1584	31.56

Regression analysis (x = mM; y = M.F. x 10^{-4})

$y = 2.37 + 15.76x \quad r = 0.938^{***}$

EPICHLOROHYDRIN



S.pombe

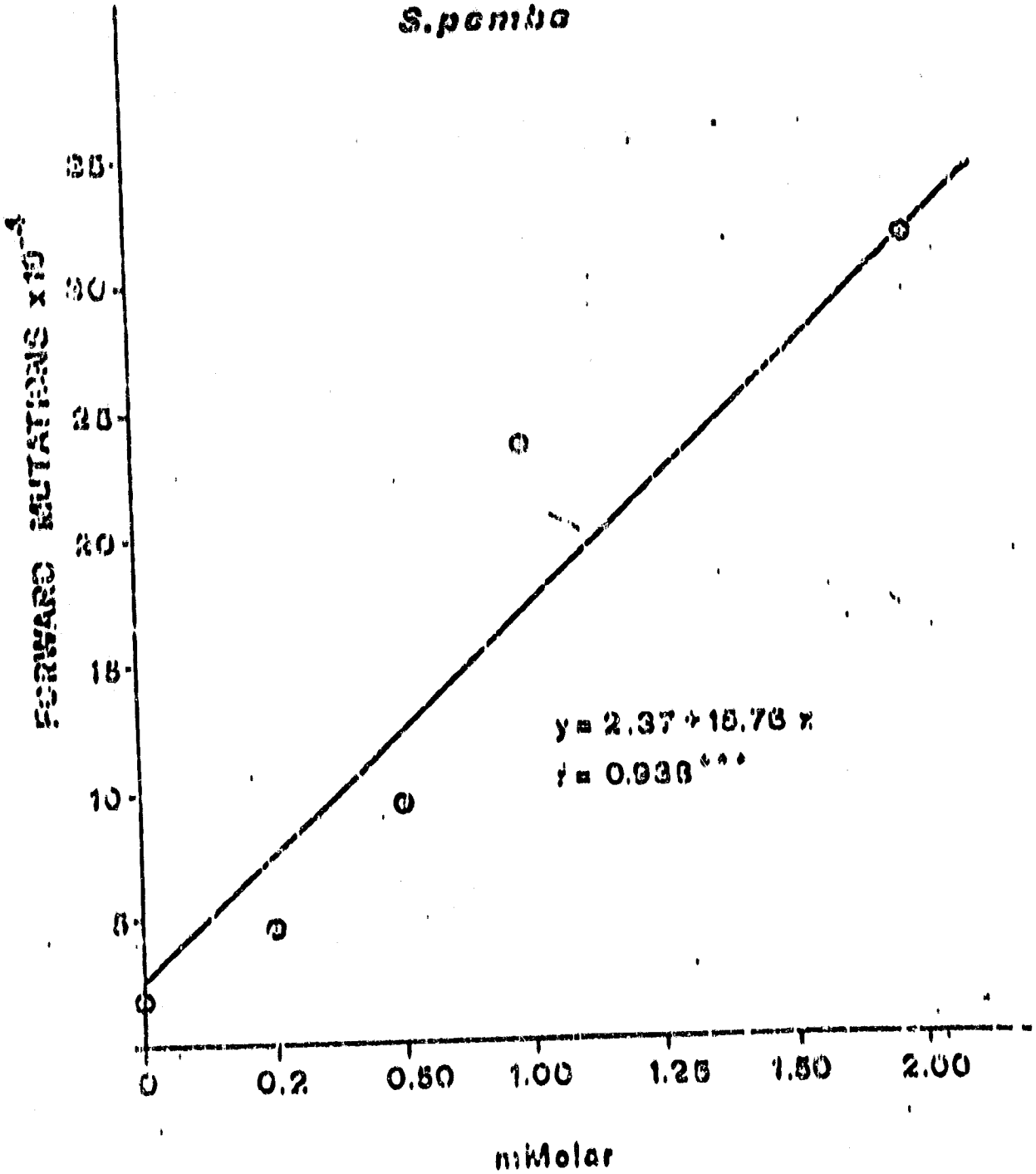


FIG. 4

TABLE 6

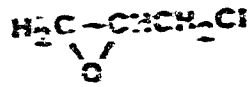
MUTAGENICITY OF EPICHLOROHYDRIN ON *S.pombe* BY MEANS OF THE HOST MEDIATED ASSAY ON B6C3F1 HYBRID MICE
(16 HOURS OF INCUBATION)

Treatment	Dose mg/kg	Animal n°	Forward Mutants n°	M.F.x10^{-4}	M±S.E.
NONE	-	1	26/135680	1.91	
"	-	2	34/100256	1.79	1.68±0.30
"	-	3	42/311520	1.34	
EPC	2	1	24/767390	0.31	
"	"	2	96/630000	1.64	1.50±1.20
"	"	3	50/680000	1.00	
"	"	4	53/160000	3.14	
EPC	10	1	47/217010	2.15	
"	"	2	40/269050	1.48	2.05±0.51
"	"	3	39/155232	2.51	
EPC	50	1	31/114576	2.70	
"	"	2	29/79772	3.63	3.71±1.05
"	"	3	35/72890	4.80	

Regression analysis (x = mg/kg; y = M.F. x 10^{-4})

$y = 1.35 + 0.0747x$ $r = 0.99^{***}$

EPICHLOROHYDRIN



S.pombe

SGCD F_1 mice

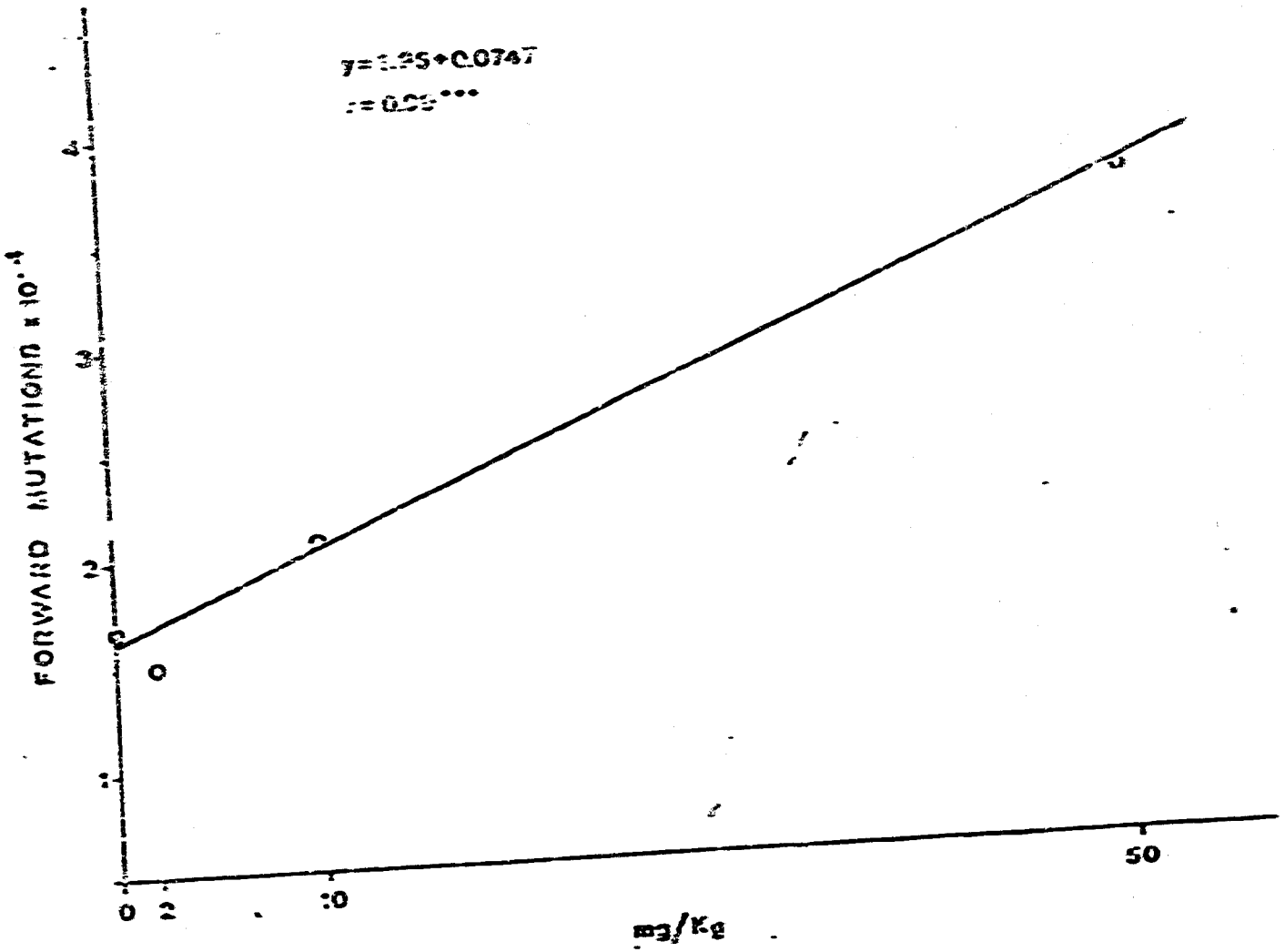


Fig. 5

TABLE 7

SUMMARY OF MUTAGENICITY DATA OF TCE SAMPLES EVALUATED FOR THE EPICHLOROHYDRINE CONTENT

Treatment		Regression analysis	Specific mutag. activity mg/kg
TCE (distilled sample)		y = 1.51 - 0.000965x	N.S.
TCE (technical sample)			
	TCE	y = 1.037 + 0.00299x	0.000299
	EPC	y = 1.038 + 0.0337x	0.0377
EPICHLOROHYDRIN		y = 1.05 + 0.0747x	0.0747

Test: FORWARD MUTATIONS
YEAST (*S. pombe*) + [illegible]

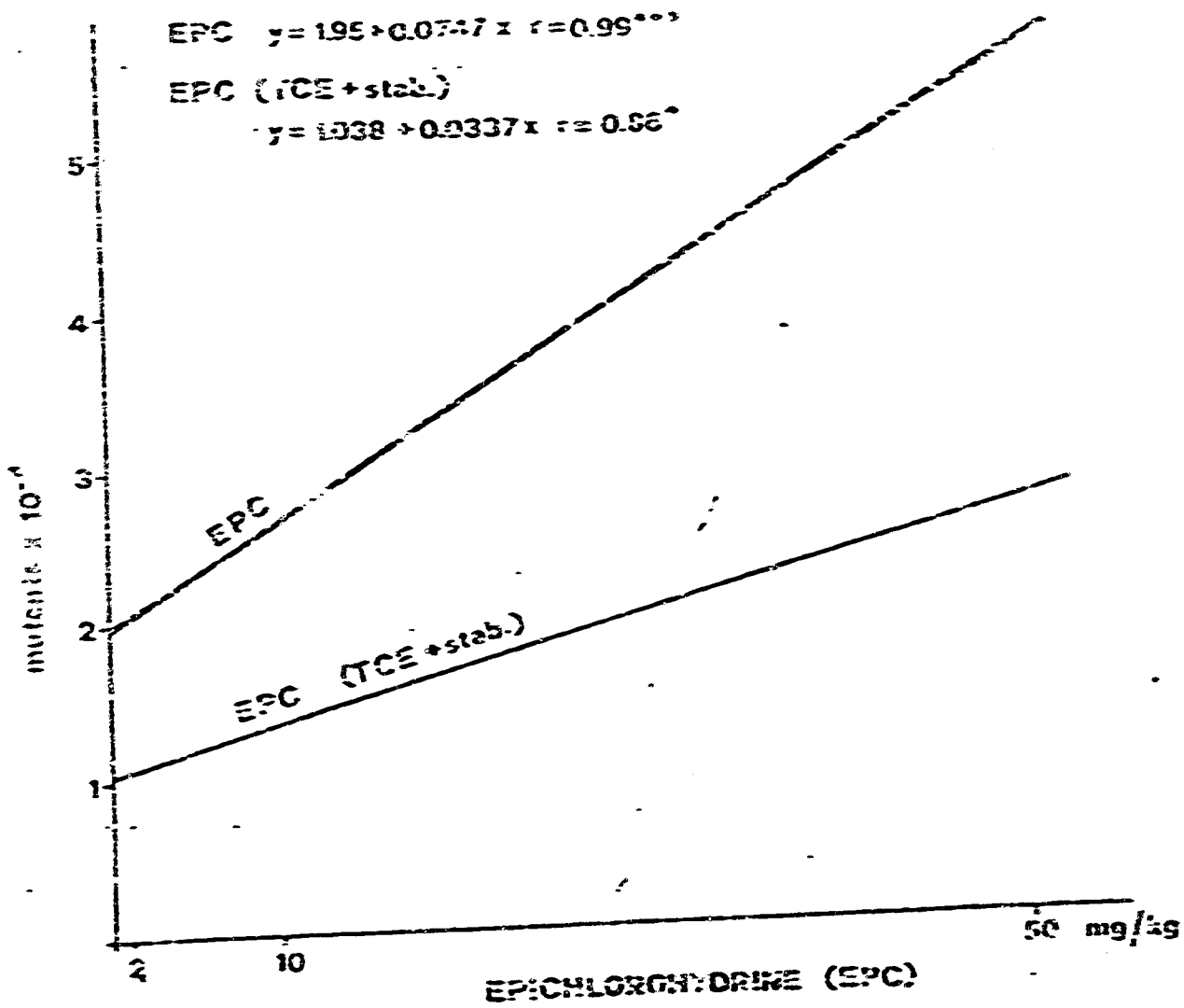


Fig. 6

TABLE 8

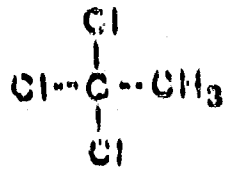
MUTAGENICITY OF 1,1,1-TRICHLOROETHANE ON S.DOMBE BY MEANS OF THE HOST MEDIATED ASSAY ON BDC3F1 HYBRID MICE

TREATMENT mg/kg	Ina.time (hours)	DOSE mg/kg	ANIMAL n°	FORWARD MUTANTS n°	M.F.x10^{-4}	M±S.E.
NONE	3h	-	1	3/36530	0.40	
"		-	2	1/39716	0.25	0.80±0.39
"		-	3	5/32140	1.55	
NONE	6h	-	1	3/39312	0.76	
"		-	2	2/37906	0.53	0.76±0.13
"		-	3	3/30435	0.99	
NONE	16h	-	1	4/18450	2.10	
"		-	2	6/29017	2.00	1.45±0.60
"		-	3	1/39716	0.25	
1,1,1-TCE	3h	5,000	1	1/20913	0.47	
"		"	2	1/29422	0.33	0.27±0.14
"		"	3	0/32479	-	
1,1,1-TCE	6h	5,000	1	6/48253	1.24	
"		"	2	2/33783	0.57	0.70±0.28
"		"	3	1/32755	0.30	
1,1,1-TCE	16h	5,000	1	4/37883	1.05	
"		"	2	7/69365	1.00	0.97±0.05
"		"	3	5/53320	0.85	

Regression analysis (x= h, y=F.M.x10^{-4})

y = 0.642 + 0.0149 r = 0.35 (NS)

1,1,1-TRICHLOROETHANE



S. pomba

B6C3 F_1 mice

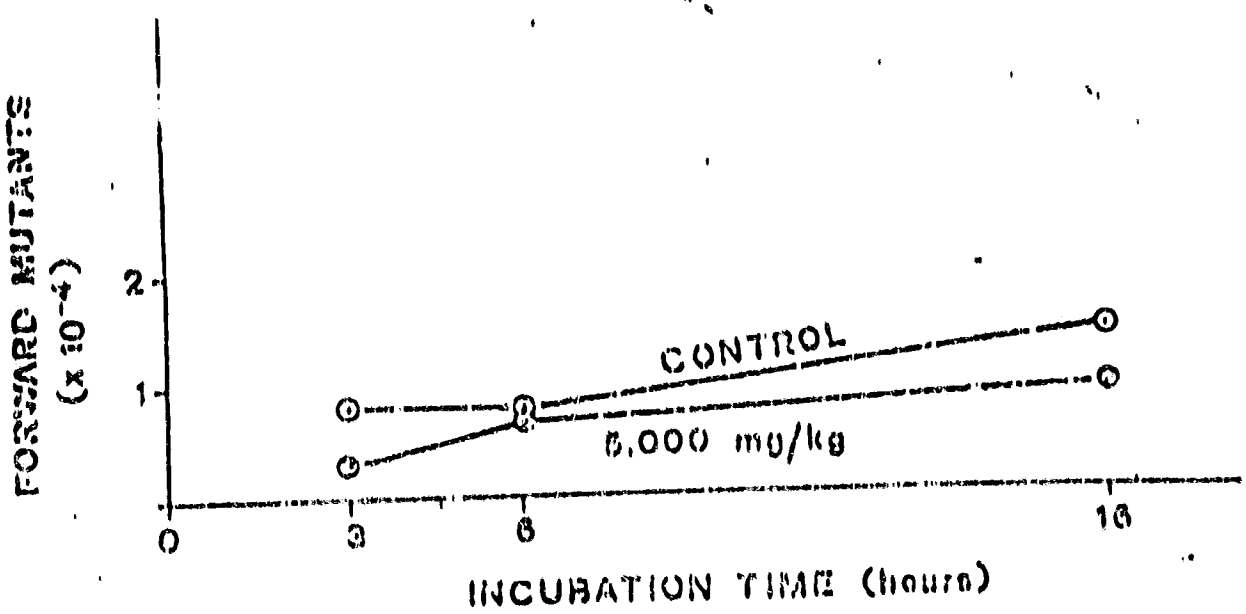


FIG. 7

TABLE 9

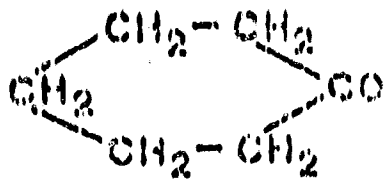
MUTAGENICITY OF CYCLOHEXANONE ON S.pombe BY MEANS OF THE HOST MEDIATED ASSAY ON B6C3F1 HYBRID MICE (INCUBATION TIME: 16 HOURS).

TREATMENT	DOSE mg/kg	ANIMAL n°	FORWARD MUTANTS n°	M.F.x10^{-4}	M±S.E.
NONE	-	1	2/66000	0.30	
"	-	2	3/68480	0.43	0.47±0.19
"	-	3	4/69500	0.60	
CYCL.	300	1	3/58400	0.51	
"	"	2	3/64000	0.46	0.46±0.05
"	"	3	2/48000	0.41	
CYCL.	600	1	2/50720	0.39	
"	"	2	3/71040	0.42	0.42±0.03
"	"	3	2/42880	0.46	
CYCL.	1,200	1	3/55360	0.54	
"	"	2	2/55500	0.36	0.42±0.10
"	"	3	2/54400	0.36	

Regression analysis (x= mg/kg y= F.M.x10^{-4})

$y = 0.486 + 0.000044x$ r = 0.87 (NS)

CYLOHEXANONE



S. pombe

B6C3F1 mice

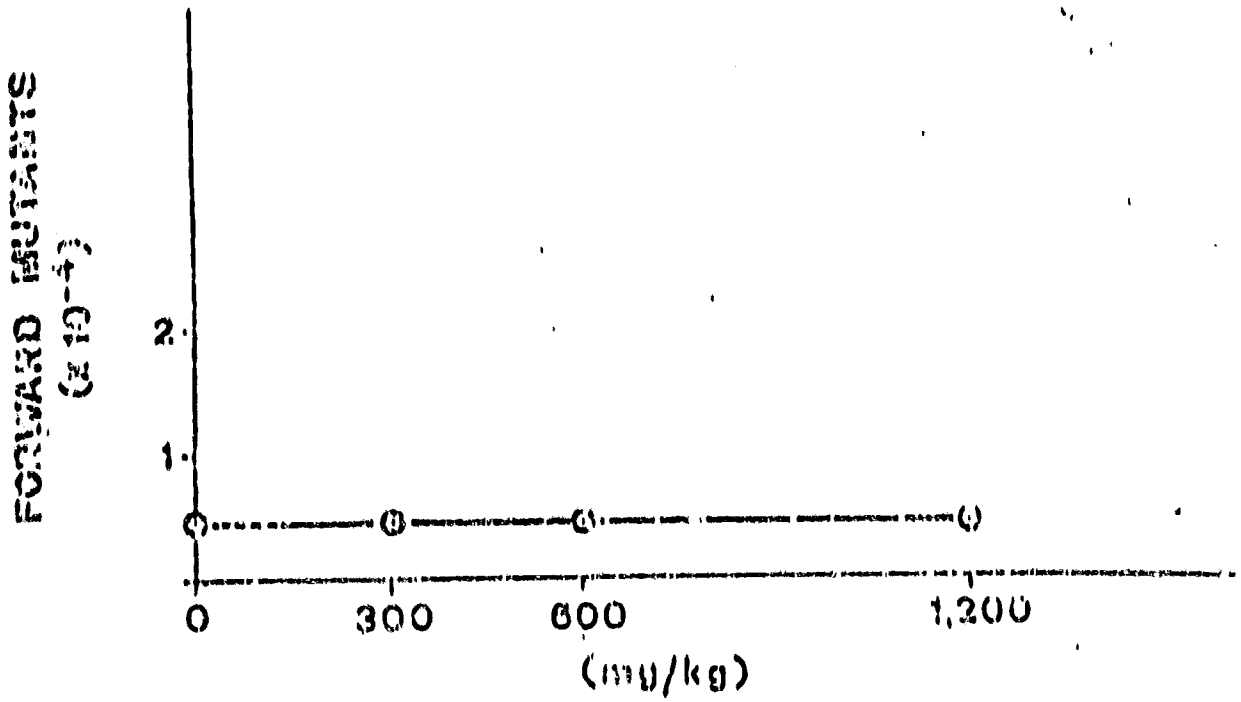


FIG. 8

8. DISCUSSION

On the basis of our studies, it seems reasonable to conclude that the carcinogenic effect described in the NCI's experiments might be due to the presence of epichlorohydrine, on the basis of mutagenic experiments presented in this paper.

In Table 10 the results of many mutagenic studies so far published for TCE are reported: in the majority of these studies no indications were included to the actual composition of samples employed in the analysis: at the present is is not possible to draw some conclusion on the possible mutagen activity of trichloroethylene (4).

In the experimental conditions employed in the present study other solvents, such as 1,1,1-trichloroethane and cyclohexanone have resulted negative.

It is therefore of extreme urgency to develop more appropriate methodological studies with trichloroethylene of known chemical composition in different mutational assays.

TABLE 10

RESULTS OF MUTAGENICITY SHORT-TERM STUDIES DEVELOPED ON UNOPPI-FIED TGE SAMPLES (*)

Organism	Technique	Results
1. *Salmonella typhimurium*	in vitro	+
2. *Escherichia coli*	in vitro	+
3. *Schizosaccharomyces pombe*	in vitro	-
	h.m.a. (mice)	+
	h.m.a. (rats)	-
4. *Saccharomyces cerevisiae*	in vitro	+
	h.m.a. (mice)	+
	h.m.a. (rats)	+
5. Chinese hamster	in vitro	-
6. *Drosophila melanogaster*	in vivo	+
7. Mouse (bone marrow)	in vivo	-
8. Hamster (bone marrow)	in vivo	-
9. Mouse (Somatic mutation)	in vivo	+
10. *Tradescantia* (Somatic mutation)	in vivo	+

8782/1394

10. REFERENCES

1. National Cancer Institute, NCI-CG-RT-Z, 1976.
2. D. DEHSCHLER et al.: Arch. Toxicol. 37, 233-236, 1977.
3. E.V. DONAHUE et al.: Cancer Res. 38, 431-439, 1978.
4. H. LOPRIENO: Comments on results of mutagenic analyses of TCE (unpublished).

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METHYLCHLOROFORM SUMMARY OF CURRENT RESEARCH (1980) PREPARED BY DEPT OF ENVIR SCIENCE OR GRADUATE CTR

Chemical Name (300 per name)	25	CAS No. (10)	26
METHYLCHLOROFORM		71-55-6	

5/31/83

1A

D-482

87821/1395

METHYLCHLOROFORM:

SUMMARY OF CURRENT RESEARCH (1980)

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RECEIVED

(February 1981)

CONTENTS

I. Measurement Program

II. Results

III. Appendices

(a) Table 1. CH_3CCl_3 Concentrations at Alaska, Hawaii, Samoa and Oregon from August 1979 through December 1980.

(b) Global atmospheric distribution and trend of methylchloroform (CH_3CCl_3).

(c) Decline in atmospheric accumulation rates of CCl_3F (F-11, CCl_2F_2 (F-12) and CH_3CCl_3.

I. Measurement Program

The overall objective of this study was to determine the lifetime of methylchloroform in the atmosphere. In order to do this, the work effort was divided into four areas: (1) measurements of CH_3CCl_3 in air samples collected routinely at remote sites in Alaska, the Pacific Northwest, Hawaii and Samoa; (2) further continuation of actively intercalibrating for CH_3CCl_3 between different laboratories; (3) preparation of a new absolute calibration standard; and (4) modeling and interpretative examination of the data obtained in this and related relevant studies. While further fine tuning of the correctness of the absolute value for CH_3CCl_3 in our standards is essential to this work, the most critical need was for a more accurate determination of the global burden of CH_3CCl_3. Accordingly, in the results section the discovery that previous latitudinal profiles of CH_3CCl_3 overestimated the burden and therefore gave a longer lifetime is discussed. Obtaining the needed latitudinal data on CH_3CCl_3's concentration distribution is by nature a painstakingly slow process. In order to determine the lifetime of CH_3CCl_3 we need as long a time series of measurements at our stations as is possible. Therefore, based on the data obtained to the present, our conclusions of the lifetime of CH_3CCl_3 must be viewed as tentative.

Work Accomplished

(1) Precision of analysis for CH_3CCl_3 at 150 pptv is ±1%. Method of analysis is standardized using a PE3920B-EC/GC and an HP3393-A reporting integrator. Conditions of analysis: 10-ft x 1/4-inch SS column packed

with 10% SP2100, Ar/CH_4 (5%) 60 mL/min, oven 69°C, ECD 350°C, sample size 5 mL. Representative analysis shown in Figure 1.

(2) Air sampling protocol of collecting triplicate samples in 800 mL SS cans internally electropolished to passivate the surface for maximum stability of CH_3CCl_3 has given excellent performance. Percent standard deviation for a given set of triplicate air samples is typically less than 2% at the 150 pptv level. No wall adsorption problems for CH_3CCl_3 have been observed for periods as long as 3 months.

(3) The number of samples collected and analysed are:

Station	Effective Dates	Number of Sample Weeks
Alaska	08/27/79 to 12/29/80	65
Hawaii	11/25/79 to 12/30/80	31
Samoa	12/20/79 to 12/20/80	33
Cape Meares, OR	01/19/79 to 12/31/80	Continuous
Newfoundland*	08/01/80 to 12/30/80	15
Barrow, AL*	08/11/80 to 12/29/80	20

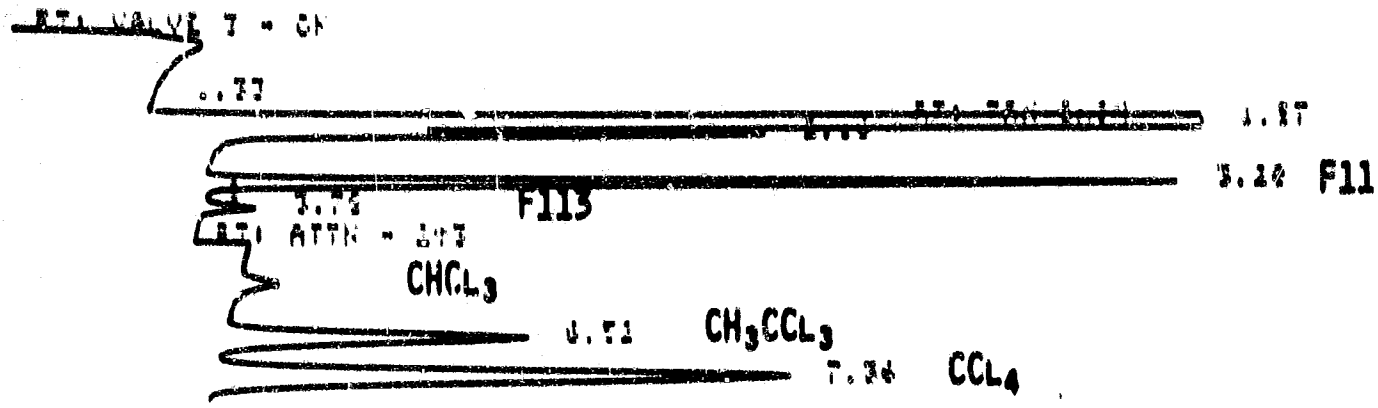
* Supplementary sites used to confirm CH_3CCl_3 data obtained at primary stations. The results of the analyses for Alaska, Hawaii, Samoa and Oregon from August 1979 through December 1980 are in Table 1 in the Appendix.

(4) The number of laboratories making atmospheric CH_3CCl_3 measurements is considerably less than the number measuring F-11 and F-12. Accordingly, the results from the present intercomparison of CH_3CCl_3 is not much different from those obtained from previous interlaboratory calibrations, i.e., ±15% about our submited values. Further efforts are being made to have all the participants return their results and the samples. The data

will be analyzed at that time and compared with the results obtained in the previous comparisons.

(5) The preparation of two sets of CH_3CCl_3 standards at ambient concentrations of ~150 pptv have confirmed earlier experiments that indicate our long term primary CH_3CCl_3 standard is ~2-4% high. These results are also consistent with a 2-4% drift identified in the low pressure standards used in 1976-1977. Further work is in progress to validate these new data before the value of our long term primary standard is adjusted. The amount of correction is not viewed as being very significant.

DIRECT ANALYSIS EC/GC, 5 ML AIR SAMPLE SP2100, 10%, 10 FT X ¼ INCH COLUMN @ 69°C.



EH-3 3311A MANUAL INJECTION @ 09:16 SEP 21, 1980
AREA %

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0.00			THRESHOLD @ START RUN = 0			
0.00			PEAK WIDTH @ START RUN = 0.14			
0.00			RPI REJECT - 1E-00			
1.87			RPI REJECT - 0			
1.88			RTI TAN SKIM			
2.14	508.34	BB	-----	89.61	541.03	12.166
3.10	1974.70	BB	0.156	213.62	509.34	44.435
3.79	110.57	BB	0.156	11.12	507.01	2.646
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7.36	1157.04	A BF	-----	63.06	502.40	27.640

TOTAL AREA = 4178.47
MULTIPLIER = 1

FIGURE 1

II. Results

(a) General discussion.

The main results of the flask sampling program are described in two papers attached to this report (R. A. Rasmussen & M. A. K. Khalil, 1981, "Global atmospheric distribution and trend of methylchloroform (CH_3CCl_3)" submitted to Geophysical Research Letters; M. A. K. Khalil & R. A. Rasmussen, 1981, "Decline in the atmospheric accumulation rates of CCl_3F (F-11), CCl_2F_2 (F-12) and CH_3CCl_3" submitted to Science.)

The data base is still too short to yield precise information on the lifetime and behavior of CH_3CCl_3 in the atmosphere. Furthermore, the "grab" sampling procedure emphasizes the atmospheric variability resulting in broad confidence bands for the calculated trends and lifetimes. Nevertheless, several new results have emerged from the previous year's work.

Perhaps the most significant result from the data obtained by flask sampling is that the global burden of CH_3CCl_3 may have been overestimated because of insufficient information on the latitudinal variation of CH_3CCl_3 which would lead to an overestimate of the lifetime based on a global mass balance model.

Past data had suggested that the latitudinal variation of CH_3CCl_3 could be represented by a constant between 30°N to 90°N and 30°S to 90°S with a linear decline with latitude in between (see Singh et al., Science 203, 900 (1978); Makide & Rowland, ACS Conference, Hawaii (1979)). Since a long time series of data was available only at 45°N (Pacific Northwest) and the south pole (Rasmussen et al., Science 211, 286 (1981)), it was used by Chang and Penner (Atm. Env. 12, 1867 (1978)) and others to calculate the

the global burden. The current flask sampling data from Cape Kumakahi, Hawaii (~24°N), suggest that there may be a faster drop off in CH_3CCl_3 concentrations with latitude, thus implying a smaller global burden. This point is represented in Figure 2 below where the solid line is the newly determined profile and the dashed line (—— - —— -) is the profile used in the past. The new profile gives a CH_3CCl_3 global burden of about 3% less than the previous profile.

It is not yet clear whether this is a real feature, seasonal effect, or an anomaly at the site's longitude. It is, therefore, apparent that the Cape Kumakahi site is extremely important to establish the global burden. More than half the earth's atmosphere lies between 30°N and 30°S latitudes and this region is also most active in terms of both transport and chemistry (HO density) relevant to CH_3CCl_3. An additional station between the Hawaii and Tasmania sites is strongly recommended to obtain an accurate estimate of the latitudinal variations in this important region of the atmosphere. We believe that Majuro on the Marshall Islands at ~7°N (172°E) would be the most suitable site since it has a U.S. postal station and other facilities necessary for a flask sampling site.

(b) Review of sites.

The entire network, supported by various projects, is as follows:

(i) Arctic (~70°N): Poker Flats and Pt. Barrow, Alaska: CH_3CCl_3 measurements have been consistent between the two sites, giving concentrations slightly less than at Cape Meares, Oregon. The trends and data are discussed elsewhere in this report.

(ii) Cape Meares (45°N): The longest time series is available from here, and the results are discussed in the appendices and data section.

(iii) St. John's, Newfoundland (48°N): This site is necessary to check how representative the Cape Meares site is for the mid northern latitudes. So far the data base from St. John's shows no difference from Cape Meares measurements. The site is, however, very recent, and we have had some problems with "pollution episodes". We are currently trying to find a more remote site on Newfoundland.

(iv) Cape Kumakahi, Hawaii (24°N): The short data base accumulated so far has provided the dip in concentrations discussed earlier. The significance of this site is connected with the measurement of the CH_3CCl_3 latidudinal profile in the important and large region of the atmosphere between the tropics.

(v) Majuro, Marshall Islands (7°N): This new site is recommended for the reasons discussed in Section (a).

(vi) Samoa (~14°S): See (iv) above.

(vii) Tasmania (42°S): This site is the counterpart of Cape Meares in the northern hemisphere, representing mid southern latitudes.

(viii) South Pole (90°S): This is the cleanest background site available, and serves to complete the latitudinal profile and to provide estimates of trends in CH_3CCl_3 concentrations far from sources.

Each of these eight sites serves a unique purpose. The continued measurements of air from these sites will resolve the many uncertainties that still remain in the estimates of the lifetime of CH_3CCl_3 and its transport throughout the earth's atmosphere.

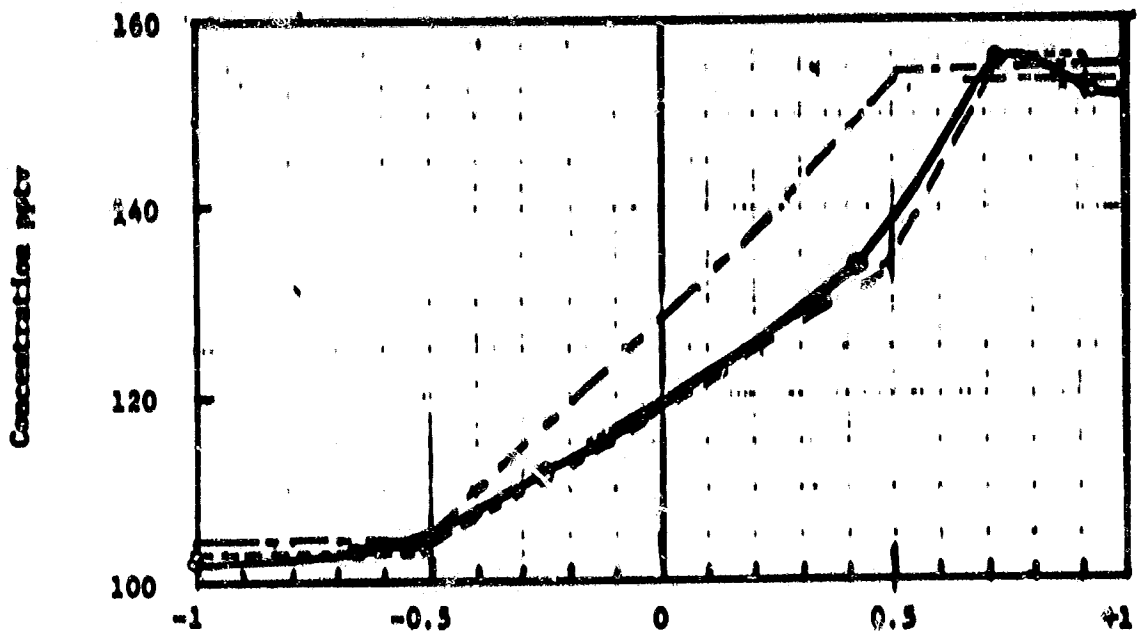

Figure 2. Latitudinal variation of CH_3CCl_3

•———• smoothed profile through data points.

—— – —— profile used in previous theoretical calculations.

- - - - - new theoretical profile.

(c) Review of results.

The following results are discussed in the two papers of the appendix.

(i) The rate of accumulation of CH_3CCl_3 has declined (based on measurements during January of each year since 1975 at 45°N & 90°S).

$$(1/C)\ (dC/dt) = \beta$$

$$\beta = a + bt$$

$$\hat{b} = -1.5\ (\pm 0.9)\%\ \text{per year}\ (1/1975\text{-}1/1981)$$

$\hat{b}$ is the average decline in the accumulation rate between 1/1975 and 1/1981.

Rate of increase during 1975: 16% (yr^{-1})

Rate of increase during 1980: 5% (yr^{-1})

(ii) Rates of increase at several sites:

Alaska	8/79-1/81	3.8% per yr^{-1} ± 2.1% yr^{-1}
Cape Meares	1/79-1/81	6.6% per yr^{-1} ± 3.2% yr^{-1}
Hawaii	11/79-1/81	4.3% per yr^{-1} ± 4.0% yr^{-1}
Samoa	2/80-1/81	4.1% per yr^{-1} ± 4.6% yr^{-1}
Tasmania	1/79-6/80	11.5% per yr^{-1} ± 1.5% yr^{-1}
South Pole	1/79-1/81	8.7% per yr^{-1} ± 5.7% yr^{-1}
Global average	1/79-1/81	6.7% per yr^{-1} ± 2% yr^{-1}

(iii) Latitudinal profile shows that CH_3CCl_3 concentration decreases rapidly beyond 45°N, giving an approximately 5% lower global burden than estimated by previous models.

(iv) Lifetime, τ, most consistent with a 6.7% yr^{-1} increase between 1/79 and 12/80 is 7 years (lower limit 5.5 years, upper limit 10 years).

(v) Comparison of trends determined by simulation of flask sampling method with "continuous" measurements.

Tasmania: (1/79-6/80)

Trend ("flask samples")[1]	11.5% yr^{-1} ± 1.5% yr^{-1}
Trend (continuous)[2]	10.4% yr^{-1} ± 1% yr^{-1}

± values are 90% confidence limits.

1. Based on 4 daily average concentrations per month.
2. Based on all data (every hour, every day).

No significant difference in trend was found.

(d) Review of other recent developments applicable to the behavior of CH_3CCl_3 in the atmosphere.

(i) Increase of CH_4 in the atmosphere (R. A. Rasmussen and M. A. K. Khalil, "Increase in the Concentration of Atmospheric Methane", Atmospheric Environment, in press; R. A. Rasmussen and M. A. K. Khalil, "Atmospheric Methane (CH_4): Trends and Seasonal Cycles", submitted to JGR). These papers show that at least over the past two years the continuous measurements of CH_4 made at Cape Meares suggest that CH_4 is increasing in the atmosphere at about 1.9 ± 0.5% per year. Since CH_4 can remove Cl in the stratosphere ($CH_4 + Cl \rightarrow HCl + CH_3 \rightarrow \ldots$), the ozone depletion by Cl from both natural (CH_3Cl) and man-made (F-11, F-12, CCl_4, CH_3CCl_3) sources will be moderated. According to Wang et al. (1981 - preprint), a net increase in the column O_3 density of ~3.5% would result by doubling CH_4 (which may double in ~40 years if current trends continue). On the other hand, depletion of tropospheric hydroxyl radicals by increased CH_4 could offset

some of this effect by increasing the lifetimes of CH_3Cl and CH_3CCl_3. (See also T. E. Graedel & J. E. McRae, GRL 7, 977-979 (1980)).

(ii) Effect of meteors on Cl, ClO removal from the stratosphere.

(E. Murad et al., Nature 289, 287 (1981)). These authors have suggested that metals in the stratosphere may be a sink of Cl and ClO. The metals can arise from the destruction of meteors which enter the upper atmosphere in sufficient quantities every year, as well as from high flying aircraft. Credible quantitative estimates of the effect on stratospheric ozone are not yet available.

(iii) Effect of increasing CO_2.

(K. S. Groves & A. F. Tuck, Quart. J. R. Met. Soc. 106, 125-157 (1980); Nature 280, 127-130 (1979); I. S. A. Isaksen et al., Nature 283, 189-191 (1980)).

This indirect mechanism for moderating the destruction of the ozone layer by Cl has been investigated for some time now. Increased CO_2 is expected to cool the upper atmosphere, thus inhibiting some of the O_3 destruction by Cl. The results are that $\Delta O_3/O_3 = -8.6\%$ from CFM's with constant CO_2, $\Delta O_3/O_3 = -2.6\%$ from CFM's with CO_2 rising to 600 ppmv (Groves and Tuck in Nature).

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Dear Sir or Madam:

We are submitting the two attached lists of Health and Safety studies as required by the referenced rule.

The first list, marked D650, is a list of studies in progress as of the date of this submission.

Please note that the study entitled "Acrylamide: A Two-Year Drinking Water Chronic Toxicity - Oncogenicity Study in CDF Fischer 344 Rats" is submitted on behalf of the following companies who are participating in the study:

Dow Chemical
American Cyanamid
Sohio
Nalco

The second list, marked D652, contains references to unpublished studies of which we are aware but do not have a copy.

Very truly yours,

R. L. Hagerman

R. L. Hagerman
Regulatory Specialist
Regulatory and Legislative Issues
Health and Environmental Sciences
1803 Building
(517)636-6055

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Dow Chemical Company
D-650
Studies in Progress as of Date of Submission

1. A Mortality Study of Men Engaged in the Manufacture of Organic Dyes.
   Purpose: Examine the mortality experience of men assigned to production areas in which aromatic amines were present as raw materials or chemical intermediates.
   Data: Mortality data
   Progress: Report submitted for publication
   Date of Completion: Unknown - when accepted for publication
   CAS Nos: 62533

2. In Vitro Reactivity Study of Alkylene Oxides
   Purpose: See title
   Data: Relative kinetic data
   Progress: Started Dec. 1, 1982
   Date of Completion: Report due 1984
   CAS Nos: 106887, 75218, 75569

3. Range-Finding Study of Methylchloroform Formulation XN 50120
   Purpose: See title
   Data: Mammalian toxicity
   Progress: Report being written
   Date of Completion: Jan. '83
   CAS Nos. 71556

4. Propylene Dichloride: Acute and Two-week Inhalation Study
   Purpose: See title
   Data: Toxicity in Rats, Mice and Rabbits
   Progress: Report being written
   Date of Completion: Jan '83
   CAS Nos: 78875

5. Methyl Chloride: Inhalation Toxicity in Female C57BL6 Mice Continuously or Intermittently Exposed for 12 Days
   Purpose: See title
   Data: See title
   Progress: Report to be written
   Date of Completion: First Quarter '83
   CAS Nos. 74873

6. Methylene Chloride: A Comparison of the Pharmacokinetics and Macromolecular Interactions of Inhaled ^{14}C-Methylene Chloride in Hamsters and Rats as Related to Toxicity
Purpose: Evaluate species differences in the fate of inhaled methylene chloride
Data: See title
Progress: Pathology in progress
Date of Completion: Sept. '84
CAS No: 79061

7. Acrylamide: A Two Year Drinking Water Chronic Toxicity - Oncogenicity Study in ICV Fischer 344 Rats
Purpose: See title
Data: See title
Progress: Pathology in progress
Date of Completion: September '84
CAS No: 79061

8. Acrylamide: Pharmacokinetics in the Rat
Purpose: See title
Data: See title
Progress: Report to be written
Date of Completion: First quarter '83
CAS No: 79061

9. Acute Range-finding - Diglycidylether of Biphenol A
Purpose: See title
Data: See title
Progress: Report being written
Date of Completion: First quarter '83
CAS No: 1675543

10. Characterization of Butylene Oxide Blood Levels, Macromolecular Binding and Hepatic Nonprotein Sulfhydryl Levels After Inhalation Exposure in Rats
Purpose: See title
Data: See title
Progress: Report being written
Date of Completion: First quarter '83
CAS No: 26249207

11. 1,1,1-Trichloroethane: Two-year Inhalation in Rats and Mice
Purpose: See title
Data:
Progress: Awaiting pathology
Date of Completion: June, '83
CAS No: 71556

12. Reduction Dechlorination of Chlorinated Methanes, Ethanes, & Ethylenes in Aqueous Solutions
Purpose: Investigate non-biological, reductive dehalogenation of a series of chlorinated hydrocarbons in aqueous solution
Data: Laboratory analytical data on concentration of chemicals in solution as a function of conditions
Progress: Underway
Date of Completion: Mid-1983
CAS Nos: 75092, 71556

13. A Case-Control Study of Renal Cancer Mortality at a Texas Chemical Plant.
Purpose: To determine if a possible etiologic agent for human renal cancer can be found related to occupation.
Data: Mortality and past presumptive exposures to chemicals produced or used in the chemical plant.
Progress: Preliminary report nearing completion
Date of Completion: Early 1983

14. A Case-Control Study of Leukemia and Occupational Exposure to Ethylene Oxide.
Purpose: To determine if past presumptive exposures to ethylene oxide are associated with leukemia.
Data: Mortality and past presumptive exposures to ethylene oxide.
Progress: Work histories on cases and controls being collected.
Date of Completion: Early 1983.

15. A Cross-Sectional Study of Employees with Potential Workplace Exposure to Ethylene Oxide.
Purpose: To determine whether those with potential exposure to ethylene oxide had a higher prevalence of abnormalities of the hematopoietic, hepatic, renal or reproductive systems than did an unexposed control group.
Data: Medical surveillance and presumptive occupational exposure
Progress: Preliminary report in process of review and revision
Date of Completion: Early 1983

16. Methyl Chloride Mortality Study.
Purpose To evaluate the mortality patterns of employees with past potential exposure to methyl chloride.
Data: Mortality and past potential occupational exposure to methyl chloride.
Progress: Collecting work history and exposure data.
Date of Completion: Mid-1983

17. 1,1,1-Trichloroethane

Purpose: Define the time course of 1,1,1-trichloroethane in human volunteers following a single six-hour inhalation exposure to 350 and 35 ppm.

Data: Human pharmacokinetic study

Progress: In progress

Date of Completion: February 1983

CAS No: 71556

18. Acrylamide

Purpose: Evaluate vibratory sensitivity in an exposed population and controls.

Data: Field survey

Progress: Preliminary data collected.

Date of completion: Unknown; Pending development and validation of methodology.

CAS No: 79061

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D-652
References to Unpublished Studies by Others

1. Studies of the visual system in chronic acrylamide poisoned monkeys. Lapham, L.W., et. al.
   Dr. L. W. Lapham, University of Rochester Medical Center, Department of Pathology, Division of Neuropathology, Rochester, NY, 14642.

2. The integration of multiple measures in behavioral toxicology. Merinon, W.H., et. al.
   Dr. W. H. Merinon, University of Rochester Medical Center, Division of Toxicology, Rochester, NY, 14642

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DETERMINATION OF TOTAL OXIDANT IN A PHOTOCHEMICAL SMOG CHAMBER: METHYLCHLOROFORM, TRICHLOROETHYLENE, PERCHLOROETHYLENE, AND METHYLENECHLORIDE

Chemical Name (300 per name) 25	CAS No. (10) 24
METHYLCHLOROFORM	71-55-6

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DETERMINATION OF TOTAL OXIDANT IN A PHOTOCHEMICAL SMOG CHAMBER: METHYLCHLOROFORM, TRICHLOROETHYLENE, PERCHLOROETHYLENE, AND METHYLENECHLORIDE

J. P. Arrington, M. J. Minta

Special Assignments
Edgar C. Britton Research Laboratory
The Dow Chemical Company
Midland, Michigan

A method has been devised to determine the total oxidant concentration resulting from simulated atmospheric photolysis of the above chlorocarbons. The amount of oxidant formed, the rate of disappearance of organic, and the effect of recent pollution control regulations on the use of these compounds will be discussed.

I. INTRODUCTION

On ~~April 27~~ JAN 30, 1971, a proposed set of National Ambient Air Quality Standards were published in the Federal Register. These standards stipulate that an air pollution alert will be declared when "oxidant" reaches a 0.1 ppm 1-hour average and an air pollution warning will be declared when "oxidant" reaches a 0.4 ppm 1-hour average. Thus those solvents which contribute markedly to oxidant formation will ~~accordingly~~ be subject to stringent controls.

The goal of this project was to devise a method to determine "total oxidant" formation, using a small (< 10 liter capacity) photoreactor already available, and to apply this method to a study of Dow's chlorinated solvents (methylchloroform, trichloroethylene, perchloroethylene, methylene chloride, chloroform) and related materials. All of these studies were to be carried out in a manner that would simulate atmospheric conditions as closely as possible. in a small chamber

II. HISTORICAL

A. Background

As a result of widespread public concern over air pollution, especially "photochemical" smog, Los Angeles enacted Rule 66 in 1966. This rule, designed to regulate emission of reactive organic compounds into the atmosphere, rated and controlled these compounds based on several criteria: eye irritation, photochemical reactivity and, to a lesser extent, "total oxidant" formation. These criteria were derived from empirical observations in studies carried out by the Los Angeles County Air Pollution Control District (LACAPCD), which measured characteristics of photochemical smog induced by various compounds.

Rule 66 was, in a sense, a landmark. Many communities across the country showed interest in it, and San Francisco soon enacted the similar Regulation 3. Unfortunately, some of these later groups have shown a lesser under-

standing of the situation than has LACAPCD, since representatives of this group have repeatedly felt it necessary to warn that atmospheric contaminants may be very different in different cities. Their recommendations have been that each case should be studied individually. As an example of the possible differences, consider Los Angeles and London. The smog in Los Angeles is oxidising, with a larger concentration of ozone than sulfur dioxide, whereas London smog is characterized by a higher sulfur dioxide concentration, making it reducing. Many other contaminants also vary greatly, depending upon local usage, weather conditions and other factors. Making the situation still more complicated is the fact that the emphasis in regulation has begun to shift more heavily toward control of "total oxidant" levels. This is particularly true of the 1971 National Air Quality Standards, and will probably be true of many local ordinances.

The restriction of trichloroethylene by Rule 66 was felt by some to be based on questionable studies (the criticism was that the concentrations used in the study did not fairly represent atmospheric conditions). Under the auspices of the Manufacturing Chemists Association (MCA) and funded by the Trichloroethylene Producers, the Stanford Research Institute (SRI) [redacted] a rather complete study of the smog-forming potential of trichloroethylene. The results of this study have now been published[1], and provide us with a large body of data that enhance our understanding of the smog-forming mechanism, as well as providing a basis for rational regulation. The results of this study will be summarized below in the discussion of the smog-forming mechanism.

Battelle Research Institute recently compiled the results of a comprehensive study[2] of a wide variety of organic compounds for the National Paint, Varnish, and Lacquer Association (NPVLA), which "tend to confirm the basis upon which Rule 66 and Regulation 3 were derived." [redacted] The Battelle report emphasized a point that is worth repeating: there is no clear correlation among oxidant formation, eye irritation, and reactivity. This not only makes regulation on the basis of any single criterion nearly impossible, but also makes rational regulation difficult. How does one assign a weight to each of the criteria? These, then, are some of the complex problems that make a complete, thorough understanding of the chemical processes involved so important to the question of control. The

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following section discusses what is currently known about photochemical smog formation.

B. Photochemical Processes in Polluted Air

For the purpose of this discussion, "photochemical smog" will be defined broadly to arise from all photochemical processes which occur in the atmosphere. Some of these processes occur in non-polluted air as well, but a survey of them is a requisite to an adequate understanding of the smog-forming process.

One of the most complicated, and yet one of the most fundamental, processes that occurs in polluted atmospheres is the accumulation of ozone. The formation of ozone has long been recognized as being an integral part of the nitric oxide-nitrogen dioxide equilibrium, but in the absence of organics, the concentration rapidly reaches a very low steady-state value. The "normal" process is thought to occur as shown in the following equations:[3,4]

$$NO_2 \xrightarrow{h\nu} NO + O\cdot \qquad (1)$$

$$O\cdot + O_2 + M \longrightarrow O_3 + M \qquad (2)$$

$$O\cdot + NO_2 \longrightarrow NO + O_2 \qquad (3)$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \qquad (4)$$

$$O_3 \xrightarrow{h\nu} O_2 + O\cdot$$

Under normal conditions, at low concentrations, nitric oxide greatly predominates.

The addition of many organic compounds to the atmosphere disrupts this equilibrium and may lead to any (or all) of the following phenomena:[5]

(1) The organic compounds are oxidized and disappear.

(2) Reaction products such as aldehydes, nitrates, PAN's*, are formed.

(3) Nitric oxide is oxidized to nitrogen dioxide.

(4) When nitric oxide disappears ozone begins to form and can reach dangerous levels.

---

*Peroxyacylnitrites and Nitrates.

The mechanism by which organic additives influence the nitric oxide-nitrogen dioxide equilibrium is not clear, but has been suggested[3] to occur by way of a chain mechanism illustrated below. This scheme is admittedly quite speculative, but it appears to be a reasonable beginning.

$$Ha + O\cdot \longrightarrow HaO\cdot\ (RO\cdot) \qquad Ha = \text{aromatic, olefin} \qquad (6)$$

$$Ha + O\cdot \longrightarrow R\cdot + OH \qquad Ha = \text{aliphatic} \qquad (7)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (8)$$

$$RO\cdot + O_2 \longrightarrow RO_3\cdot \qquad (9)$$

$$RO_2\cdot + NO \longrightarrow RO\cdot + NO_2 \qquad (10)$$

$$RO_3\cdot + NO \longrightarrow RO_2\cdot + NO_2 \qquad (11)$$

$$RO_2\cdot + O_2 \longrightarrow RO\cdot + O_3 \qquad (12)$$

$$RO\cdot + NO_2 \longrightarrow RONO_2 \qquad (13)$$

The reaction (12) is thus responsible for the accumulation of ozone, and reactions 10-12 are the chain carriers. Although this mechanistic scheme accounts fairly well for most of the salient features of the "system," it is not completely satisfactory. It fails, for example, to offer a clue to the reason a mass balance in nitrogen is lacking in nearly all the studies carried out to date. Further, this mechanistic scheme is not sufficiently sophisticated to explain the dependence of the maximum ozone level upon both the ratio and absolute concentration of organic and nitrogen oxide, as was reported in the SRI study.[1]

The SRI results on trichloroethylene are certainly worthy of comment, particularly since they are so pertinent to this study. It was shown[1] that at a given ratio of trichloroethylene to nitrogen oxides, the mole yield of ozone increased as the absolute concentration of the reactants decreased. It was also found that photolysis at low ratios (8:1 or less) of trichloroethylene to nitrogen oxides generates smaller amounts of ozone than does irradiation at higher ratios (8:1). Both these findings are illustrated in Table I. It is unfortunate that a wider range of ratios was not studied, as this might lead to rather interesting changes. The SRI data also serve to illustrate the difficulty of basing regulations upon a single characteristic of smog and testing only at a given set of concentration and ratio parameters. Other factors, such as stabilizers and relative humidity, have also been found

TABLE I

Ozone Yield as a Function of Absolute Concentration and Concentration Ratios

Ratio(trichlor/NO_2)	[trichlor]mm	Max[O_3]mm	% O_3 Yield
8:1	8	0.8	10
8:1	0.8	0.17	21
2:1	4	<0.05	<1
2:1	8	<0.1	<5

to influence the reactivity of trichloroethylene, although the effect on oxidant formation was not investigated.

The Battelle group[5] examined a series of 45 individual organic-solvent materials in a study conducted for the NYSA. Their study was extensive in the number of smog characterization measures. Unfortunately, each of their experiments was done at a fixed ratio (5:1) of organic to nitrogen oxides, and it has already been shown that this doesn't always give the complete picture.

An excited state ($^1\Delta_g$) of molecular oxygen has recently been suggested[6] as a reactant in the photooxidation of nitric oxide to nitrogen dioxide. A mechanism by which this might occur is shown below.

$$O_2(^1\Delta_g) + RH \longrightarrow R\text{-}OOH \quad R = \text{olefin} \qquad (14)$$

$$ROOH \xrightarrow{\Delta} RO\cdot + OH \qquad (15)$$

$$RO\cdot + O_2 \longrightarrow RO_3\cdot \qquad (9)$$

$$RO_3\cdot + NO \longrightarrow RO_2\cdot + NO_2 \qquad (11)$$

This is simply one way of producing RO· without the necessity for invoking a reaction of the organic molecule with a free oxygen atom (both species are present at very low concentrations). A number of recent reviews[6-8] attest to the reactivity of singlet oxygen with a wide variety of unsaturated organic molecules. In fact, the usual reaction of singlet oxygen with olefins is illustrated by Rxn (14) above. From the point of view of reactivity, then, it is quite reasonable to assume that singlet oxygen plays a part in the oxidation of nitric oxide to nitrogen dioxide in polluted atmospheres. The formation of singlet oxygen in polluted air is also quite credible. Many organic molecules are known to sensitize the conversion of the ground state ($^3\Sigma$) of oxygen to its excited state ($^1\Delta$). Almost any carbonyl-containing compound or aromatic hydrocarbon is capable of sensitizing this transformation quite efficiently, so the presence of some singlet oxygen in polluted atmospheres is quite possible. This reactive state of oxygen has also been suggested to arise

$$\text{Organic} \xrightarrow{h\nu} \text{Org.}\,^1* \longrightarrow \text{Org.}\,^3* \qquad (16)$$

$$\text{Org.}\,^3* + O_2(^3\Sigma) \longrightarrow \text{Org.} + O_2\,(^1\Delta g) \qquad (17)$$

from other reactions such as the photolysis of ozone,[9,10] and bimolecular

reaction between ozone and nitric oxide (reaction 4).[11] Although the formation of singlet oxygen and its participation in the conversion of nitric oxide to nitrogen dioxide in polluted atmospheres seems plausible, it has not yet been demonstrated to occur in the lower atmosphere. Among others, Pitts' group at Riverside, California, is actively studying this problem.

The accumulation of ozone in polluted atmospheres is thus a result of a disruption of the nitric oxide-nitrogen dioxide-ozone equilibrium by the addition of certain organic molecules. Some conclusions can be drawn from the proposed mechanism, even though it may not be complete. The first is that compounds that do not readily react with oxygen atoms (benzene, paraffins) should exhibit a low rate of ozone formation. It is also clear that nearly all of these reactions are initiated from the photodissociation of nitrogen dioxide to nitric oxide and an oxygen atom, and everything also occurs in a dark, or secondary reaction. Further, in the complete absence of either added organics or nitrogen oxides, the symptoms of photochemical smog endemic to Los Angeles should be removed. Since it is unlikely that we shall ever attain "zero" concentrations of either organics or nitrogen oxides, it is important to determine the degree to which each organic material contributed to the symptoms of photochemical smog, and to enact regulations on this basis. It is on this premise that Rule 66 was enacted and the work described below was initiated.

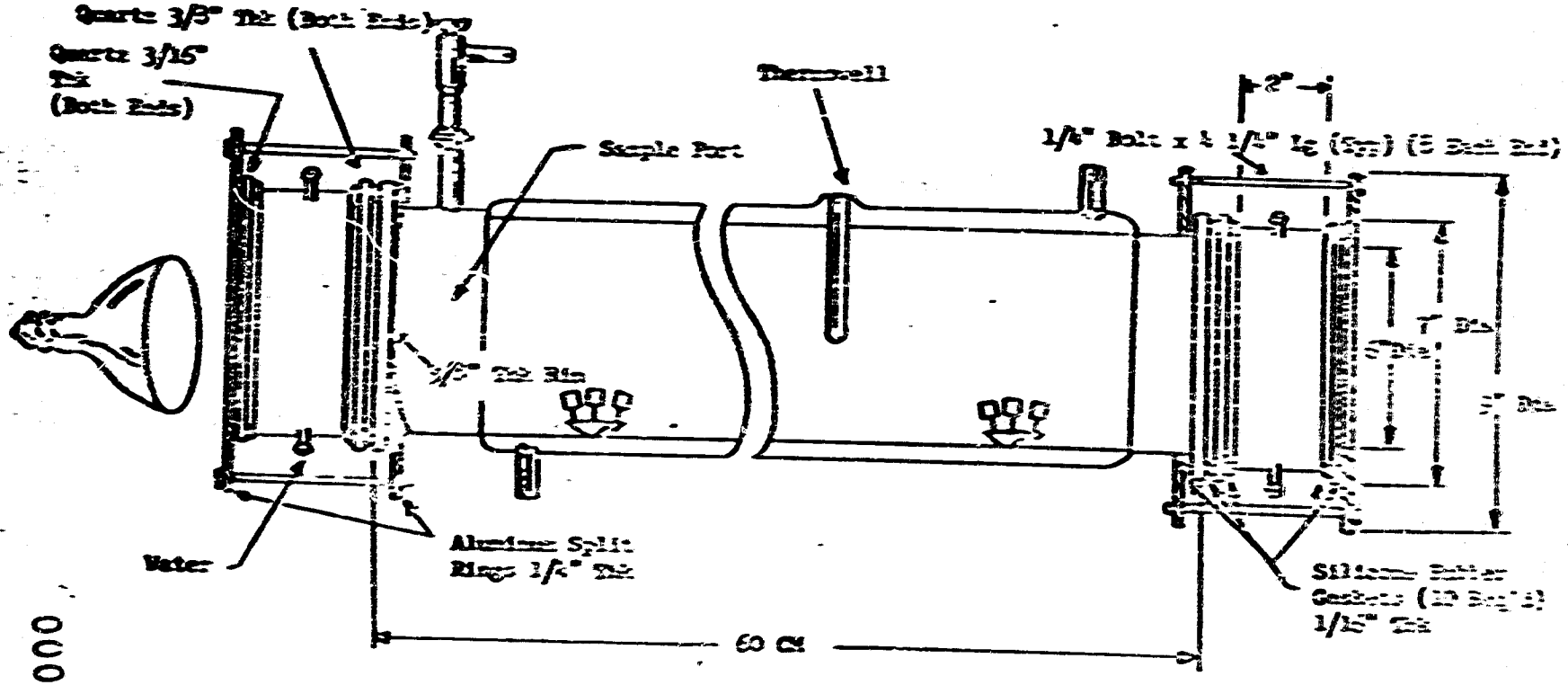
III. RESULTS AND DISCUSSION

A. General Comments

As discussed above, many workers[3-9] have reported that ozone does not begin to appear until the nitric oxide has been converted to nitrogen dioxide. It is also clear from these data that the same maximum ozone level is attained no matter which of these two nitrogen oxides is part of the starting mixture. In order to avoid this "induction period" and to thereby shorten the analysis time, nitrogen dioxide was used in all of these experiments. The concentration of the organic used was often as high as 50 ppm; this was done in order to facilitate gc monitoring (response of flame ionization detectors to chlorocarbons is very poor). A ratio of 4:1 for organic/NO_2 was chosen for use in each of the experiments. The range for most of the earlier work was from 2:1 to 8:1; it was felt that 4:1 is a good compromise.

Figure 1

Photochemical Cooler Design[7]



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The precision with which oxidant could be measured in these experiments suffers from several factors. The major one is, of course, the fact that each reading comes from what is actually a separate experiment. Other factors are the difficulty of introducing nitrogen dioxide reproducibly and the large volume of air being flushed through the absorbing reagent. A rough estimate of the precision in oxidant measurement would be on the order of ± 10-15%. While this is far from being as quantitative as one might wish, the data obtained still seem to give quite adequate representation of ozone formation, particularly when one is concerned with relative characteristics of various compounds.

B. Method for Oxidant Measurement

A number of problems were encountered in devising a method to measure ozone at levels below 1 ppm in the photochamber. A method which seems to be quite satisfactory was devised, however, and it is briefly described below.

The contents of the chamber were flushed with nitrogen through a neutral-buffered 1% KI solution[12] in a gas absorbing tower of the type described by Smith.[13] The optimum conditions were a flow rate of 1 l/min with 25 ml of the absorbing reagent; smaller quantities of KI and/or higher flow rates gave consistently low readings, as determined by titration with thiosulfate. The validity of the method was tested by generating small quantities of ozone with an electric discharge in a flask, and removing two aliquots by syringe. One was injected into the photochamber and flushed through a KI solution as just described; the other was directly bubbled slowly through an equivalent volume of KI solution. Titration of each solution (several runs) indicated that over 95% of the ozone in the chamber could be accounted for.

The next step was to compare results obtained from an actual irradiation with literature values. Toluene was chosen to serve as a comparison, since it had been studied by other groups[8] who found it to lead to "moderate" quantities of ozone at a relatively rapid rate. Thus, the study of toluene can function as a benchmark for the work reported here and help to assess the validity of the overall method being used.

C. Toluene

The photolysis of toluene was carried out at 16 ppm in the presence of 4 ppm nitrogen dioxide. Figure 2 shows the results of this irradiation. It can be seen that the maximum oxidant concentration (0.8 ppm) was reached after

4 hr of irradiation. Battelle reported[9] that a maximum ozone concentration of 0.49 ppm was attained after 3.3 hr, starting with 4 ppm toluene and 8 ppm nitric oxide. In earlier work at Dow, Bradeway found the half-life for disappearance of toluene was 6.75 hr, starting with 10 ppm toluene and 9 ppm nitric oxide, whereas the data obtained in this study indicate a half-life of about 4 hr. Bearing in mind the differences in starting concentrations, light intensities, and reaction times for nitric oxide versus nitrogen dioxide, the agreement in data seems quite satisfactory.

It should be mentioned that it is not possible to assess separately the quantity of nitrogen dioxide as compared to ozone from the data obtained in this study. Although it is simple to irradiate nitrogen dioxide in the absence of organics (see Figure 3) and to follow its rapid rate of disappearance (nitrogen dioxide reacts with aqueous potassium iodide, although non-stoichiometrically), the ozone concentration cannot be obtained by substracting the nitrogen dioxide curve from the "total oxidant" curve with the difference being ozone. This is because the addition of organic can drastically alter the nitric oxide-nitrogen dioxide equilibrium. The only manner in which we could determine ozone by itself would be to run a separate series of experiments to determine nitrogen dioxide in the presence of organic and ozone. Because of the lack of precision and the time involved when this particular chamber is used, it is probably not worthwhile to separate "total oxidant" into its various components.

D. Methylchloroform

The photolysis of methyl chloroform was studied at two concentrations, 50 ppm and 10 ppm. The results are illustrated in Figures 5 and 6. The data at 10 ppm indicate that oxidant level (which includes a contribution from nitrogen dioxide) rapidly decreases until it approaches zero. (The lowest level that could be measured is about 0.05 ppm). The curve for the 50 ppm reaction again rapidly decreases, but asymptotically approaches 0.1 ppm, which is very low, considering the high initial concentration of methylchloroform. As before, it is not clear whether the "total oxidant" is due to ozone or to residual nitrogen dioxide. Since methylchloroform is itself unreactive, and no oxidant (or almost none) is formed from its photolysis, it can be expected that methylchloroform will be exempt from air pollution-control regulations that are concerned with the standard symptoms of photochemical smog (eye irritation, oxidant formation, reactivity).

E. Trichloroethylene

Trichloroethylene is by far the most reactive of the compounds studied for this report, and this fits in well with other studies.[1] The data (see Figure 4) for photolysis of 50 ppm trichloroethylene also indicate significant oxidant formation, again in agreement with the GRI study.[1] The rapidity with which oxidant forms is perhaps surprising. That it is real, however, is borne out by the fact that most of the points in Figure 4 were obtained in duplicate. Again, however, some of the oxidant may be due to a slower decrease in the nitrogen dioxide concentration.

F. Perchloroethylene

Perchloroethylene was found to be rather reactive from the standpoint of disappearance of organic, dropping from 50 ppm to ≤ 5 ppm in 4 hours. In this respect it is quite similar to trichloroethylene; however, perchloroethylene is rather dramatically different from trichloroethylene with respect to oxidant formation. A comparison of Figures 8 and 9 with Figure 3 shows that photolysis of perchloroethylene leads to a slight oxidant formation initially but that the final oxidant levels reached after 13 hours of irradiation are lower than those for the blank. This same behavior was borne out in a lower concentration experiment where total oxidant with perchloroethylene decreased from 0.66 ppm to 0.17 ppm in 4.38 hours compared to a final level of 0.52 ppm for the blank (the initial organic and NO_2 were 12.5 ppm and 2.74 ppm respectively).

G. Methylene Chloride

Methylene chloride behaved in an identical manner as methylchloroform under simulated atmospheric photolysis at both 50 and 12.5 ppm. It produced oxidant levels essentially identical with background and showed no disappearance of organic in 13 hours or irradiation. Thus methylene chloride should be given a clean bill of health by control legislation which emphasizes either chemical reactivity and/or oxidant formation in evaluating atmospheric pollutants.

H. General Discussion

The value for total oxidant is plotted as though it were entirely due to ozone, which reacts stoichiometrically and completely with neutral-buffered 1% potassium iodide.[14] At the early stages of the irradiation, however, this obviously is not true, as the major portion is due to nitrogen dioxide. Nitro-

gen dioxide reacts with potassium iodide, but at less than 1:1 stoichiometry. A generally accepted value is about 50%. Thus, if we have 5 ppm nitrogen dioxide, we could expect approximately the same value under those conditions as 1 ppm ozone. The points at the early stages of the reaction should therefore be considered as "effective oxidant concentration."

While it is not surprising that methylchloroform is unreactive under these conditions, this obviously raises some problems. What happens to methylchloroform in air? Methylchloroform absorbs in the uv at wavelengths [illegible] and under these conditions C-Cl bond cleavage might be predicted, eventually leading to phosgene, formaldehyde and HCl, among others. It is difficult to believe, however, that a sufficient number of photons of high enough energy would be found in the lower atmosphere to cause this reaction to occur to any significant extent, so we are still faced with the same problem.

Methylene chloride presents a similar problem to that encountered with methyl chloroform; we still do not know its fate in air. Further studies are currently in progress to establish whether either material is susceptible to oxidative photolysis in the upper atmosphere where higher energy radiation is available or whether decomposition at sea level is real but simply too slow to be detected on our experimental time scale.

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IV. CONCLUSIONS

A method has been developed to measure "total oxidant" formation resulting from irradiation of mixtures of organic solvents and nitrogen dioxide in a small (10 liter) photochamber. The precision of this method suffers from the size of the chamber since each point obtained requires a separate experiment.

Methylene chloride has been found to be unreactive when subjected to simulated atmosphere photolysis ($\lambda > 295$ mμ), with no oxidant formation observed at initial concentrations of either 50 or 18.5 ppm. Methylchloroform has been found to be quite unreactive, and no "oxidant" could be detected at a level of 10 ppm methylchloroform and 2.5 ppm of nitrogen dioxide. Even at 50 ppm, only a very small amount of oxidant could be detected, where the detectable limit is approximately 0.05 ppm. Perchloroethylene was found to be quite

reactive, disappearing at about the same rate as trichloroethylene, but producing only a small amount of oxidant. In confirmation of earlier work, both trichloroethylene and toluene were found to be moderately reactive and to lead to significant oxidant formation. It can be reasonably assumed that methylchloroform and methylene chloride will be exempt from future pollution-control restrictions based on photochemical smog symptoms. It is likely that perchloroethylene will remain exempt if oxidant formation is a primary criterion.

V. LIST OF FIGURES

Figure 1	Photochemical Chamber Design
Figure 2	Photooxidation of Toluene with Nitrogen Dioxide
Figure 3	Irration of Nitrogen Dioxide
Figure 4	Photooxidation of Trichloroethylene with Nitrogen Dioxide
Figure 5	Photooxidation of Methylchloroform (50 ppm) with Nitrogen Dioxide
Figure 6	Photooxidation of Methylchloroform (10 ppm) with Nitrogen Dioxide
Figure 7	Photooxidation of Methylene Chloride with Nitrogen Dioxide
Figures 8,9	Photooxidation of Perchloroethylene with Nitrogen Dioxide

VI. REFERENCES

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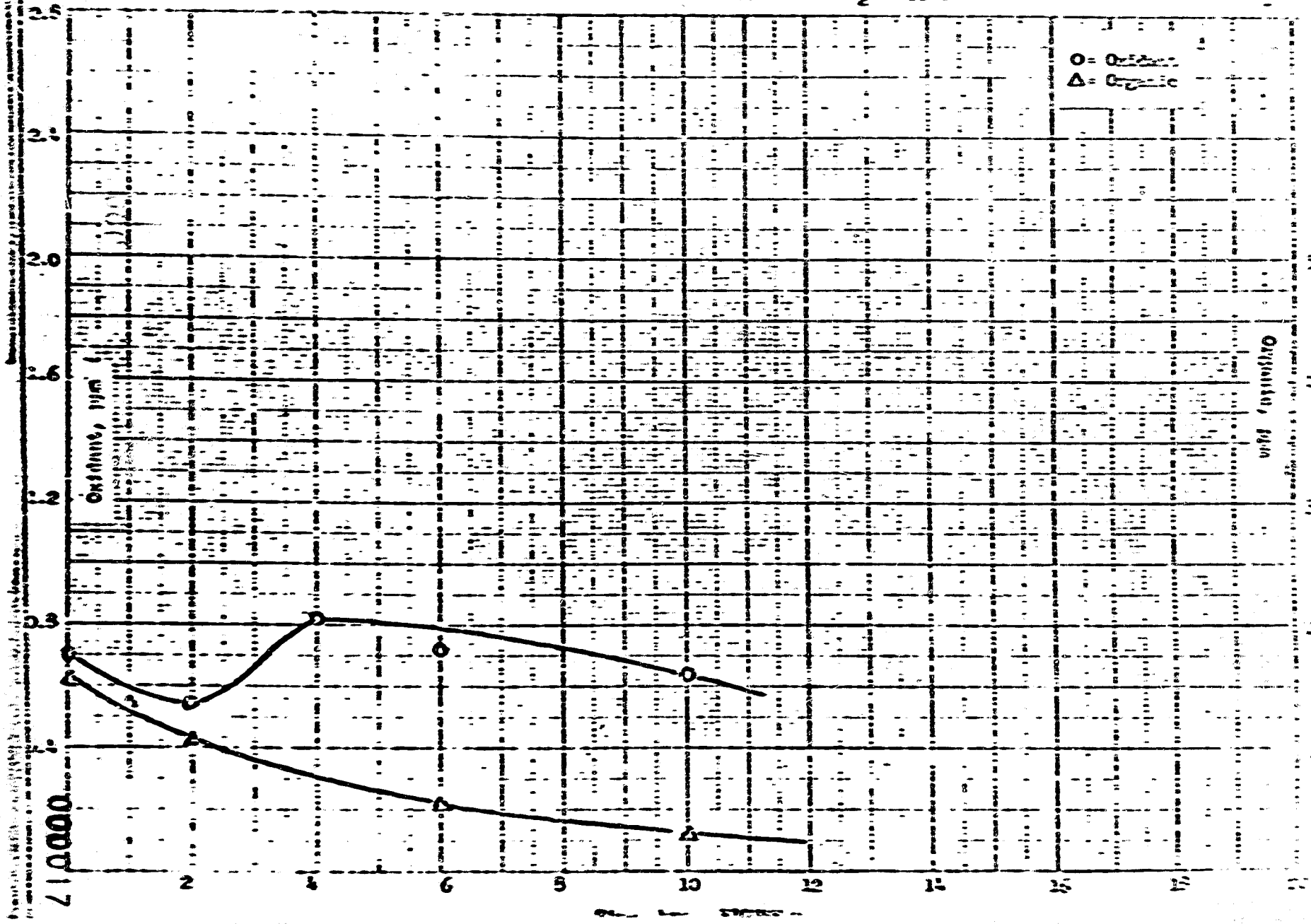
Photooxidation of Toluene (16 ppm) with NO_2 (4 ppm)



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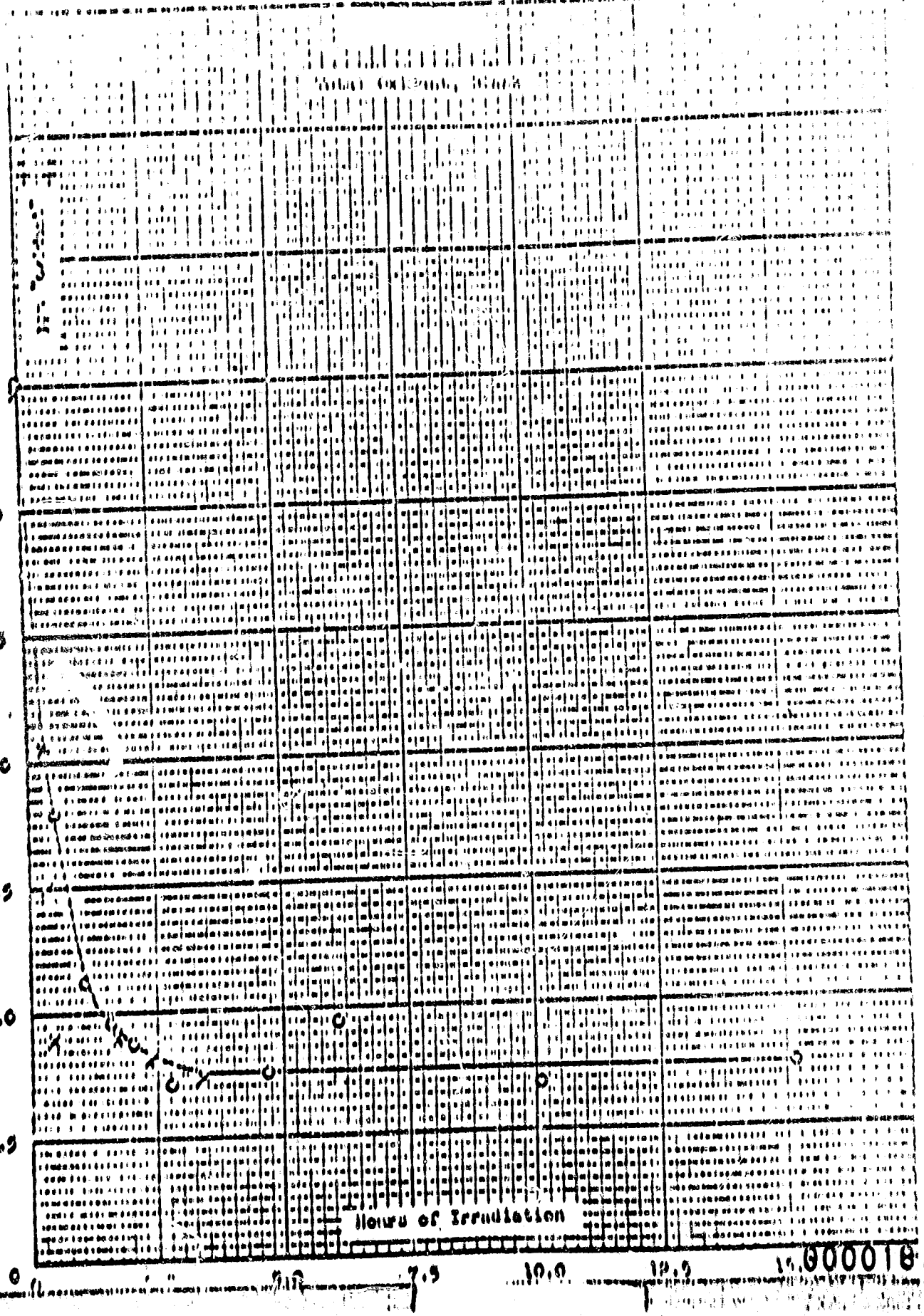

Figure 3

Photooxidation of Trichloroethylene (90 ppm) with NO_2 (12 ppm)

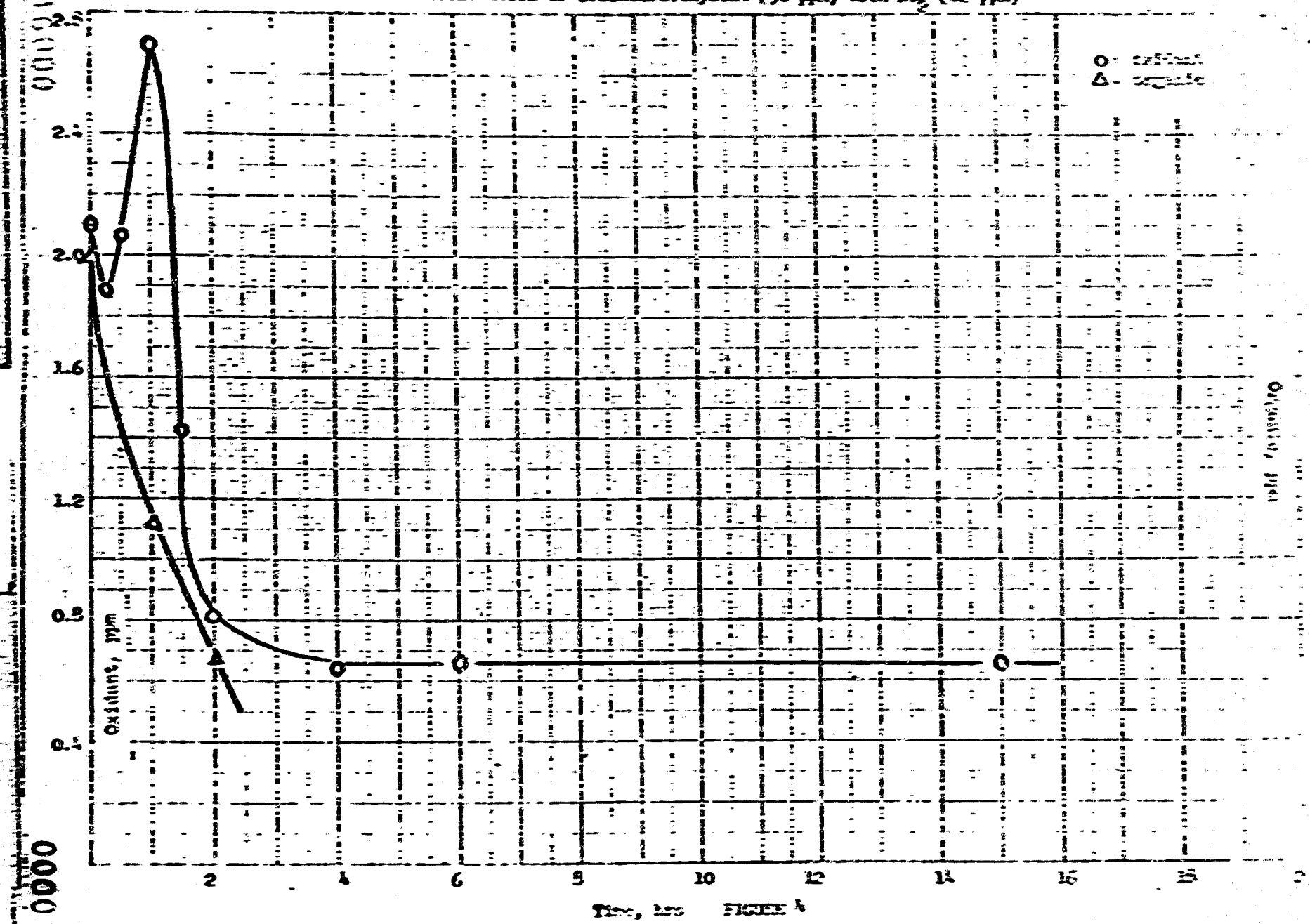

FIGURE 4

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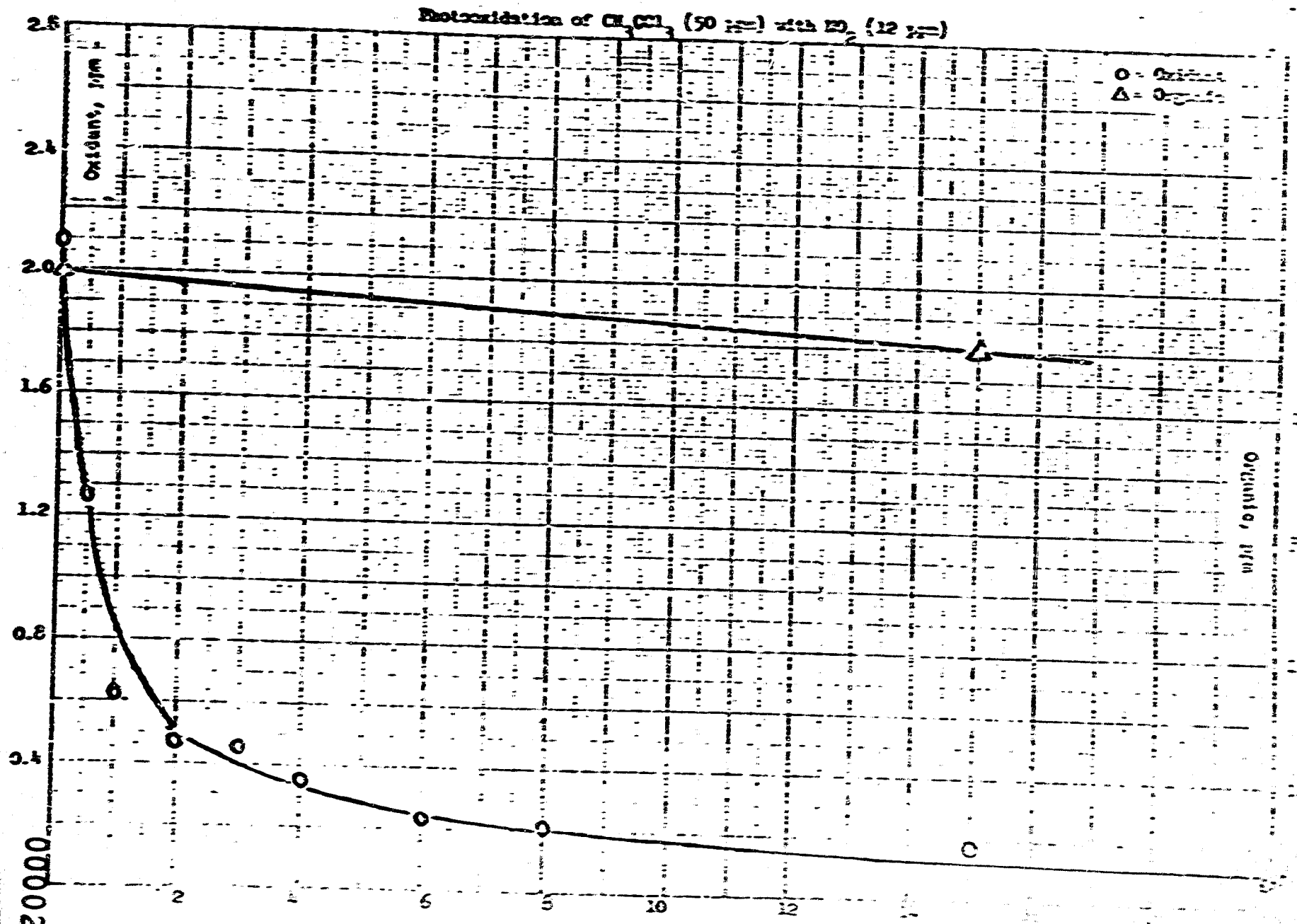
Photooxidation of CH_3CCl_3 (50 μm) with NO_2 (12 μm)
O - Oxidant
Δ - Oxygen
Oxidants, μm
Oxygen, μm
2.8
2.4
2.0
1.6
1.2
0.8
0.4
2
4
6
8
10
12
Time, hrs

FIGURE 5

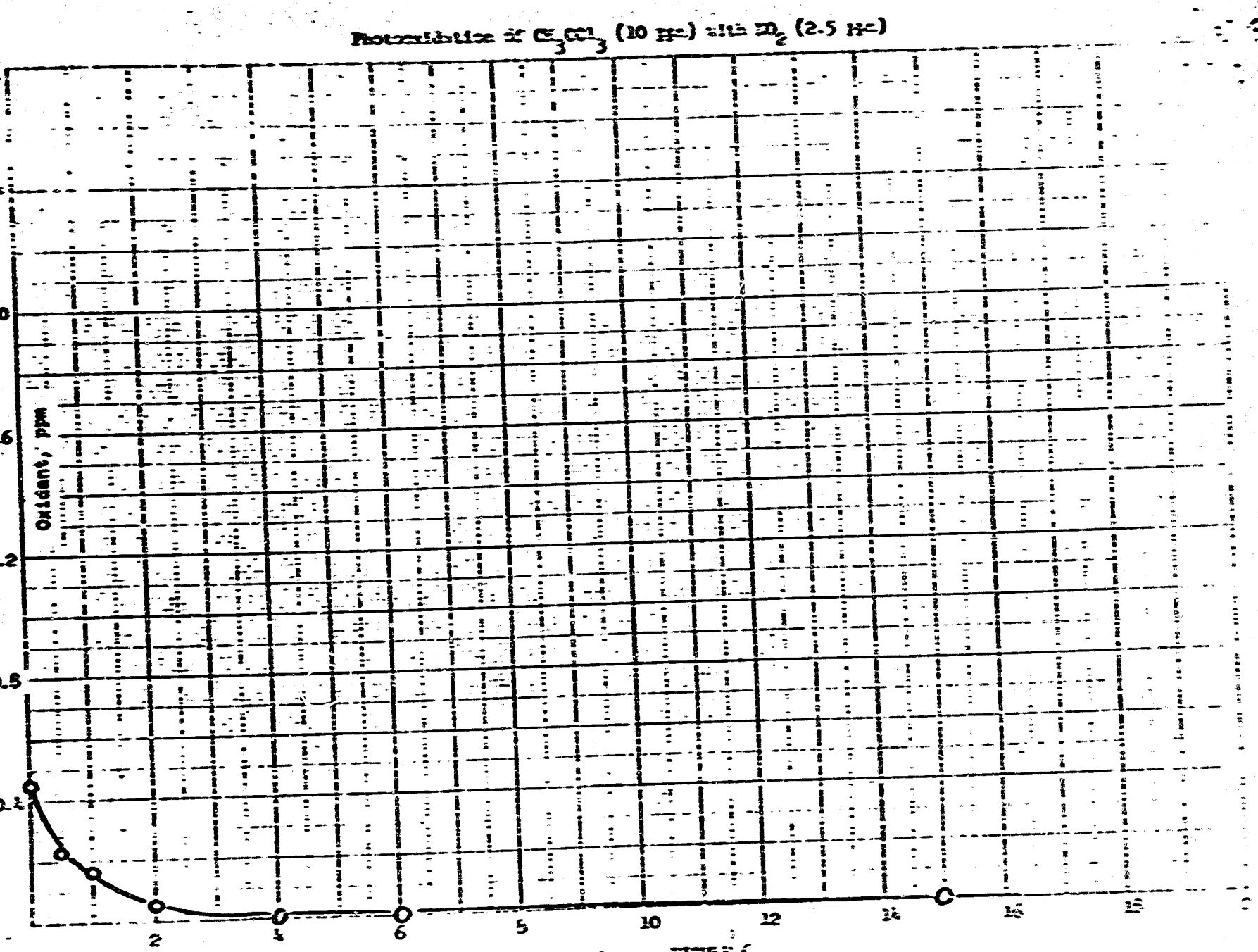

FIGURE 6

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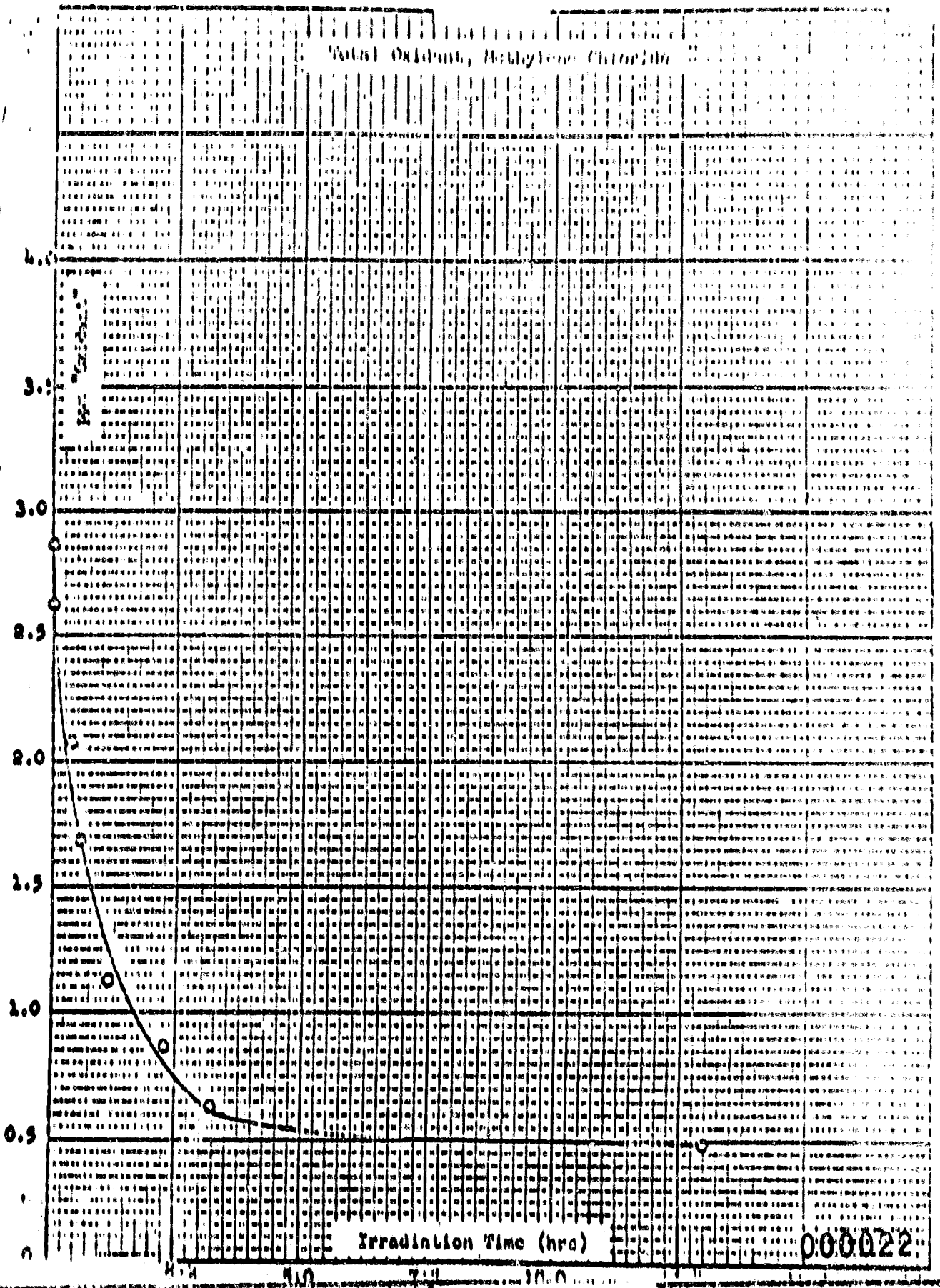

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Total Dalkane Perchloroethylene

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

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