ATMOSPHERIC METHYL IODIDE

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ATMOSPHERIC METHYL IODIDE

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Chapter 1

INTRODUCTION

Methyl iodide is present in the atmosphere in minute quantities, but it and other iodine species have been suggested to play an important role in tropospheric photochemistry (Chameides and Davis, 1980). Although the atmospheric concentration of CH_3I is very small -- of the order of a few parts per trillion by volume (pptv) or even a fraction of a part per trillion -- the sensitivity of the electron capture detector (ECD) towards CH_3I makes it possible to readily measure this species and determine its atmospheric concentration. CH_3I is the only gaseous organo-iodine species that has been quantitatively measured in the atmosphere.

Atmospheric iodine compounds can be divided into three categories: organically-bound iodine (gaseous), inorganic gaseous iodine, and particulate iodine. Over the years several investigators have measured several of these species. Lovelock (1973), Lillian et al. (1975), Singh et al (1977), and Rasmussen et al. (1982), using electron capture gas chromatography, were the first to observe CH_3I in the atmosphere. In addition, Rasmussen et al. (1980) observed CH_3I using an O_2-doped ECD during the investigation of atmospheric CH_3Cl. Inorganic gaseous iodine concentrations have been measured by Rahn et al. (1976), Rancher and Kritz (1980), and Cicerone (1981). Their work was focused on determining the total gaseous inorganic iodine concentration. Total gaseous organically bound iodine has also been measured by the same investigators, whereas Moyers and Duce (1972) have measured particulate iodine concentration. In all these studies, except the determination of CH_3I, the measurements were done by neutron activation analysis methods.

When Chameides and Davis (1980) examined the importance of iodine (I) in tropospheric photochemistry, they assumed the major source of atmospheric iodine to be from the photolysis of CH_3I, i.e.,

$$CH_3I \xrightarrow{h\nu} CH_3^{\circ} + I^{\circ}$$

These iodine atoms then combined with other atoms and molecules to form inorganic iodine species:

$$I^{\circ}\ \underset{\text{etc.}}{(O_3,\ H_xO_y,\ NO_x)} \longrightarrow IX\ \underset{\text{etc.}}{(IO,\ HOI,\ IONO_2)}$$

Production of IX and the conversion of these IX species back to iodine can lead to chemical cycles that can remove tropospheric O_3, increase NO_2/NO ratio, and destroy H_xO_y free radicals.

IX is ultimately removed by heterogeneous processes. Models indicate iodine may have a strong impact upon the atmospheric O_3-NO_x-H_xO_y system. The magnitude of these effects depends upon several uncertain rate constants, concentrations of CH_3I, and other organic and inorganic iodine species.

$$O_2 \xrightarrow{h\nu} 2O$$

$$O + O_2 + M \rightarrow O_3 + M.$$

Cl and Br can also react with O_3 in a catalytic destruction cycle:

$$\begin{array}{c} O_3 + Cl^{\circ} \rightarrow O_2 + ClO \\ \underline{ClO + O \rightarrow Cl^{\circ} + O_2} \\ O_3 + O \rightarrow 2O \end{array}$$

Similarly for Br°.

Competing chain termination reactions with CH_4 and HO_2 remove Cl in the stratosphere as HCl, which is removed by rainout.

$$HCl + HO \rightarrow H_2O + Cl^{\circ} \qquad \text{(A)}$$

However, this reaction (A) is not very significant in the troposphere because of lower HO° concentrations. Also, if HO° concentrations are high in tropical-subtropical marine boundary layer, washout or rainout of HCl is also high. Additionally H-Cl and H-Br bond strengths are stronger than that of H-I. Therefore, $Cl^{\bullet}$ and $Br^{\bullet}$ are not as important as I in the tropospheric O_3 budget.

Unlike Br and Cl, I forms very weak covalent bonds with C, H, N, and O. This enables IX compounds to be very easily photo-dissociated in near UV or visible light. As a result, the IX system can be highly catalytic.

I.A. Effect of IX on O_3 Photochemistry

Since

$$CH_3I \xrightarrow{h\nu} CH_3^{\circ} + I^{\circ}$$

$$I + (O_3, H_xO_y, NO_x, \text{etc.}) \longrightarrow IX\ (IO, HOI, IONO_2, \text{etc.})$$

$$[IX] \propto [CH_3I]$$

i.e.,

$$[IO], [HOI], \text{etc.} \propto [CH_3I]$$

$$2I + 2O_3 \rightarrow 2IO + 2O_2$$

$$\underline{IO + IO \rightarrow 2I + O_2}$$

$$2O_3 \rightarrow 3O_2 \qquad \text{IO + IO path}$$

$$I + O_3 \rightarrow IO + O_2$$

$$IO + HO_2 \rightarrow HOI + O_2$$

$$HOI \xrightarrow{h\nu} I + OH$$

$$OH + CO \rightarrow CO_2 + H$$

$$\underline{H + O_2 + M \rightarrow HO_2 + M}$$

$$CO + O_3 \rightarrow CO_2 + O_2 \qquad \text{HOI + } h\nu \text{ path}$$

Let's take loss of O_3 due to some path A as $D_{O_3}(A)$:

$$D_{O_3}\ (HOI + h\nu) \propto [CH_3I]$$

$$D_{O_3}\ (IO + IO) \propto [CH_3I]^2$$

∴ At low [CH_3I] values, D_{O_3}(HOI + $h\nu$) is important
& at higher [CH_3I] values, D_{O_3}(IO + IO) is important
The crossover point is between 10 pptv and 25 pptv [CH_3I]
D_{O_3}(IX) $\sim$ D_{O_3}(H_xO_y) for [CH_3I] = 10 pptv
D_{O_3}(IX) > D_{O_3}(H_xO_y) significantly for [CH_3I] $\gtrsim$ 25 pptv

For example, at [CH_3I] = 50 pptv, D_{O_3}(IX) is a factor of 100 greater than D_{O_3}(H_xO_y)! The photochemical lifetime of O_3 decreases to 0.1 days (from 10 days with H_xO_y).

I.B. Effect of IX on NO_x Photochemistry

Iodine can enhance the NO_2/NO ratio:

$$I + O_3 \rightarrow IO + O_2$$

$$IO + NO \rightarrow NO_2 + I$$

At [CH_3I] = 10 pptv, NO_2/NO is enhanced by 10%; at [CH_3I] = 25 pptv, NO_2/NO is enhanced by 25%.

I.C. Effect of IX on H_xO_y PHotochemistry

OH• radicals act as scavengers for several atmospheric trace gases, such as CO, CH_4, CH_3Cl, CH_3CCl_3, etc. To a large extent, the steady state OH concentrations depend on reactions:

$$\left.\begin{array}{l} O_3 + h\nu \rightarrow O'(D) + O_2 \\ O'(D) + H_2O \rightarrow 2OH \\ \\ HO_2 + NO \rightarrow NO_2 + OH \end{array}\right\}$$

production of OH radicals

if NO is present, $HO_2 + NO \rightarrow NO_2 + OH$

$$\left.\begin{array}{l} CO + OH \rightarrow CO_2 + H \\ CH_4 + OH \rightarrow CH_3 + H_2O \end{array}\right\}$$

loss of OH radicals

conversion of $HO_2 \rightarrow OH$

$$I + O_3 \rightarrow IO + O_2$$

$$IO + HO_2 \rightarrow HOI + O_2$$

$$HOI \xrightarrow{h\nu} OH + I$$

$$\overline{O_3 + HO_2 \rightarrow 2O_2 + OH}$$

i.e., OH is produced at the cost of O_3 and HO_2

$$HO_2 + I \rightarrow HI + O_2$$

$$HI + OH \rightarrow I + H_2O$$

loss of H_xO_y

Overall:

$[CH_3I] \simeq 10$ pptv up to 20% increase in [OH]

$[CH_3I] \simeq 50$ pptv 10-100% increase in [OH]

(depending on the model used)

There are several iodine species involved in these catalytic cycles. To completely understand the importance of iodine in the tropospheric photochemical system, one must determine the concentrations of all the iodine species involved and also their rate constants.

Since CH_3I is assumed to be the major source of atmospheric iodine, it is important to know the atmospheric concentration of this compound, its flux from the ocean, and its distribution over the globe.

Lovelock and Maggs (1973) were the first to measure the atmospheric concentration of CH_3I at levels of 1-2 pptv. They also determined CH_3I in seawater. Large local variations were also observed in the surface seawater samples but not any obvious changes in concentration with latitude. In a separate experiment Lovelock (1975) found that marine algae were a strong source of CH_3I. He concluded that the source of atmospheric CH_3I is the ocean, that it is biological in origin, and that it is the natural carrier of iodine between the seas and the land. Lovelock (1975) observed CH_3I in all his seawater samples, suggesting that it is a common metabolic product of marine algae. To quote from an earlier work of Lovelock and Maggs (1973):

> "Biological methylation is a ubiquitous tendency; nevertheless it was surprising to find a familiar organic chemical reagent distributed through the oceans."

Open ocean concentrations (Atlantic, Antarctic, and Caribbean) were around 1.35×10^{-9} mL of gas per mL of water. Coastal seawater concentrations are much higher, especially if seaweed beds are present.

The large brown kelp, "Laminaria," produces very high levels of CH_3I according to Lovelock. Ten times the open ocean concentrations of CH_3I were observed in the vicinity of "Laminaria digitata" beds in southwestern Ireland. But inshore algal beds like "Fucus" did not show such increases of CH_3I.

Lillian et al. (1975) observed CH_3I in the atmosphere to range from less than 1 pptv (background) to 3800 pptv (Bayonne, N.J.). They stated that a noteworthy characteristic feature of CH_3I is its general non-detectability at sites remote from the oceans. They attributed this non-detectability to its tropospheric reactivity.

Singh et al. (1977) observed average background concentrations between 2 and 3 pptv (the extremes being 1 and 120 pptv). Ambient CH_3I values as high at 61 pptv were observed during thunderstorms. They observed a significant difference between summer and winter background CH_3I values, the summer values being higher. They also observed gradients between marine and continental air masses.

Moyers and Duce (1972) studied the gaseous and particulate components of iodine in the marine atmosphere. Total gaseous iodine (both organically bound and inorganic) samples were collected on specially cleaned activated charcoal, after removing the particulate matter with an electrostatic precipitator. Simultaneously particulate samples were collected using a cascade impactor. The iodine collected was analyzed by NAA. Their observations were:

No correlation between gaseous iodine and

(i) particulate chlorine;

(ii) total seasalt (as Na) concentration in the atmosphere;

(iii) wind speed;

(iv) gaseous bromine.

Gaseous iodine correlated with particulate iodine and the I/Cl ratio of particulate matter. Gaseous iodine concentration was 3-4 times the particulate iodine concentration.

Rahn et al. (1976) measured the atmospheric iodine species as: particulate iodine, gaseous inorganic iodine, and gaseous organic iodine from the same air sample using different filters. The particulate matter was collected on Nuclepore® filters followed by inorganic iodine which was collected on LiOH-impregnated filters, and finally the organically bound iodine on activated charcoal, and all were analyzed by NAA. They concluded that of the inorganic and organic components of gaseous tropospheric halogens measured at four remote locations, the organic component contained the bulk of the halogen mass.

Rancher and Kritz (1980) studied the diurnal fluctuation of iodine in the tropical marine atmosphere. They measured only the particulate and inorganic iodine. They used Nuclepore® filters for trapping particulate matter and LiOH-impregnated cellulose filters for trapping inorganic iodine species, while passing organically bound iodine such as CH_3I. The analysis was by NAA. Unlike chlorine and bromine, they observed iodine to be greatly enriched in the marine aerosol compared to seawater. [This has also been observed by other investigators before: Miyaki and Tsunogai, 1963; Duce and Winchester, 1963]. Rancher and Kritz (1980) observed that gaseous inorganic iodine shows a pattern of day-night variation with daytime concentration being significantly higher than the preceding or following nighttime value. But there was no statistically significant difference between daytime and nighttime values of particulate iodine concentrations, and they suggested that marine aerosol is not a source of gaseous inorganic iodine. The observed nighttime depletion of gaseous inorganic iodine is not reflected in a corresponding increase in nighttime particulate iodine, nor can this depletion be attributed to the absorption at the sea surface since the coefficient of dry deposition is too small to account for the observed fast change in inorganic gaseous iodine. Therefore, they suggested that the only possibility is the dominance at nighttime of a gaseous inorganic iodine species not effectively trapped by LiOH-impregnated filters like $IONO_2$. [Chameides and Davis' (1980) model calculations predict a nighttime increase of $IONO_2$!]

Cicerone (1981) mentioned the trapping of gaseous inorganic iodine by bubbling air through aqueous solutions of KOH, LiOH, or K_2CO_3 after filtering out the particulate matter by Duce et al. (1965).

In the following chapters of this thesis the experimental techniques used in these measurements of CH_3I concentrations will be discussed, together with the distribution of CH_3I over the world.

I have measured the atmospheric concentration of CH_3I using Temperature-Programmed Electron-Capture Gas-Chromatography with freeze-out (TP-EC-GC). In addition to CH_3I, other trace gases such as N_2O, F-12, F-11, F-113, $CHCl_3$, CH_3CCl_3, CCl_4, TCE, and PCE have also been measured by this method. CH_3Br, F-21, and F-114 also have been observed though not quantitatively measured.

F-11 and CH_3CCl_3 are used as internal standards to check the precision of TP-EC-GC since they are also measured from the same sample cans using isothermal EC-GC with direct injection whose precision is maintained at ±1% at the 100 pptv level.

Several hundred air samples have been analyzed, dating back to 1977, from Point Barrow (Alaska) down to the South Pole, with Cape Meares (Oregon), Hawaii [at sea level and at Mauna Loa Observatory (MLO)], the Marshall Islands, Samoa, and Cape Grim (Tasmania). In addition, samples have been obtained from Cape Point (South Africa), Niwot Ridge and Parachute Creek (Colorado), Whiteface Mountain (New York), Irafoss (Iceland), and from off the Peruvian coast. Special studies have been done to find the altitudinal profiles of these trace gases at Barrow, Hawaii, Samoa, and Australia. Latitudinal variations have been studied from the samples collected during the GAMETAG flight, other ocean cruises, and from the samples routinely obtained from sites at Barrow to the South Pole.

In addition to these air samples, CH_3I concentrations in seawater, lakewater, rainwater, snow, and ice core samples have also been studied. Before analyzing these samples by TP-EC-GC, they were extracted using a modified McAuliffe technique (Hoyt, 1982).

Chapter 2

EXPERIMENTAL METHOD

Methyl iodide is analyzed in ambient air samples by Temperature-Programmed Electron-Capture Gas-Chromatography (TP-EC-GC). A Perkin-Elmer 3920B gas chromatograph is used with a Hewlett Packard 3388A Integrator. The electron capture detector on the gas chromatograph has a ^{63}Ni source and is operated at 350°C. The column is 10% SP2100 on 100/120 mesh Supelcoport of length 10' x 1/4" O.D. stainless steel. The temperature of the oven is programmed to start at +10°C with an initial time of 4 minutes followed by a rate of temperature increase of 16°C per minute to +80°C. The total run time for a sample is 20 minutes though CH_3I has a retention time of about 8 minutes, because, in addition to CH_3I, other species having longer retention times such as F-113, $CHCl_3$, CH_3CCl_3, CCl_4, TCE, and PCE are also studied by this method of TP-EC-GC. N_2O, F-12, and F-11 are also quantitatively measured. F-11 and CH_3CCl_3 are used as internal standards as they are routinely measured independently from the same air sample containers by direct analysis by isothermal EC-GC. The carrier gas is 95% argon and 5% CH_4 with a 62 cm^3 per minute flow rate.

When analyzing northern hemispheric samples, the same size used is 100 mL. For southern hemispheric samples and high altitude samples, 200 mL samples are used. This because TCE and PCE peaks are sometimes too small to be integrated, with the latter category, with the precision required if 100 mL samples are used. Also, South Pole samples sometimes have so little CH_3I the peak cannot be observed with just a

100 mL sample. For rainwater, seawater, snow, ice, and lakewater extractions, usually 100 mL samples are used, but in some instances 50 mL are used if the samples are suspected of having high concentrations of the species measured or if the sample size is limited.

The first and every fourth sample thereafter are from the calibration standard tank.

The samples (50, 100, or 200 mL) are trapped in a 6" x 1/4" O.D. U-tube filled with glass beads (60/80 mesh) by freezing out with liquid oxygen (at -183°C) and then thermally desorbing with hot water (at about 70°C) and injecting into the column.

Before loading up each sample, the whole sample loading system -- sample lines, syringe, and sample loop -- is flushed with 100 mL of zero air to avoid any contamination from the sample that was run earlier. If any sample was unusually "dirty" (i.e., concentration of any of the species measured was much larger than the usually observed levels), the sample loading system was flushed with even more zero air.

2.A. Verification of the CH_3I Peak and Calibration of Standard

Verification of the CH_3I peak was done by GC/MS at A.E.R.E., Harwell, England, and at the Oregon Graduate Center; the latter was done using the Finnigan GC/MS system. The GC/MS work at OGC was done using a "Scott Standard" having 9.37 ppm CH_3I (Figures 2.1 and 2.2).

The primary CH_3I standard was made by R. A. Rasmussen and S. A. Penkett at A.E.R.E., Harwell, England, by static dilution and gas chromatographic-mass spectrometry techniques.

C_{0-108} = CH_3I concentration in tank 0-108

C_I = CH_3I concentration in primary standard

C_{II} = CH_3I concentration in secondary standard; made by diluting the primary standard

V_{0-108} = volume of sample used from tank 0-108

V_I = volume of primary standard used to make secondary standard

V_{II} = volume of secondary standard used to calibrate 0-108

H_{0-108} = peak height of CH_3I for tank 0-108

H_{II} = peak height of CH_3I for secondary standard

$$C_{0-108} = \frac{C_{II}\ V_{II}\ H_{0-108}}{H_{II}\ V_{0-108}}$$

where

$$C_{II} = \frac{C_I\ V_I}{V_{II}}$$

From propagation of errors it can be shown that

$$\left(\frac{\Delta C_{0-108}}{C_{0-108}}\right)^2 = \left(\frac{\Delta C_{II}}{C_{II}}\right)^2 + \left(\frac{\Delta V_{II}}{V_{II}}\right)^2 + \left(\frac{\Delta H_{0-108}}{H_{0-108}}\right)^2 + \left(\frac{\Delta H_{II}}{H_{II}}\right)^2 + \left(\frac{\Delta V_{0-108}}{V_{0-108}}\right)^2$$

where

$$\left(\frac{\Delta C_{II}}{C_{II}}\right)^2 = \left(\frac{\Delta V_I}{V_I}\right)^2 + \left(\frac{\Delta C_I}{C_I}\right) + \left(\frac{\Delta V_{II}}{V_{II}}\right)$$

where Δx = error or uncertainty in x; that is, uncertainty in C_I is ΔC_I.

Therefore,

$$\left(\frac{\Delta C_{0-108}}{C_{0-108}}\right)^2 \approx 2\left(\frac{\Delta V_{II}}{V_{II}}\right)^2 + \left(\frac{\Delta V_I}{V_I}\right)^2 + \left(\frac{\Delta C_I}{C_I}\right)^2 + \left(\frac{\Delta H_{0-108}}{H_{0-108}}\right)^2 + \left(\frac{\Delta H_{II}}{H_{II}}\right)^2 + \left(\frac{\Delta V_{0-108}}{V_{0-108}}\right)^2$$

From the primary static dilutions done at A.E.R.E., Harwell, the absolute accuracy in C_I (in the primary standard) has been determined as ±25%. That is

$$\frac{\Delta C_I}{C_I} = \pm 0.25$$

$$\frac{\Delta H_{0-108}}{H_{0-108}} = \pm 0.02; \quad \frac{\Delta H_{II}}{H_{II}} = \pm 0.05; \quad \frac{\Delta V_{II}}{V_{II}} = \pm 0.05; \quad \frac{\Delta V_I}{V_I} = \pm 0.05;$$

$$\frac{\Delta V_{0-108}}{V_{0-108}} = \pm 0.01$$

Therefore

$$\frac{\Delta C_{0-108}}{C_{0-108}} = 0.27$$

The uncertainty in the absolute concentration in tank 0-108 is ±27%.

Zero air was used to dilute the more concentrated standard so that its concentration was of the same order as that of the working standard, which was assumed to be a few parts per trillion by volume, as the working standard was made of ambient air. (The work of Lovelock, Singh, etc., had showed the background CH_3I concentration to be around a few parts per trillion by volume.)

2.B. Linearity of the CH_3I Peak Height with Sample Size

50, 100, 150, and 200 mL samples from the standard calibration tank were run several times to check the linearity of the CH_3I peak height with sample size. The peak heights of N_2O, F-12, F-11, and CH_3CCl_3 were also recorded (Table 2.1).

The mean peak heights for each of these species for each sample size were normalized against the mean peak height at 50 mL. This was done to show the relative linearities of the peak heights with sample size. (By doing this we assume that the perfectly linear line for peak height vs. sample size passes through the origin and the 50 mL peak height point.) (Figure 2.3).

For CH_3I the normalized peak heights were within +3.0% and -7.7% of the perfectly linear values. These discrepancies may be due to minor leaks around the barrel of the sample syringe rather than to the efficiency of the freezeout system. The liquid oxygen trap we assumed to be perfect (Table 2.2).

2.C. Precision and Reproducibility

Two different sample sizes were used when analyzing samples by this method (TP-EC-GC): 100 mL and 200 mL. 100 mL samples were used for analyzing northern hemispheric samples and snow, rainwater, lakewater, and seawater extractions. For southern hemispheric samples, high altitude samples (including northern hemispheric), and when studying altitudinal profiles, 200 mL samples were used. This was done because, in general, the northern hemispheric samples usually had higher concentrations of almost all the trace gases studied by TP-EC-GC and could be determined quantitatively even with a 100 mL sample. In high altitude samples, CH_3I and other reactive trace gases were in lower concentrations, and therefore 200 mL samples were required. In the case of southern hemispheric samples, though CH_3I concentration could be determined with 100 mL samples, species such as PCE required 200 mL of the sample.

Over a period of 1-1/2 years, 100 mL-size samples from the standard tank (#0-108) were run 485 times with a mean peak height (CH_3I) of 11.71 units with a standard deviation of 1.09 units. Over the same period 200 mL samples from the standard tank were run 411 times with a mean peak height (CH_3I) of 22.76 units and a standard deviation of 2.52 units. Each day the samples were run the mean CH_3I peak height of the standard and the standard deviation were calculated. Also calculated was the precision for the day for the standard, defined as:

$$\text{Precision} = \frac{\text{standard deviation of } CH_3I \text{ peak height for standard tank}}{\text{mean peak height } (CH_3I) \text{ for standard tank}} \times 100\%$$

The precision was within 5%.

2.D. Stability of CH_3I in Sample Containers

In ALE tanks:

The stability of CH_3I in ALE tanks was studied over a period of 9 months. A total of 11 tanks were studied. The CH_3I concentration in these tanks remained within about 25% of the initial concentrations.

This was so except in the case of #0-083, which lost the CH_3I concentration by about 40% from the initial concentration (Table 2.3 and Figure 2.4).

The stability of CH_3I in ALE tanks is important as our calibration standards are ALE tanks, and the concentration of CH_3I in ALE tanks should not drift over long periods of time.

In 800 mL cans:

To study the stability of CH_3I in 800 mL stainless steel cans, in which most of our sampling is done, six cans were filled with ambient air and analyzed. They were analyzed again after two weeks to see whether the CH_3I concentration had changed. Two weeks were allowed because that is about the time lapse between time of collection and time of analysis of our regular samples. Only one can showed any significant change in CH_3I concentration (Table 2.4). In addition to this special study, all cans that repeatedly gave significantly higher CH_3I concentrations were noted, and the corresponding numbers were not considered when analyzing the CH_3I data. These included 1 L beaker type cans. Another special study was done with some of these "problem" 1 L cans. The six cans under study were flushed well and filled with air at Cape Meares. When analyzed soon after, two cans showed high CH_3I concentration. After two weeks, the analyses showed no change in CH_3I concentration while the three others showed very high concentrations, including the two cans that initially showed high levels of CH_3I (Table 2.5).

2.E. Comparison of TP-EC-GC with Routine Isothermal EC-GC

The temperature-Programmed EC-GC method was compared with the Routine Isothermal EC-GC method using two internal standards, namely F-11 and CH_3CCl_3. These two trace gases were used because both are measured by both methods. Another reason for selecting the Routine EC-GC method to check the reliability of the TP-EC-GC method is that it has been used over several years to measure F-11 and CH_3CCl_3 (also N_2O, F-12, and CCl_4), and is known to be reliable (for precision, reproducibility, and interlaboratory comparison studies).

The F-11 and CH_3CCl_3 concentrations of 72 ALE tanks were used for the comparison. Using the F-11 and CH_3CCl_3 peak height for the #0-108 standard tank, the precision of analysis for F-11 and CH_3CCl_3 was calculated:

$$\text{precision} = \frac{\text{standard deviation}}{\text{mean peak height}} \times 100\%$$

for F-11, precision = $100\ p_{F-11}\ \% = 3.2\%$

for CH_3CCl_3, precision = $100\ p_{CH_3CCl_3}\ \% = 2.7\%$

It has been observed that the responses of the TP-EC-GC instrument and the Routine EC-GC instrument are linear with the F-11 and CH_3CCl_3 concentrations.

Since the comparison of TP-EC-GC was done against the Routine EC-GC, which is a well-established method for measuring F-11 and

CH_3CCl_3, it was assumed that the concentrations obtained from it (the Routine EC-GC method) were the actual concentrations.

The linear correlation coefficient (r) was calculated between the two methods for both gases.

$$r = \frac{N\Sigma x_i y_i - \Sigma x_i y_i}{[N\Sigma x_i^2 - (\Sigma x_i)^2]^{\frac{1}{2}}[N\Sigma y_i^2 - (\Sigma y_i)^2]^{\frac{1}{2}}}$$

i.e., r_{F-11} and $r_{CH_3CCl_3}$ were calculated.

The "x" concentrations correspond to the Routine EC-GC.

The "y" concentrations to the TP-EC-GC.

$$r_{F-11} = 0.87$$

$$r_{CH_3CCl_3} = 0.97$$

χ^2 tests were done for F-11 and CH_3CCl_3 to see how well the concentrations from TP-EC-GC agree with the concentrations from the Routine EC-GC method.

$$\chi^2 = \Sigma\{ \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2\}$$

for ν degrees of freedom

$$\nu = N - n - 1$$

Since both instruments (TP-EC-GC and Routine EC-GC) have linear responses for concentrations we are observing, n can be taken as 1. $\therefore$ $\nu = 70$ because we have considered 72 ALE tanks for the study. Since $y(x_i) = x_i$, $\chi^2 = \Sigma\{\frac{1}{\sigma^2} [y_i - x_i]^2\}$. Recall that precision for F-11 and CH_3CCl_3 peak heights was 3.2% and 2.7% respectively.

$$p_{F-11} = 0.032 \text{ and } p_{CH_3CCl_3} = 0.027$$

Therefore, the uncertainties in y_i(i.e., σ_i) can be taken as $\sigma_i = py_i$; i.e., $\sigma_{i_{F-11}} = p_{F-11}y_i$ and $\sigma_{i_{CH_3CCl_3}} = p_{CH_3CCl_3}y_i$.

$$\chi^2 = \frac{1}{p^2} \Sigma {\frac{y_i - x_i}{y_i}}^{2}$$

For F-11 $$\chi^2 = \frac{1}{(0.032)^2} \Sigma {\frac{y_i - x_i}{y_i}}^{2}$$

and for CH_3CCl_3 $$\chi^2 = \frac{1}{(0.027)^2} \Sigma {\frac{y_i - x_i}{y_i}}^{2}$$

Reduced chi square = $\chi^2_\nu = \chi^2/\nu$ $\quad \nu = 70$

For the 72 ALE tanks that were used for the comparison of the two methods:

$$\chi^2{}_{\nu_{F-11}} = 0.812$$

$$\chi^2{}_{\nu_{CH_3CCl_3}} = 0.541$$

By studying χ^2 tables (for $\nu = 70$), for CH_3CCl_3 $P > 99\%$ and for F-11 $90\% > P > 80\%$. One can see that F-11 does not compare as well as CH_3CCl_3 between the two methods. The correlation coefficients were also better for CH_3CCl_3 than for F-11 (0.97 and 0.87 respectively).

One would expect the two gases to behave similarly in the comparison between the two methods. The calculations show otherwise. There is a reason for the dissimilarity of how the two gases compare.

The TP-EC-GC instrument has a temperature program with a 4-minute hold at 10°C followed by a temperature increase at a rate of 16°C per minute up to 80°C, which is the final temperature. The F-11 peak comes out in the region of the temperature program when the temperature is rising with the liquid N_2 supply still on (the liquid N_2 supply shuts off at about 55°C). The F-11 peak height is sensitive to the temperature of the GC oven and therefore to any change in the rate of temperature rise. Ideally one would expect the temperature program to be perfect each time the instrument is run since the output pressure of the liquid N_2 tank is preset and any changes or deviations from the set temperature programm corrected by the GC oven heater. But depending on when the liquid N_2 tank was filled and when the sample was run, the temperature can deviate from the set programs slightly, and as a result the F-11 peak height can deviate slightly from the ideal behavior. Considering this and the fact that the TP-EC-GC method uses a much larger sample size than the Routine EC-GC (100 mL or 200 mL vs. 5 mL), the agreement of F-11 results between the two methods is quite good.

Overall, when we consider F-11 and CH_3CCl_3 to compare the TP-EC-GC with the Routine EC-GC method, we can say that there is a good agreement between the two methods.

Table 2.1

Linearity of CH_3I (and N_2O, F-12, F-11, and CH_3CCl_3) Peak Height with Sample Size*

Sample Size (mL)		N_2O	F-12	F-11	CH_3I	CH_3CCl_3
50	n	8	8	8	7	8
	$\bar{x}$	1576.59	237.14	430.73	5.27	134.15
	σ	16.66	5.91	18.10	0.90	3.62
	$\sigma/\bar{x} \times 100$	1.1%	2.5%	4.2%	17.2%	2.8%
100	n	15	15	15	15	15
	$\bar{x}$	2915.92	423.62	899.99	9.74	240.37
	σ	47.21	13.56	54.80	1.78	6.08
	$\sigma/\bar{x} \times 100$	1.5%	3.1%	6.2%	18.6%	2.7%
150	n	8	8	8	8	8
	$\bar{x}$	4350.02	606.99	1393.69	16.29	353.00
	σ	67.20	17.11	64.63	2.51	16.35
	$\sigma/\bar{x} \times 100$	1.4%	2.8%	4.5%	15.3%	4.5%
200	n	8	8	8	8	8
	$\bar{x}$	5716.22	786.19	1837.98	19.46	460.11
	σ	39.09	16.97	64.48	2.04	13.80
	$\sigma/\bar{x} \times 100$	0.6%	2.3%	3.4%	10.5%	3.1%

*Data from special test done on July 17, 21, and 22, 1981.

Table 2.2

The peak heights were normalized for each species (N_2O, F-12, F-11, CH_3I, and CH_3CCl_3) against the peak height at 50 mL sample size, i.e., peak height of the 50 mL sample size was taken to be 1.000 to show the relative linearity in peak height against sample size.

Sample Size (mL)		N_2O	F-12	F-11	CH_3I	CH_3CCl_3
50	x	1.000	1.000	1.000	1.000	1.000
	σ	0.011	0.025	0.042	0.172	0.028
100	x	1.850	1.786	2.089	1.848	1.792
	σ	0.031	0.058	0.128	0.337	0.046
150	x	2.759	2.560	3.326	3.091	2.631
	σ	0.042	0.073	0.150	0.478	0.122
200	x	3.626	3.315	4.267	3.693	3.430
	σ	0.025	0.071	0.150	0.387	0.102

Table 2.3

Stability of CH$_3$I in ALE Tanks
Concentrations and Percentage Deviations from Initial Analysis

	Feb. 1981	Apr. 1981	June 1981	July 1981	Aug. 1981	Sept. 1981	Nov. 1981
Tank #	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation
0-091				0.7	1.1	0.9	0.7
A				0.0%	+60.9%	+24.6%	-5.8%
0-057				1.0	0.9	0.7	0.8
B				0.0%	+15.0%	-28.0%	-18.0%
0-070	0.6			0.6		0.5	0.4
C	0.0%			0.0%		-15.8%	+24.6%
0-077	2.0			2.0		1.7	1.7
D	0.0%			0.0%		-12.6%	-15.2%
0-026	0.4			0.4		0.5	0.4
E	0.0%			0.0%		+34.3%	+25.7%
0-029	1.6			1.3		1.3	1.7
F	0.0%			-16.0%		-15.3%	+10.3%

Table 2.3 (continued)

	Feb. 1981	Apr. 1981	June 1981	July 1981	Aug. 1981	Sept. 1981	Nov. 1981
Tank #	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation	Conc. pptv Deviation
0-083	4.7					3.2	2.8
G	0.0%					-32.6%	-41.0%
-0-50	0.6			0.6		0.5	
H	0.0%			-1.7%		-8.6%	
0-161			1.4	1.3	1.3		
I			0.0%	-9.0%	-8.4%		
0-011		8.0				7.3	
J		0.0%				-8.6%	
0-123		1.3		1.2			
K		0.0%		-7.5%			

Table 2.4

CH_3I Stability Test - 800 mL Cans

Filled 12/27/82 at Cape Meares, Oregon

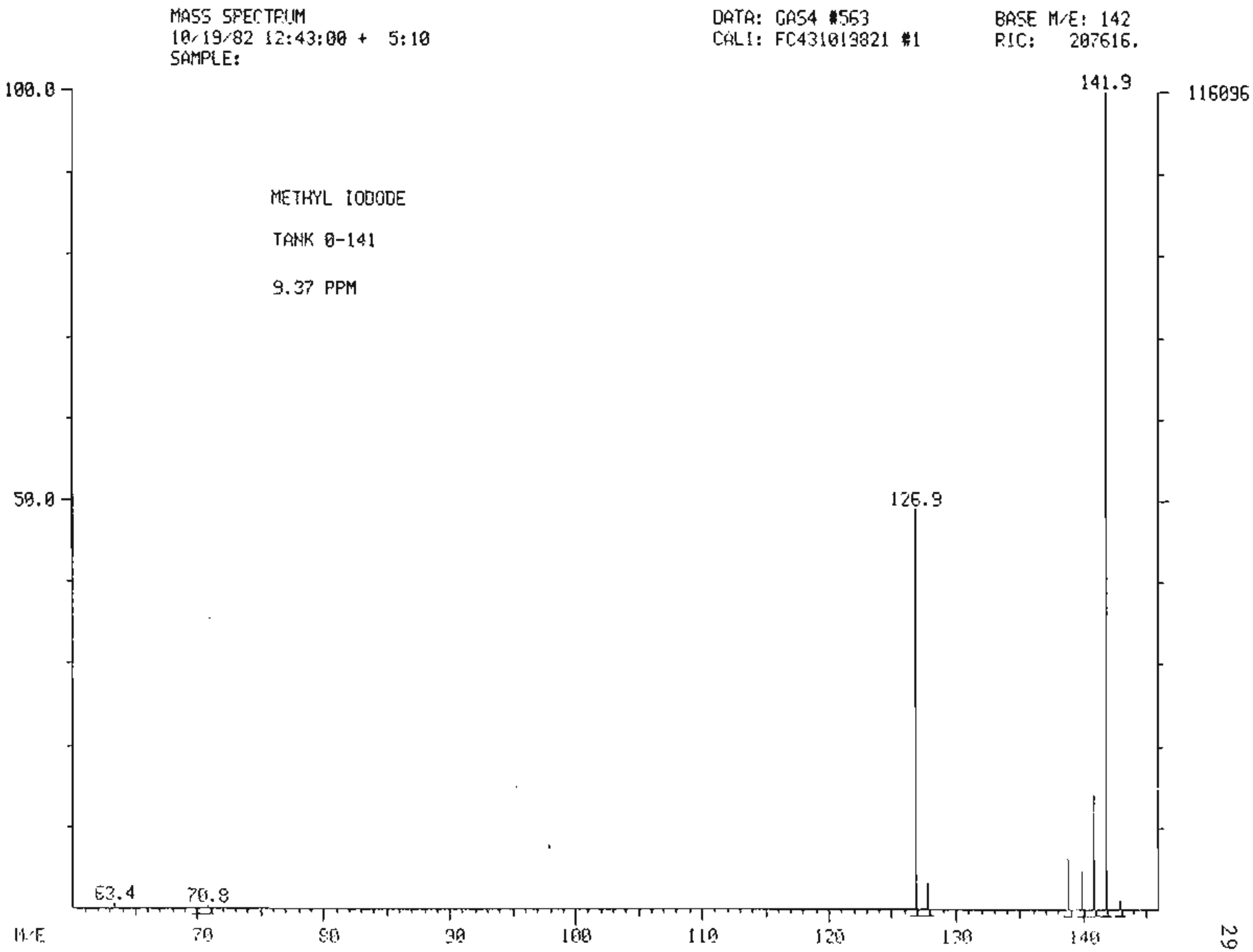
	CH_3I Concentration (pptv)	
Can #	First Analysis 12/29/82	Second Analysis 01/11/83
900	0.3	0.5
901	0.4	0.9
902	0.7	3.3
903	0.4	0.5
904	0.5	0.5
905	0.5	0.5

Table 2.5

CH_3I Stability Test - 1 L Cans

Filled 12/27/82 at Cape Meares, Oregon

Can #	CH_3I Concentration (pptv) First Analysis 12/30/82	Second Analysis 01/10/83
80	0.9	1.1
98	3.4	4.8
64	0.8	12.8
26	3.4	14.1
109	0.4	0.6
35	0.5	0.5



MASS SPECTRUM
10/19/82 12:43:00 + 5:10
SAMPLE:

DATA: GAS4 #563
CALI: FC431019821 #1

BASE M/E: 142
RIC: 207616.

METHYL IODODE

TANK 0-141

9.37 PPM

Figure 2.1

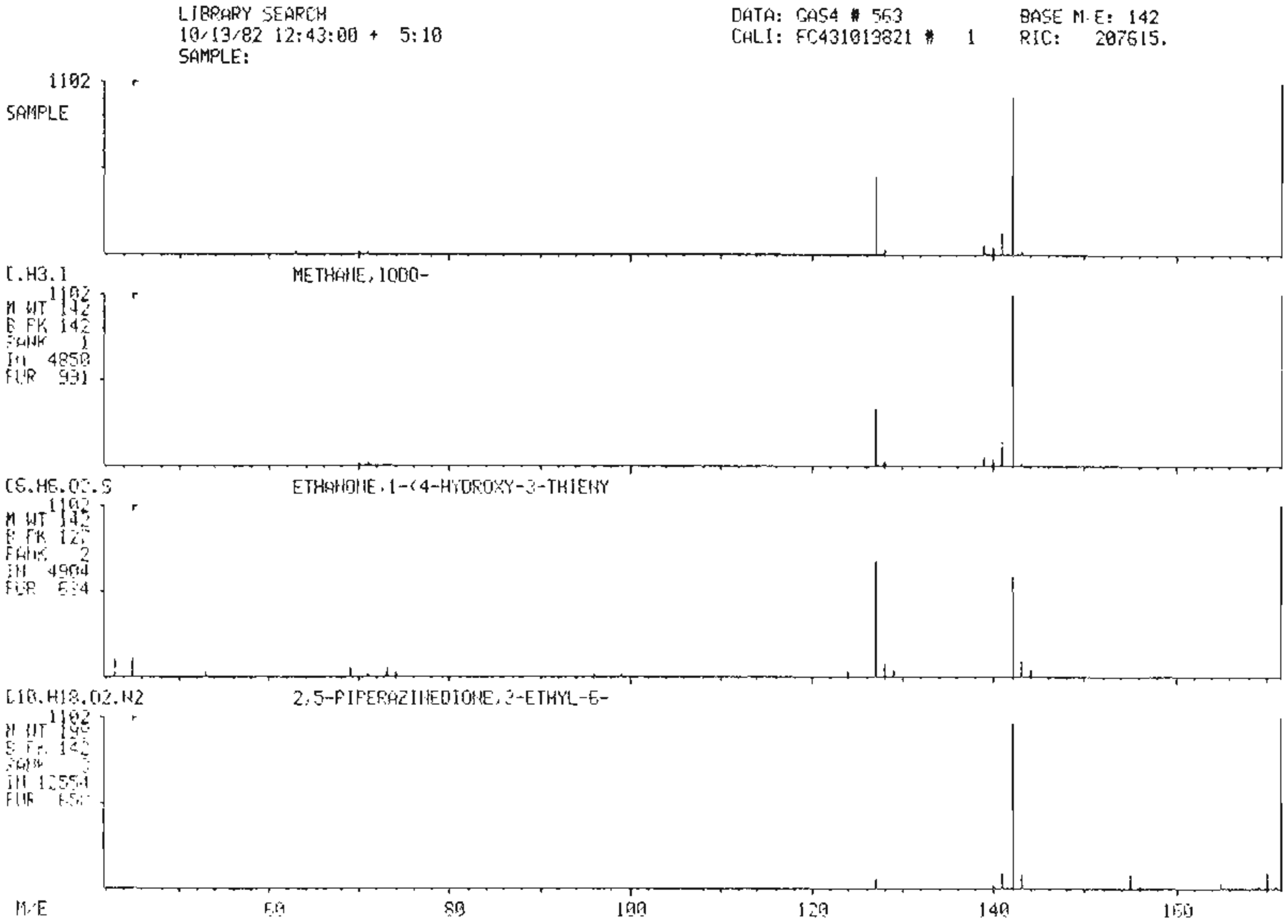

LIBRARY SEARCH
10/13/82 12:43:00 + 5:10
SAMPLE:
DATA: GAS4 # 563
CALI: FC431013821 # 1
BASE M/E: 142
RIC: 207615.
1102
SAMPLE
C.H3.I
METHANE, IODO-
1102
M WT 142
B PK 142
RANK 1
IN 4850
PUR 931
C6.H6.O2.S
ETHANONE, 1-(4-HYDROXY-3-THIENY
1102
M WT 142
B PK 127
RANK 2
IN 4904
PUR 634
C10.H18.O2.N2
2,5-PIPERAZINEDIONE, 3-ETHYL-6-
1102
M WT 198
B PK 142
RANK 3
IN 12554
PUR 650
M/E
60
80
100
120
140
160

Figure 2.2

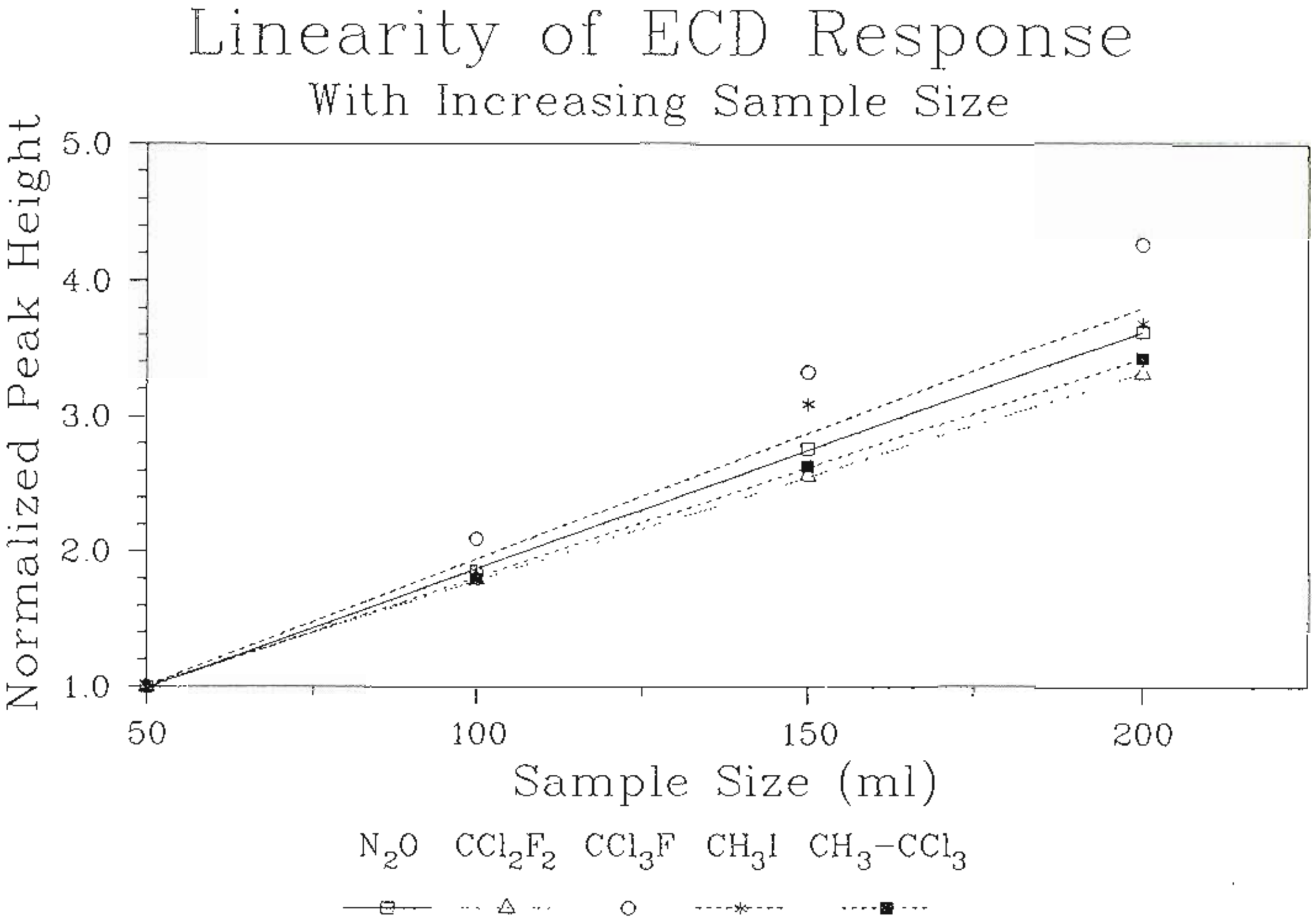

Linearity of ECD Response
With Increasing Sample Size
Normalized Peak Height
5.0
4.0
3.0
2.0
1.0
50
100
150
200
Sample Size (ml)
N_2O
CCl_2F_2
CCl_3F
CH_3I
CH_3-CCl_3

Figure 2.3

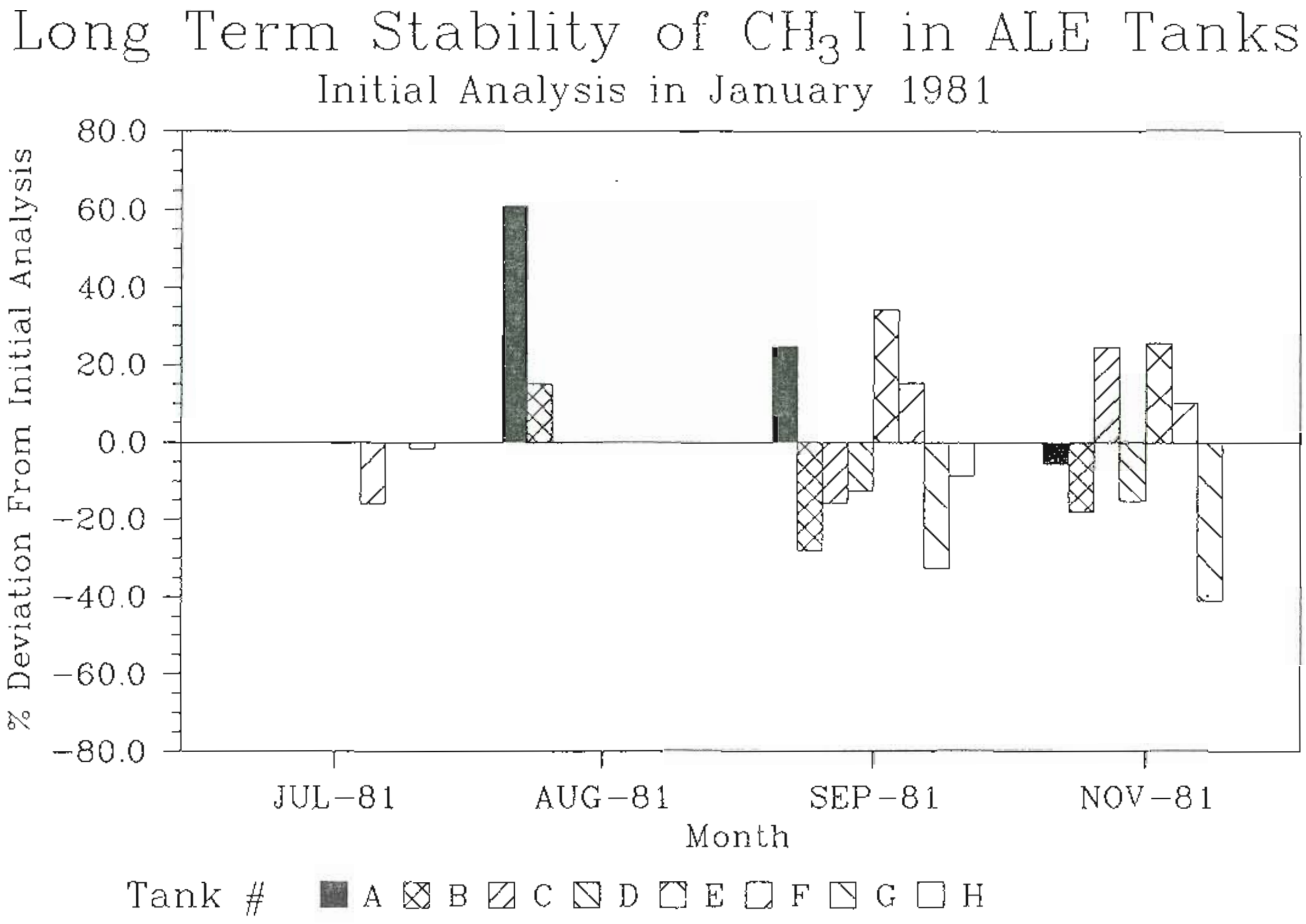

Long Term Stability of CH_3I in ALE Tanks
Initial Analysis in January 1981
% Deviation From Initial Analysis
80.0
60.0
40.0
20.0
0.0
-20.0
-40.0
-60.0
-80.0
JUL-81
AUG-81
SEP-81
NOV-81
Month
Tank #
A
B
C
D
E
F
G
H

Figure 2.4

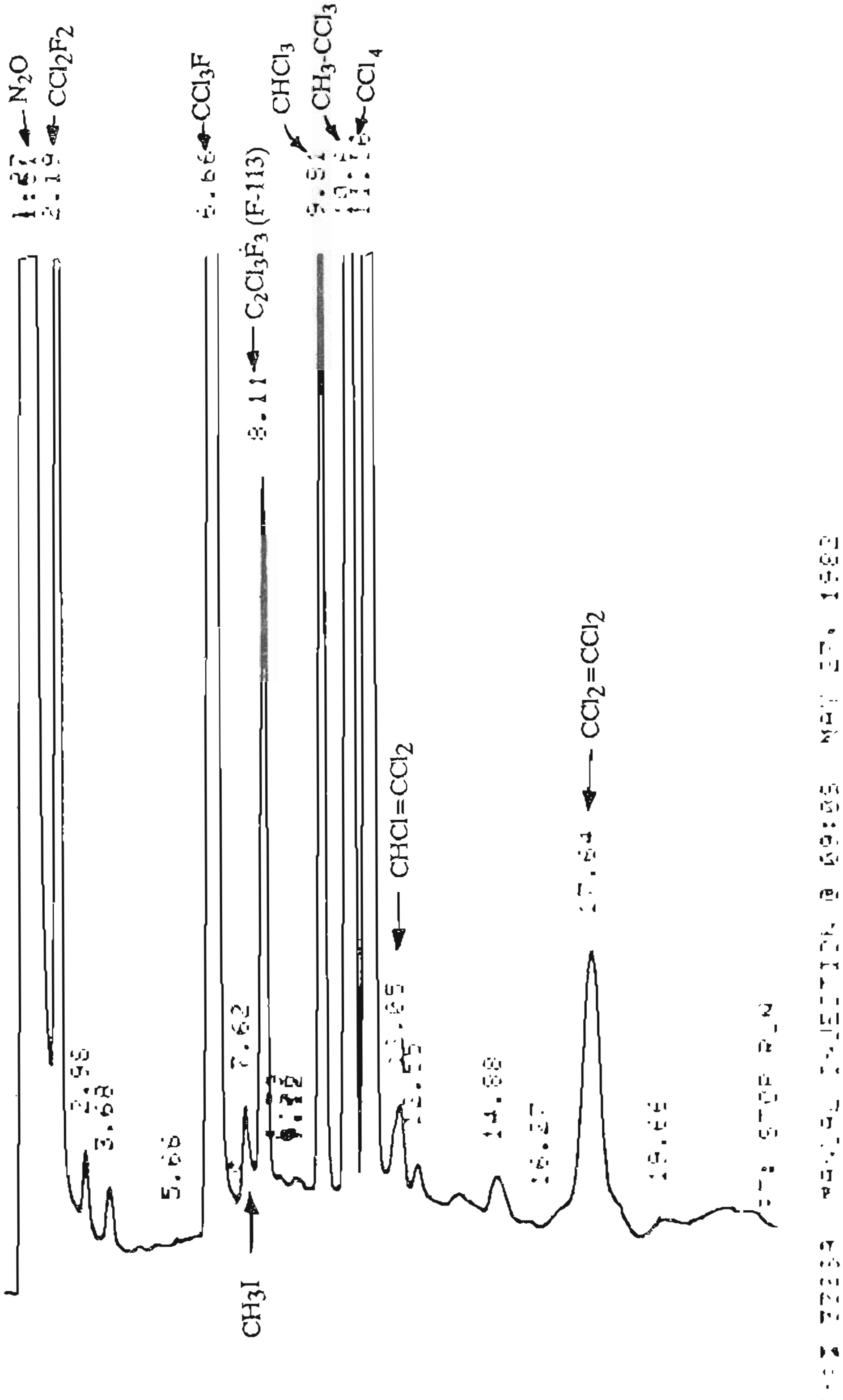

N$_2$O
CCl$_2$F$_2$
CCl$_3$F
C$_2$Cl$_3$F$_3$ (F-113)
CHCl$_3$
CH$_3$-CCl$_3$
CCl$_4$
CH$_3$I
CHCl=CCl$_2$
CCl$_2$=CCl$_2$
1.27
2.19
3.68
5.66
6.66
7.62
8.11
14.88
16.27
17.64

Figure 2.5

Chapter 3

SEASONAL VARIATIONS AND LONGTERM TRENDS OF CH_3I CONCENTRATION

The seasonal variations of atmospheric CH_3I concentration can be studied from samples obtained from five sampling stations. Point Barrow, Alaska; the Pacific Northwest, Cape Meares, Oregon; Mauna Loa and Cape Kumukahi, Hawaii; Samoa.

Point Barrow, Alaska: From a direct observation of the plot of CH_3I concentration with time, it is difficult to see seasonal variations clearly, but a plot of monthly average CH_3I concentration with month shows a low in April and a high in July (0.4 and 1.5 pptv, respectively), with the rest of the months showing a concentration around 0.8 pptv (except June, which is also high at 1.3 pptv) (Table 3.1 and Figure 3.1).

Pacific Northwest, Cape Meares, Oregon: The monthly average CH_3I concentration, when plotted against the month, shows a maximum around August-September-October of about 1.8 pptv and a minimum of about 1.0 pptv around February-March-April (Table 3.2 and Figure 3.2).

Cape Kumukahi and Mauna Loa, Hawaii: Cape Kumukahi has a maximum monthly averaged CH_3I concentration of 4.0 pptv in July, with the lowest in February and March (of 1.7 pptv). January 2.4 pptv) and June (2.5 pptv) are also higher than the rest of the year between 1.8 and 2.0 pptv. Mauna Loa on the other hand is just the opposite, with the highest concentrations in February and March (of 0.9 pptv) and the lowest in June (0.3 pptv). When Cape Kumukahi and Mauna Loa CH_3I concentrations (monthly averages) are plotted on the same graph, it is readily observed that the maximum at Mauna Loa coincides (the months) with the lowest concentration months at Cape Kumukahi and vice versa. It is interesting to see that the difference in monthly average concentration between Cape Kumukahi and Mauna Loa also follows a seasonal variation similar to that of Cape Kumukahi, with a low in February-March and a high in June-July (Figure 3, Tables 3.3 and 3.4).

Samoa: The lowest monthly average CH_3I concentration is in April (1.1 pptv) and the highest in August (2.6 pptv). The rest of the months the concentration varies between about 1.4 and 1.9 pptv (Figure 3.4 and Table 3.5).

3.A. Longterm Variations of CH_3I Concentration

There are no apparent longterm changes in the CH_3I concentration. The CH_3I data for Cape Meares, Oregon, do not show any increasing (or decreasing) trend. The plot of CH_3I concentration vs. time, going back to 1978, shows seasonal variations but no longterm trend. Though the data are limited to a little over a year for the other stations (Barrow, Cape Kumukahi, Mauna Loa, and Samoa), they also do not show any longterm variations in the CH_3I concentration (Figure 3.5 and Table 3.6).

Table 3.1

Monthly Average CH_3I Concentration

Barrow, Alaska

Month	Number of Samples	CH_3I pptv
January	7	0.7 ± 0.1
February	14	1.0 ± 0.4
March	33	0.6 ± 0.3
April	27	0.4 ± 0.2
May	14	0.8 ± 0.5
June	6	1.3 ± 0.3
July	10	1.5 ± 0.7
August	9	0.6 ± 0.3
September	9	0.7 ± 0.2
October	2	0.7 ± 0.0
November	--	
December	8	0.7 ± 0.2

Table 3.2

Monthly Average CH_3I Concentration

Pacific Northwest - Cape Meares, Oregon
1978-1982

Month	Number of Samples	CH_3I pptv
January	7	1.1 ± 0.4
February	8	1.0 ± 0.8
March	4	1.0 ± 0.2
April	30	1.0 ± 0.4
May	2	1.5 ± 0.8
June	6	1.4 ± 0.3
July	11	1.4 ± 0.2
August	5	1.8 ± 0.3
September	5	1.6 ± 0.2
October	17	1.7 ± 0.8
November	12	1.1 ± 0.3
December	7	1.3 ± 0.4

Table 3.3

Monthly Average CH_3I Concentration

Cape Kumukahi, Hawaii

Month	Number of Samples	CH_3I pptv
January	4	2.4 ± 1.0
February	10	1.7 ± 0.4
March	16	1.7 ± 0.6
April	18	1.8 ± 0.6
May	15	1.8 ± 0.5
June	5	2.5 ± 0.4
July	14	4.0 ± 1.9
August	8	1.8 ± 0.5
September	8	2.0 ± 0.9
October	--	
November	--	
December	9	2.0 ± 0.5

Table 3.4

Monthly Average CH_3I Concentration

Mauna Loa Observatory, Hawaii

Month	Number of Samples	CH_3I pptv
January	3	0.7 ± 0.2
February	11	0.9 ± 0.4
March	19	0.9 ± 0.5
April	18	0.8 ± 0.3
May	20	0.6 ± 0.4
June	11	0.3 ± 0.2
July	11	0.4 ± 0.3
August	8	0.4 ± 0.3
September	10	0.4 ± 0.3
October	3	0.6 ± 0.4
November	--	
December	5	0.3 ± 0.2

Table 3.5

Monthly Average CH_3I Concentration

Samoa

Month	Number of Samples	CH_3I pptv
January	6	1.7 ± 0.9
February	13	1.6 ± 0.7
March	9	1.8 ± 0.6
April	18	1.1 ± 0.5
May	13	1.6 ± 0.4
June	7	1.4 ± 0.4
July	9	1.7 ± 0.4
August	13	2.0 ± 1.5
September	8	1.9 ± 0.8
October	5	1.8 ± 1.0
November	3	1.5 ± 0.6
December	6	1.5 ± 0.2

Table 3.6

Pacific Northwest Monthly CH_3I Concentrations - ALE Tanks

Date Collected (Month/Year)	n	CH_3I (pptv)
April/1978	12	1.2 ± 0.2
June	4	1.4 ± 0.1
October	6	1.1 ± 0.1
November	5	0.8 ± 0.0
December	1	0.8
January/1979	3	0.8 ± 0.1
February	2	1.0 ± 0.3
April	2	1.1 ± 0.2
May	1	1.8
July	1	0.8
August	3	2.0 ± 0.4
October	5	2.3 ± 0.2
November	1	0.8
January/1980	3	1.2 ± 0.1
February	1	0.5
March	2	1.0 ± 0.2
April	4	1.0 ± 0.2
June	2	1.1 ± 0.0
July	6	1.3 ± 0.1
August	2	1.5 ± 0.1
September	2	1.7 ± 0.1
October	3	1.2 ± 0.1
November	4	1.2 ± 0.1
December	4	1.4 ± 0.2
January/1981	3	0.7 ± 0.0
February	4	0.7 ± 0.3
March	1	1.2
April	3	1.2 ± 0.3
May	1	0.9
July	4	1.4 ± 0.1
August	1	2.1
September	2	1.7 ± 0.2
November	2	1.4 ± 0.4
December	3	1.1 ± 0.2
January/1982	1	1.0
February	3	0.8 ± 0.2
March	1	0.9
April	2	0.7 ± 0.4
May	1	1.1
June	1	1.3

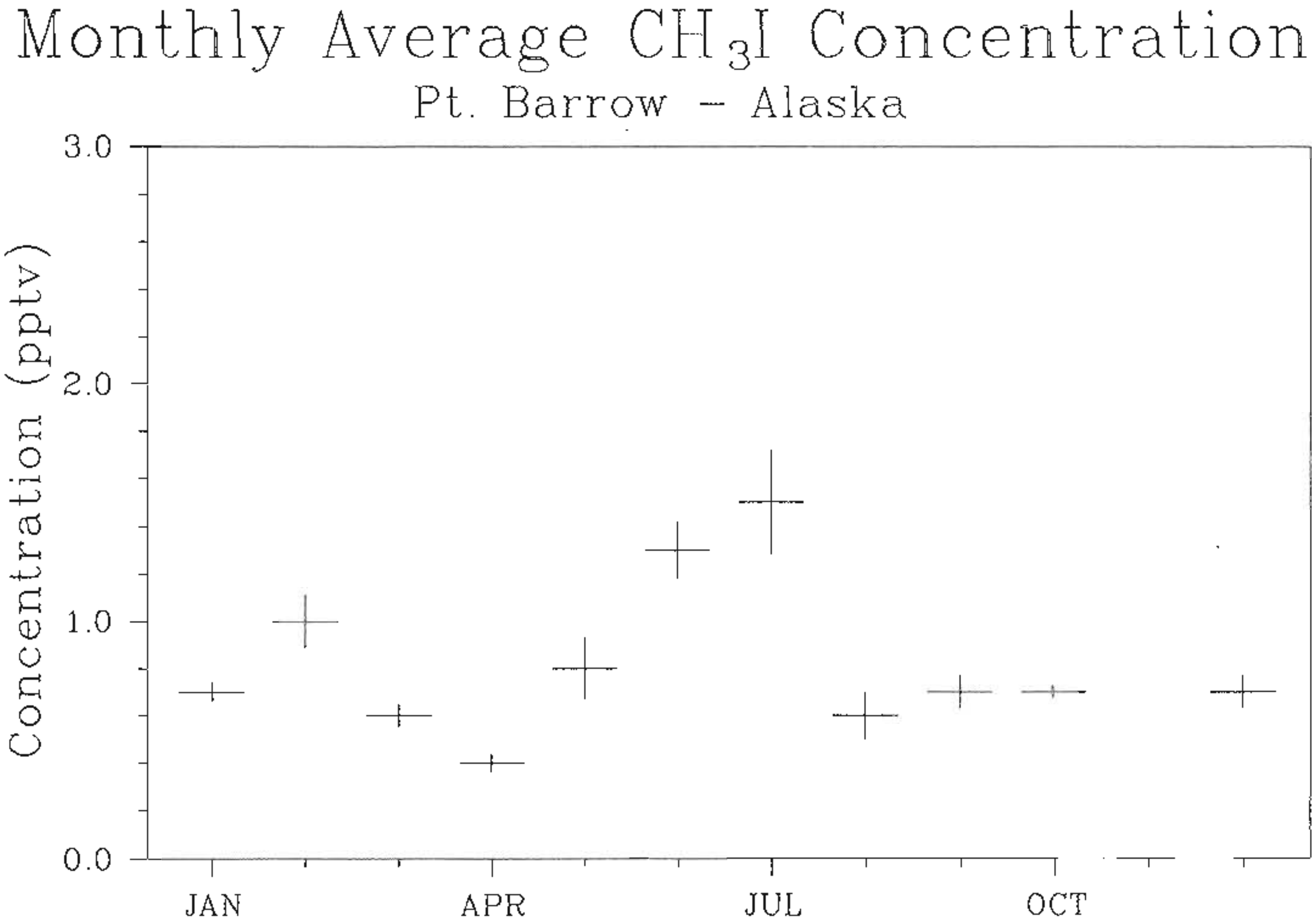

Monthly Average CH_3I Concentration
Pt. Barrow - Alaska
Concentration (pptv)
3.0
2.0
1.0
0.0
JAN
APR
JUL
OCT

Figure 3.1

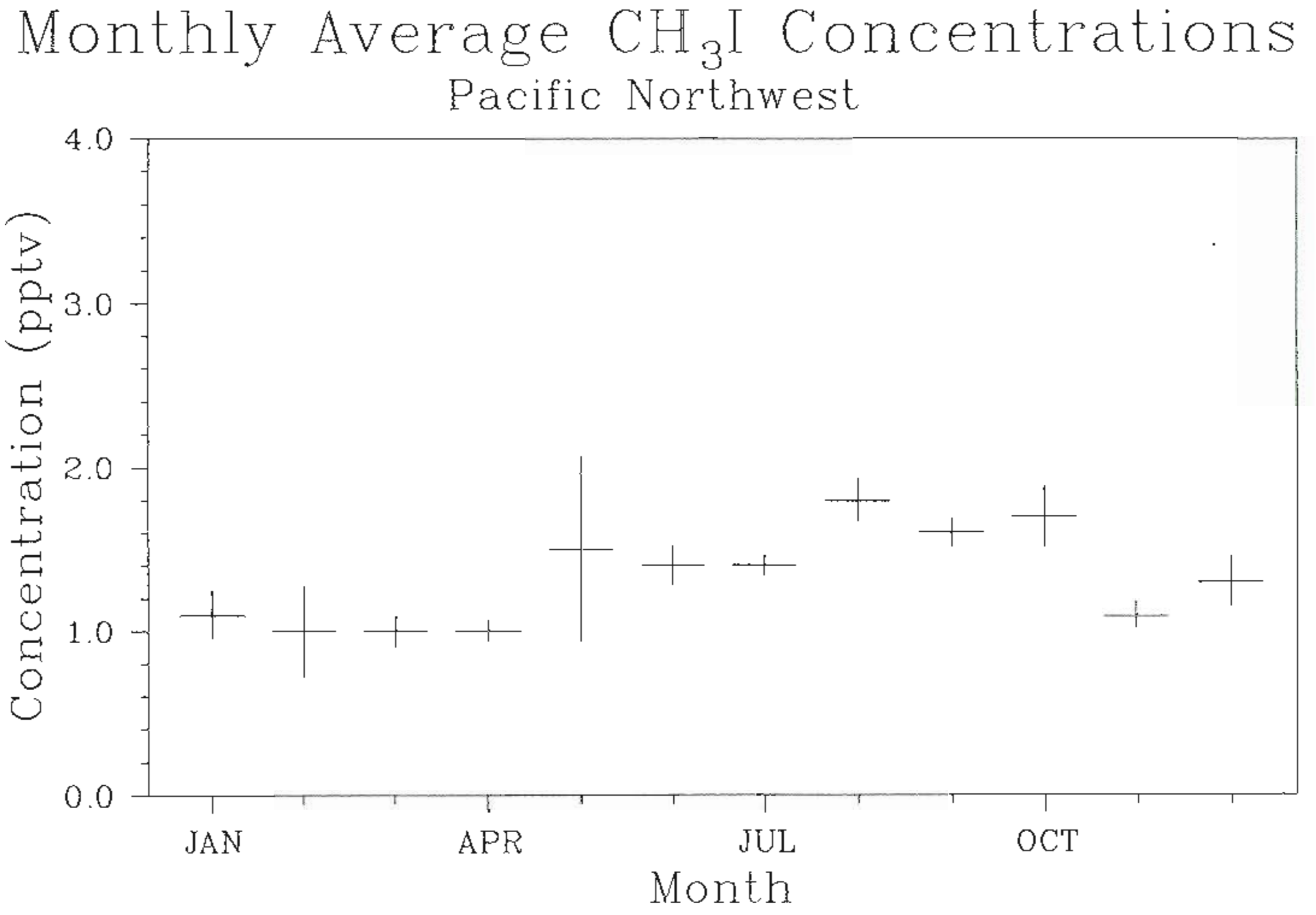

Monthly Average CH_3I Concentrations
Pacific Northwest
Concentration (pptv)
4.0
3.0
2.0
1.0
0.0
JAN
APR
JUL
OCT
Month

Figure 3.2

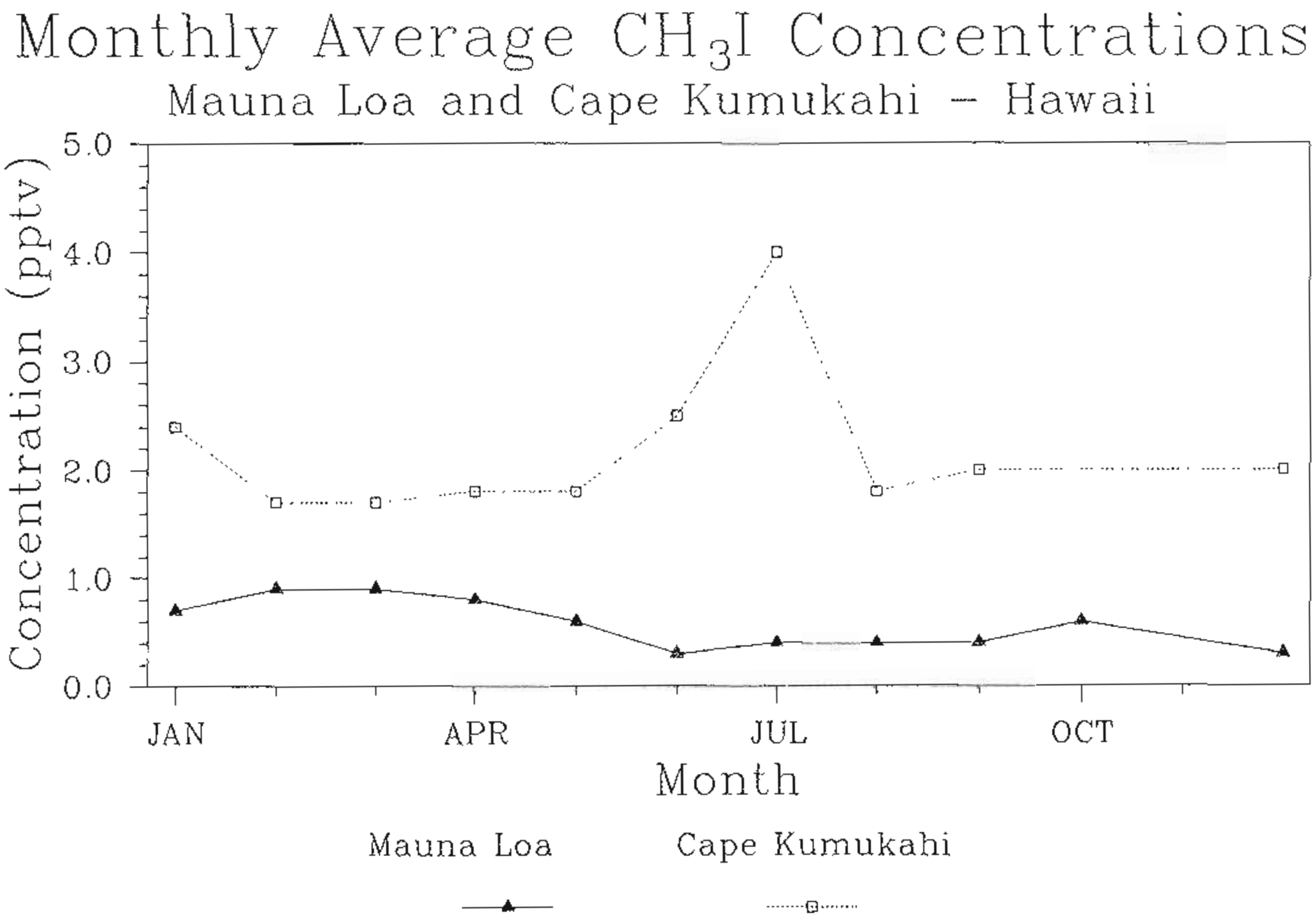

Monthly Average CH3I Concentrations
Mauna Loa and Cape Kumukahi - Hawaii
Concentration (pptv)
5.0
4.0
3.0
2.0
1.0
0.0
JAN
APR
JUL
OCT
Month
Mauna Loa
Cape Kumukahi

Figure 3.3

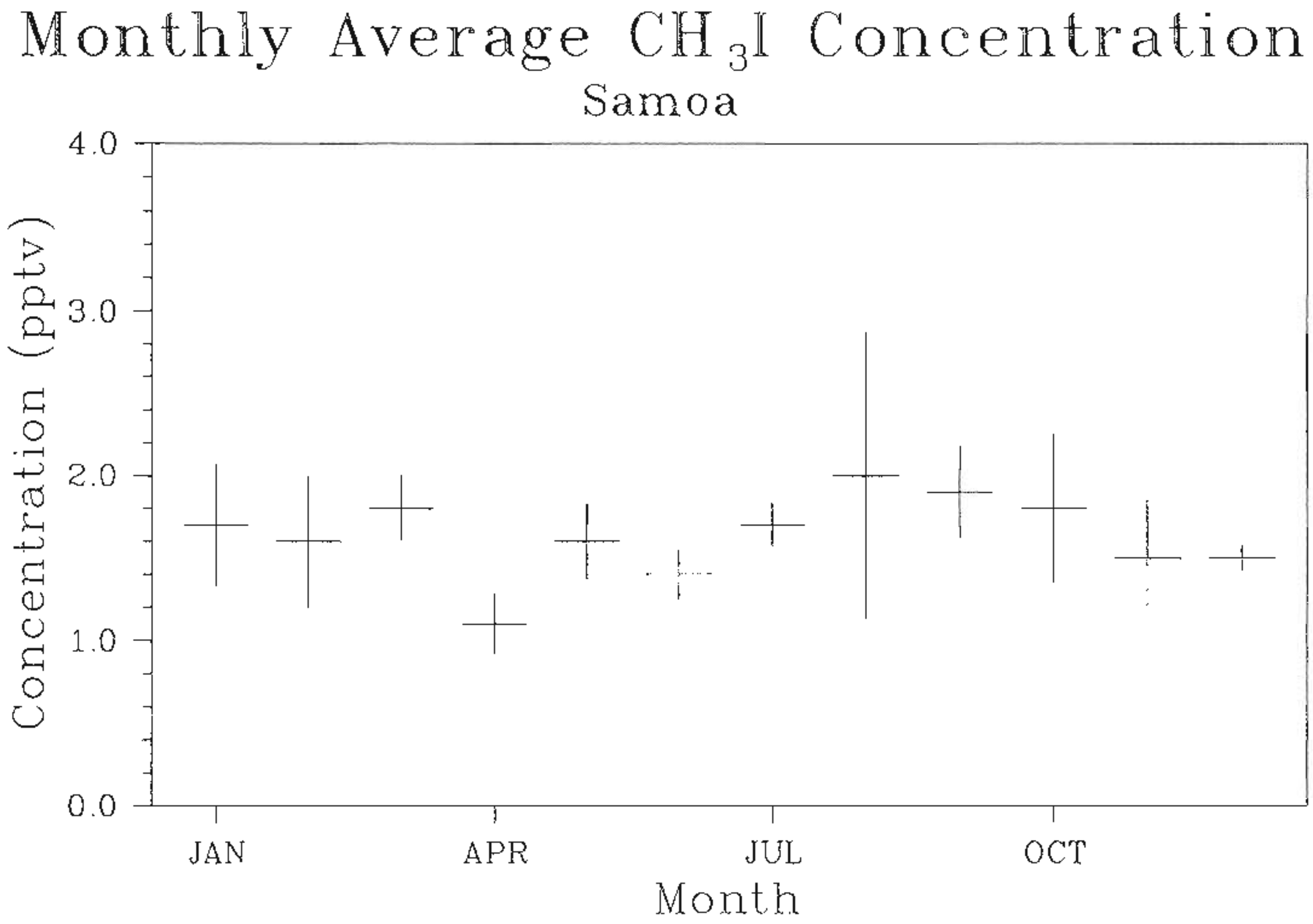

Monthly Average CH_3I Concentration
Samoa
Concentration (pptv)
4.0
3.0
2.0
1.0
0.0
JAN
APR
JUL
OCT
Month

Figure 3.4

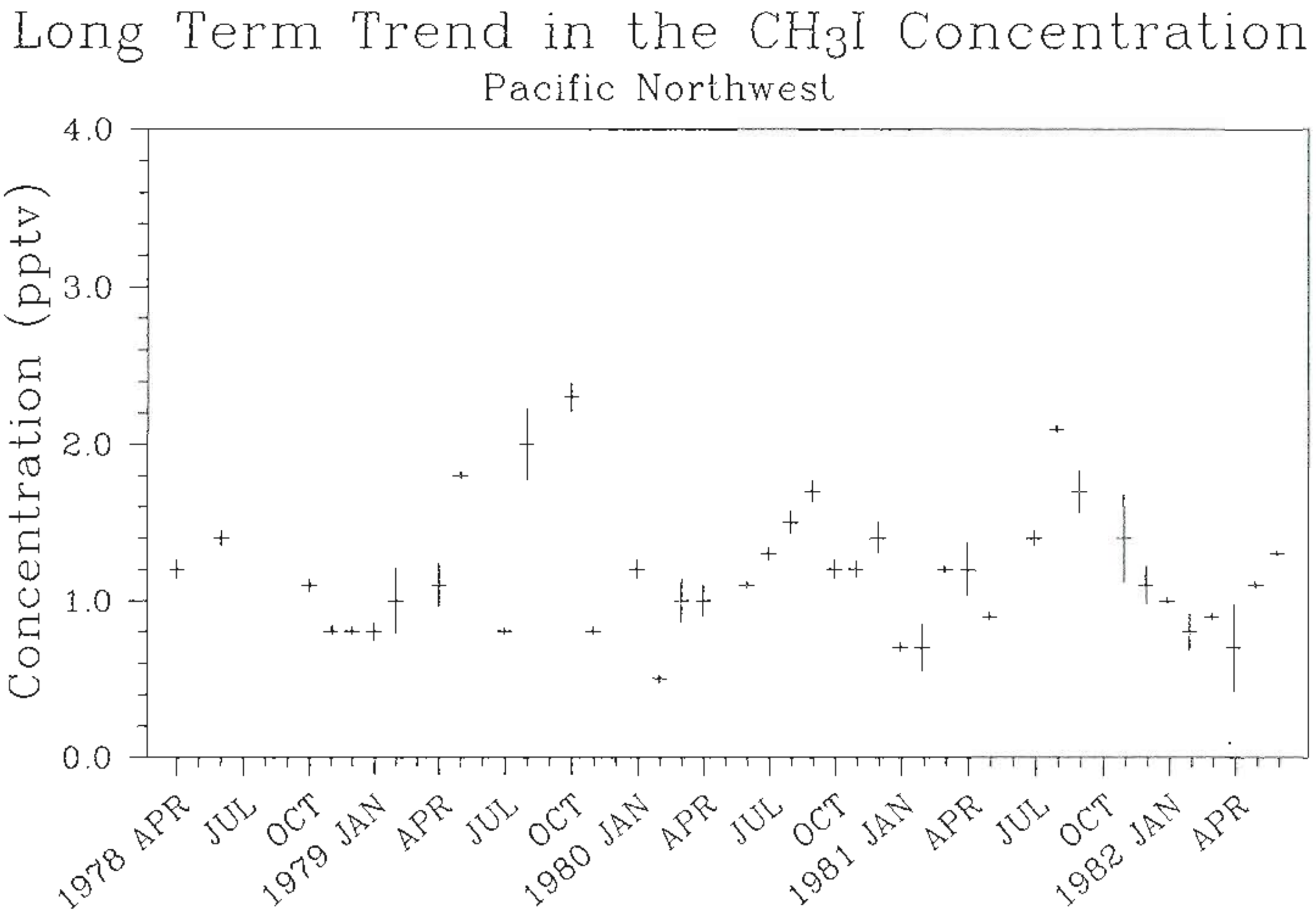

Long Term Trend in the CH3I Concentration
Pacific Northwest
Concentration (pptv)
4.0
3.0
2.0
1.0
0.0
1978 APR
JUL
OCT
1979 JAN
APR
JUL
OCT
1980 JAN
APR
JUL
OCT
1981 JAN
APR
JUL
OCT
1982 JAN
APR

Figure 3.5

Chapter 4

LATITUDINAL VARIATIONS OF CH_3I CONCENTRATION

From the plot of mean annual CH_3I concentration vs. latitude, it can be seen that the CH_3I concentration is a maximum around the equator and tapers off towards the poles (Figure 4.1 and Table 4.1), not considering hot spots such as Cape Point (South Africa), Irafoss (Iceland), and the Peruvian coast.

This higher abundance of CH_3I around the equator may be attributed to the higher abundance of sunshine, which is necessary for the growth of algae. It has been observed that certain types of marine algae produce CH_3I. (Though solar radiation is also involved in the destruction of CH_3I by photodissociation, it may be offset by its role towards algal growth.)

The average annual CH_3I concentration for the Marshall Islands has been calculated using data from the months of July through October. At other locations these months show the maximum CH_3I concentration (see the chapter on "Seasonal Variations of CH_3I Concentration"). Therefore, using the data from July through October may overestimate the average annual concentration. But again, since the Marshall Islands are close to the equator (at 7°N), seasonal variations may be small, minimizing the overestimation.

For Tasmania the CH_3I concentration used as an estimate for the average annual concentration is the value of May.

For the South Pole the average annual CH_3I concentration has been calculated using data from December through February. Because these are summer months in the southern hemisphere, the average annual CH_3I concentration calculated may be an overestimation. (In the higher northern latitudes CH_3I concentration is higher in summer months.)

Studying the CH_3I concentrations in the GAMETAG samples, it appears that CH_3I is more abundant in the tropics compared to the higher latitudes in both northern and southern hemispheres. From this data set it can be seen that the CH_3I concentration below the boundary layer is more variable with latitude than that above the boundary layer (2.7±1.3 pptv below the boundary layer and 1.0±0.8 pptv above the boundary layer).

Table 4.1

Latitudinal Variations of Atmospheric CH_3I

Station	Latitude	n	Annual Mean CH_3I Concentration (pptv)
Barrow (Alaska)	70°N	139	0.75 ± 0.05
Pacific Northwest	45°N	115	1.20 ± 0.10
Cape Kumukahi (Hawaii)	20°N	107	2.15 ± 0.10
Mauna Loa (Hawaii) 11,000 ft.	20°N	119	0.60 ± 0.05
Marshall Islands	7°N	23	3.15 ± 0.20
Samoa	15°S	110	1.70 ± 0.15
Tasmania	40°S	5	1.05 ± 0.05
South Pole	90°S	21	0.45 ± 0.10

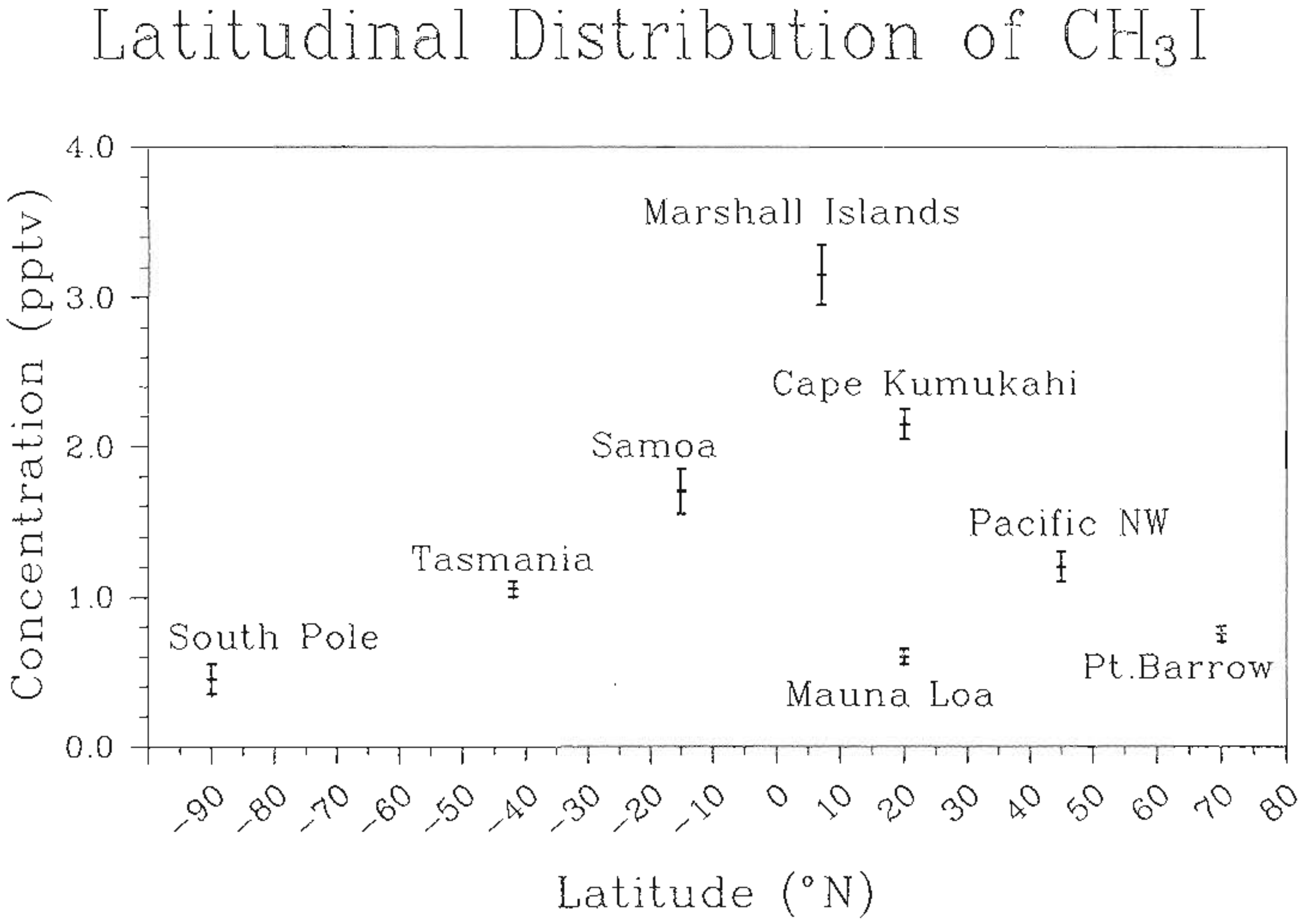

Latitudinal Distribution of CH_3I
Concentration (pptv)
4.0
3.0
2.0
1.0
0.0
Marshall Islands
Cape Kumukahi
Samoa
Pacific NW
Tasmania
South Pole
Pt.Barrow
Mauna Loa
-90
-80
-70
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
80
Latitude (°N)

Figure 4.1

Chapter 5

ALTITUDINAL VARIATION OF CH_3I CONCENTRATION

The altitudinal variation of CH_3I concentration can be observed from several special studies and also by studying the differences in CH_3I concentration between Cape Kumukahi and Mauna Loa in Hawaii. The special studies are:

two special studies at Point Barrow, Alaska;
one in Hawaii;
one in Samoa;
one in Australia.

The CH_3I concentration data at Cape Kumukahi and Mauna Loa span over about a year and a half. Therefore they allow us to observe seasonal cycles (if any) between these two stations, though they do not give any additional profile, just above and below the boundary layer. The CH_3I concentration at Mauna Loa is always lower than that at Cape Kumukahi (Table 5.1 and Figure 5.1). Also the monthly averaged CH_3I concentrations are anti-correlated between these two stations, i.e., whenever the CH_3I concentration is high at Cape Kumukahi, the value at Mauna Loa is at a low and vice versa. This may be due to the fact that the production of CH_3I and its destruction are governed by the same factor(s), namely, solar radiation. At Cape Kumukahi, which is at sea level, the solar radiation is not as strong as at Mauna Loa, which is at an elevation of 11,000 feet. Also, Cape Kumukahi is at an altitude near the source of CH_3I, and Mauna Loa is at an altitude, above the boundary layer, where the air is "older" and far from the source of CH_3I. (Also see the chapter on "Sources and Sinks of Atmospheric CH_3I and Its Lifetime.").

The fact that CH_3I concentrations at Cape Kumukahi and Mauna Loa are anti-correlated can also be seen from the plot of Cape Kumukahi vs. Mauna Loa.

Data from "special Hawaii samples" show that CH_3I concentrations decrease with increasing altitude, with a maximum concentration around sea level at 2.6 pptv and dropping off to less than about 0.2 pptv at 12,000 feet. This is seen when the CH_3I concentration is plotted against the altitude. The rate at which CH_3I concentration decreases with increasing altitude is greater at lower altitudes up to about 3,000 feet (Table 5.7 and Figure 5.6).

The regular samples collected at Cape Kumukahi (at sea level) and Mauna Loa (at 11,000 feet) also seem to fit with the data from the special Hawaii samples, at sea level and 11,000 feet.

It was interesting to see that the sample collected at the cloud base (at 2,700 feet) showed elevated CH_3I, of 2.1 pptv, since at the rate the CH_3I concentration falls off with increasing altitude one would expect the CH_3I concentration to be between 0.5 and 1.0 pptv (from the special Hawaii data). We have observed elevated levels of CH_3I in rainwater and snowmelt extractions. (See chapter on "CH_3I in Seawater, Rainwater, Lakewater, Snow, and Glacial Ice Extractions.")

From the "special Barrow samples" also can be seen that the CH_3I concentration drops off with increasing altitude, from about 0.5 pptv at ground level to about 0.1 pptv at 10,000 feet. Again as in the case of the "special Hawaiian samples," the drop-off in CH_3I concentration with increase in altitude is greater at lower altitudes, up to about 4,000 feet (Tables 5.2 and 5.3, Figure 5.2).

Special Samoa samples (i.e., the altitudinal profile) show that the CH_3I concentration is a maximum around 500 feet, at about 2.5 pptv, with the concentration about 2.0 pptv at sea level but dropping only to about 1.0 pptv at 12,000 feet.(Table 5.4, Figure 5.3).

A similar variation of CH_3I concentration is observed in the special study done in Australia but with the CH_3I concentration dropping to less than 0.4 pptv at 13,500 feet. Here also the CH_3I concentration is higher at 500 feet than at sea level.(Table 5.5, Figure 5.4).

GAMETAG samples also show a difference in CH_3I concentration below and above the boundary layer. It can be clearly seen that the CH_3I concentration drops to a half or less above the boundary layer as compared to the level below.(Table 5.6, Figure 5.5).

Table 5.1

Difference in CH_3I Concentration Between Cape Kumukahi and Mauna Loa Observatory

(Monthly Average Concentrations Are Considered in pptv)

Month	Cape Kumukahi	Mauna Loa Observatory	Cape Kumukahi/Mauna Loa Observatory
January	2.4	0.7	1.7
February	1.7	0.9	0.8
March	1.7	0.9	0.8
April	1.8	0.9	0.9
May	1.8	0.6	1.2
June	2.5	0.3	2.2
July	4.0	0.4	3.6
August	1.8	0.4	1.4
September	2.0	0.4	1.6
October	--	0.6	--
November	--	--	--
December	2.0	0.3	1.7

Table 5.2

Special Barrow Samples - I

Sampled 05/07/82

Altitude (ft.)	CH_3I Concentration (ppt)
Ground (cryo T)	2.5
500	0.3 ± 0.1
2,000	0.2 ± 0.1
4,000	0.1
6,000	0.2 ± 0.0
8,000	0.1 ± 0.0
10,000	0.1 ± 0.0
12,000	0.1 ± 0.0
13,900	0.2 ± 0.1

Table 5.3

Special Barrow Samples - II

Sampled 05/07/82

Altitude (ft.)	CH_3I Concentration (ppt)
Ground	0.5
500	0.2 ± 0.1
700	0.5
2,700	0.3 ± 0.1
4,000	0.3 ± 0.2
6,000	0.1 ± 0.0
8,000	0.1 ± 0.1
10,000	0.1 ± 0.0
12,000	0.1 ± 0.0
14,000	0.1

Table 5.4

Special Samoa Samples - January 1982

Altitude (ft.)	Number of Samples	CH_3I Concentration (pptv)
0	3	2.0 ± 0.3
500	5	2.5 ± 1.5
1,000	6	1.8 ± 1.0
5,000	5	1.1 ± 0.6
8,000	8	0.8 ± 0.6
12,000	5	1.1 ± 0.4

Table 5.5

Australian Samples - Space Shuttle, November 1981

Altitude (ft.)	Number of Samples	CH_3I Concentration (pptv)
0	7	1.8 ± 0.8
1,000	4	1.2 ± 0.3
7,000	1	1.1
9,000	1	1.2
10,000	2	1.1 ± 0.1
13,000	4	0.2 ± 0.1
13,500	5	0.4 ± 0.3

Table 5.6

Gametag Samples - Pacific Ocean, 1978

Date	Latitude°	Longitude°	Altitude (m)	CH_3I Concentration (pptv)
04/27	36.12	120.59	4,820	0.8
05/02	18.47	158.84	5,500	0.8
05/02	18.35	163.23	315	3.1
05/03	10.00	172.21	340	4.0
05/03	-2.42	171.79	340	2.7
05/04	-10.19	171.57	5,508	1.2
05/04	-13.01	171.31	340	2.2
05/07	-40.88	173.10	5,500	0.3
05/10	-57.39	171.98	5,810	1.2
05/10	-46.32	172.00	124	2.2
05/11	-32.21	173.21	285	2.6
05/11	-18.78	176.91	5,500	0.5
05/13	-6.50	175.49	5,817	1.2
05/13	-3.59	172.54	400	1.4
05/13	1.18	171.12	365	2.5
05/13	16.65	169.68	200	1.1
05/14	18.12	162.73	5,300	0.2
05/14	18.48	160.10	212	5.6

Table 5.7

Special Hawaii Samples

Altitude (ft)	n	CH_3I Concentration (pptv)
50	15	1.1 ± 0.1
1,900	2	0.9 ± 0.1
4,000	2	0.7 ± 0.2
6,000	2	0.5 ± 0.2
11,000	2	0.4 ± 0.0

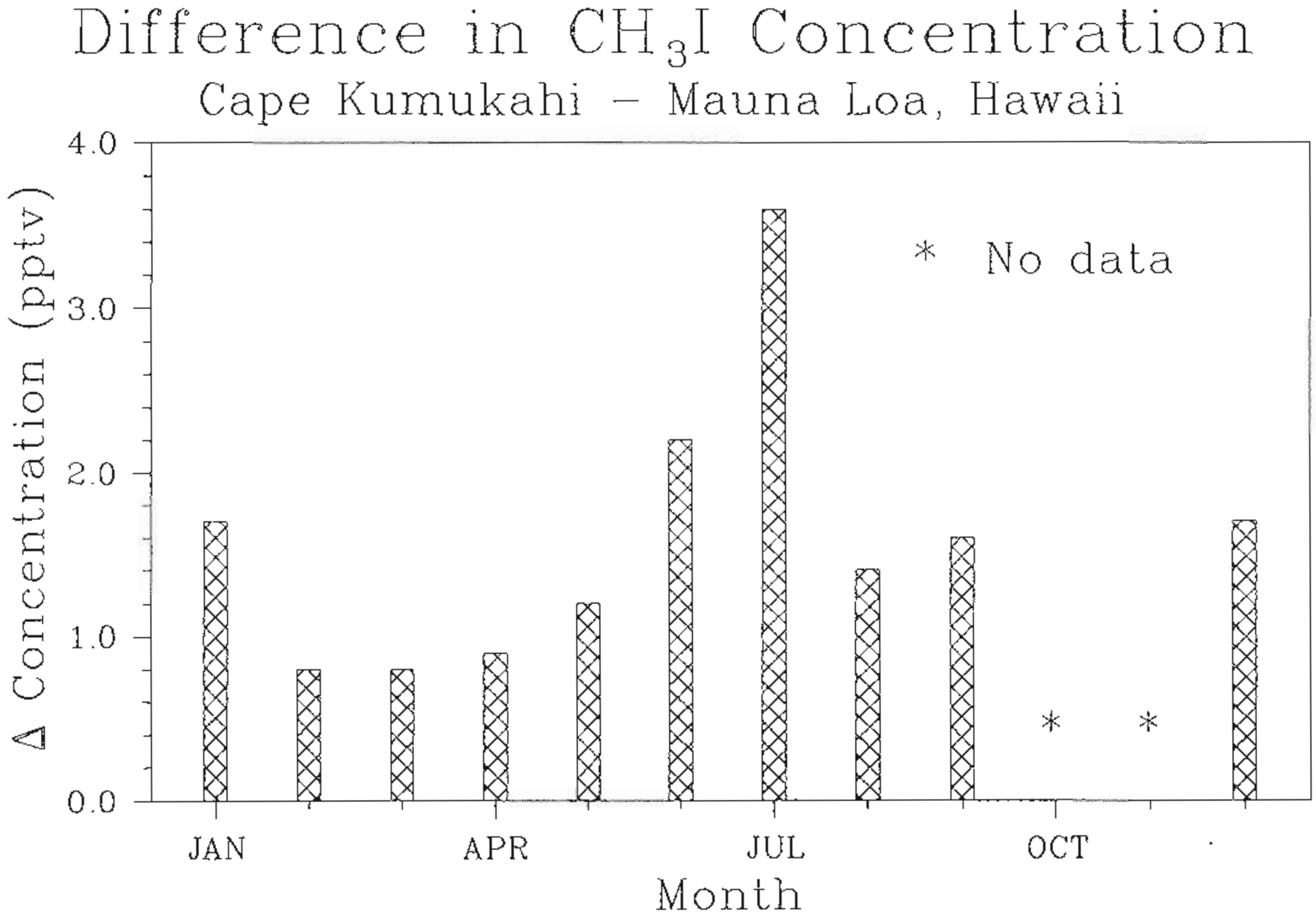

Difference in CH_3I Concentration
Cape Kumukahi – Mauna Loa, Hawaii
Δ Concentration (pptv)
4.0
3.0
2.0
1.0
0.0
* No data
*
*
JAN
APR
JUL
OCT
Month

Figure 5.1

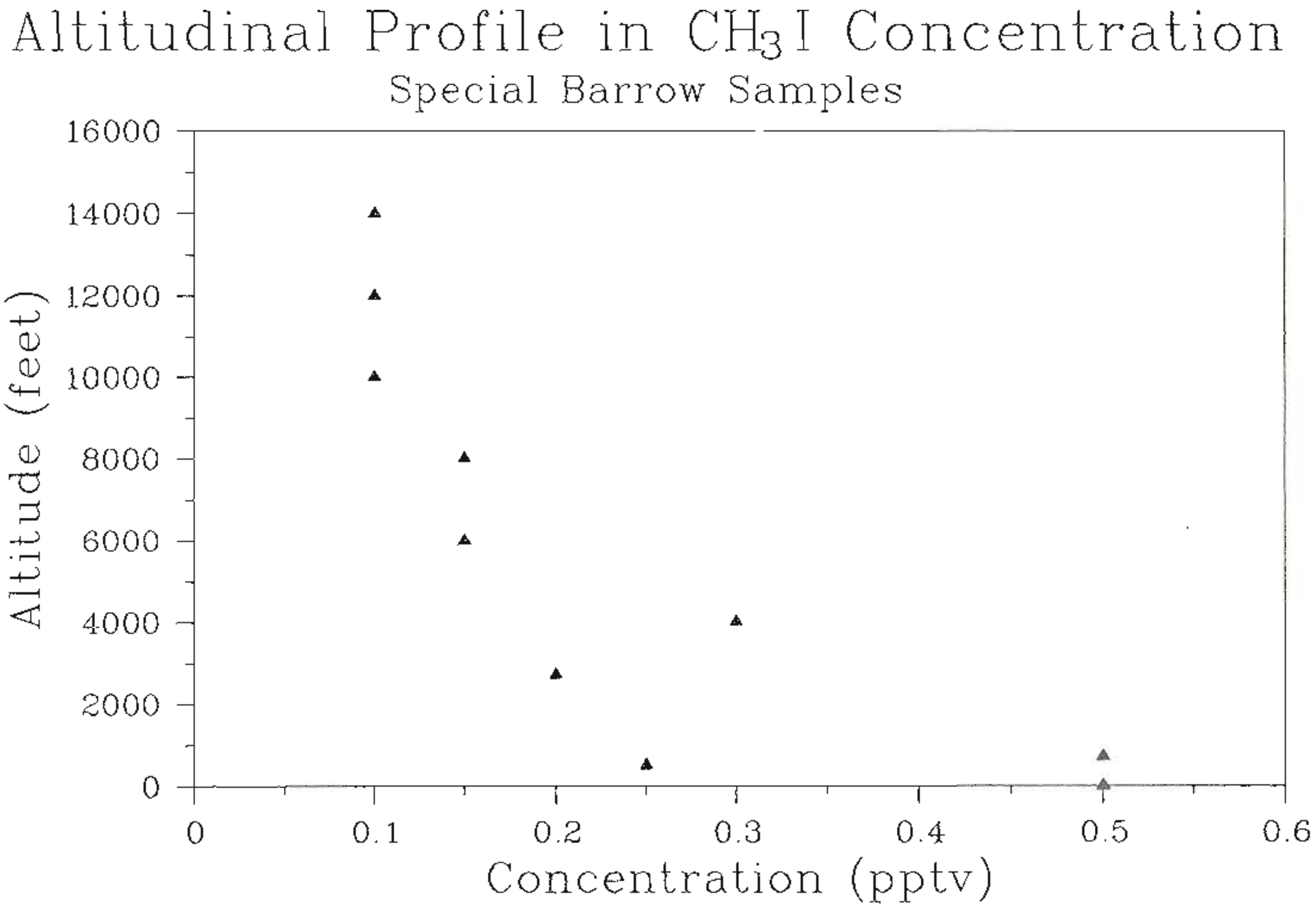

Altitudinal Profile in CH_3I Concentration
Special Barrow Samples
Altitude (feet)
16000
14000
12000
10000
8000
6000
4000
2000
0
0
0.1
0.2
0.3
0.4
0.5
0.6
Concentration (pptv)

Figure 5.2

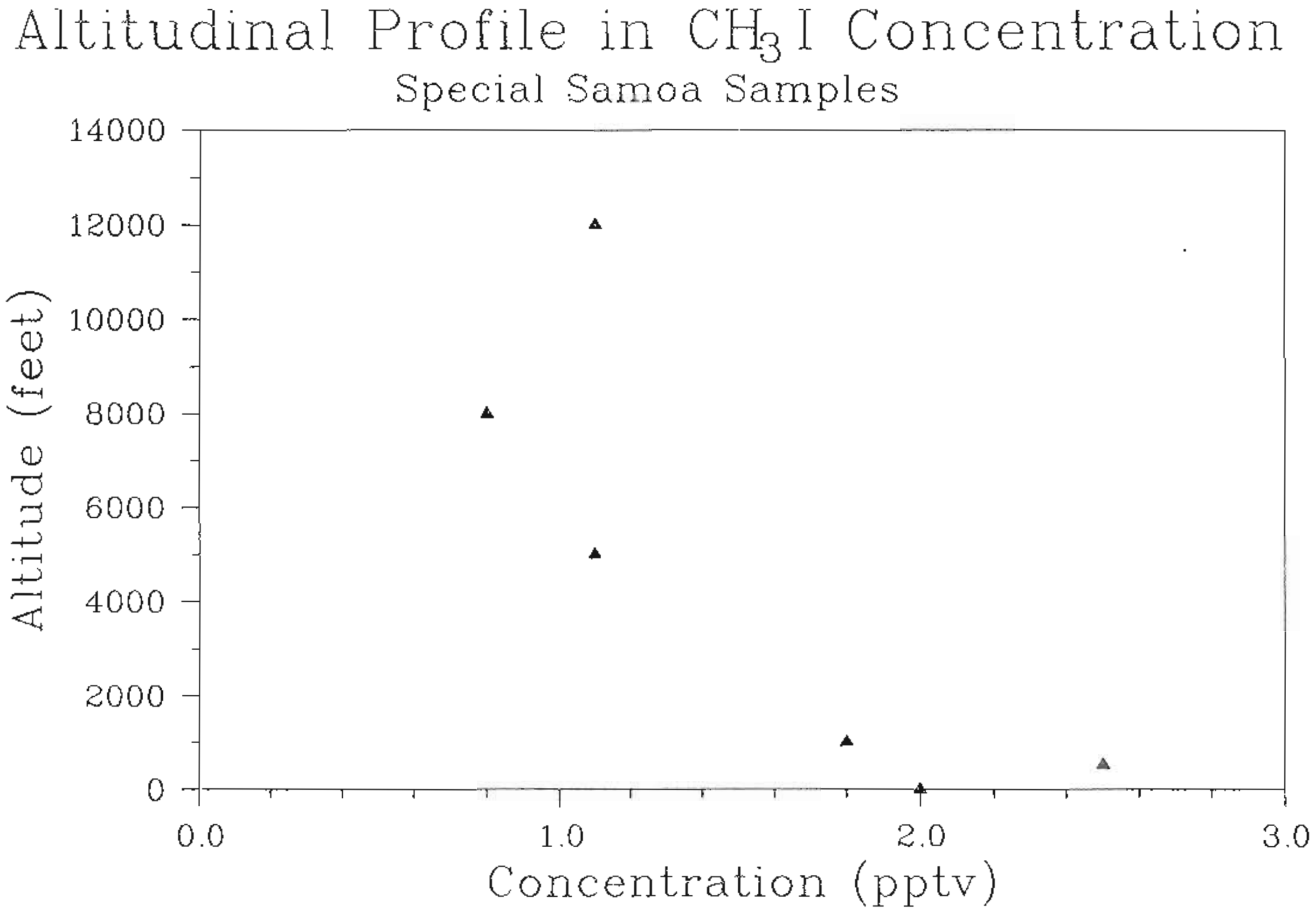

Altitudinal Profile in CH_3I Concentration
Special Samoa Samples
Altitude (feet)
14000
12000
10000
8000
6000
4000
2000
0
0.0
1.0
2.0
3.0
Concentration (pptv)

Figure 5.3

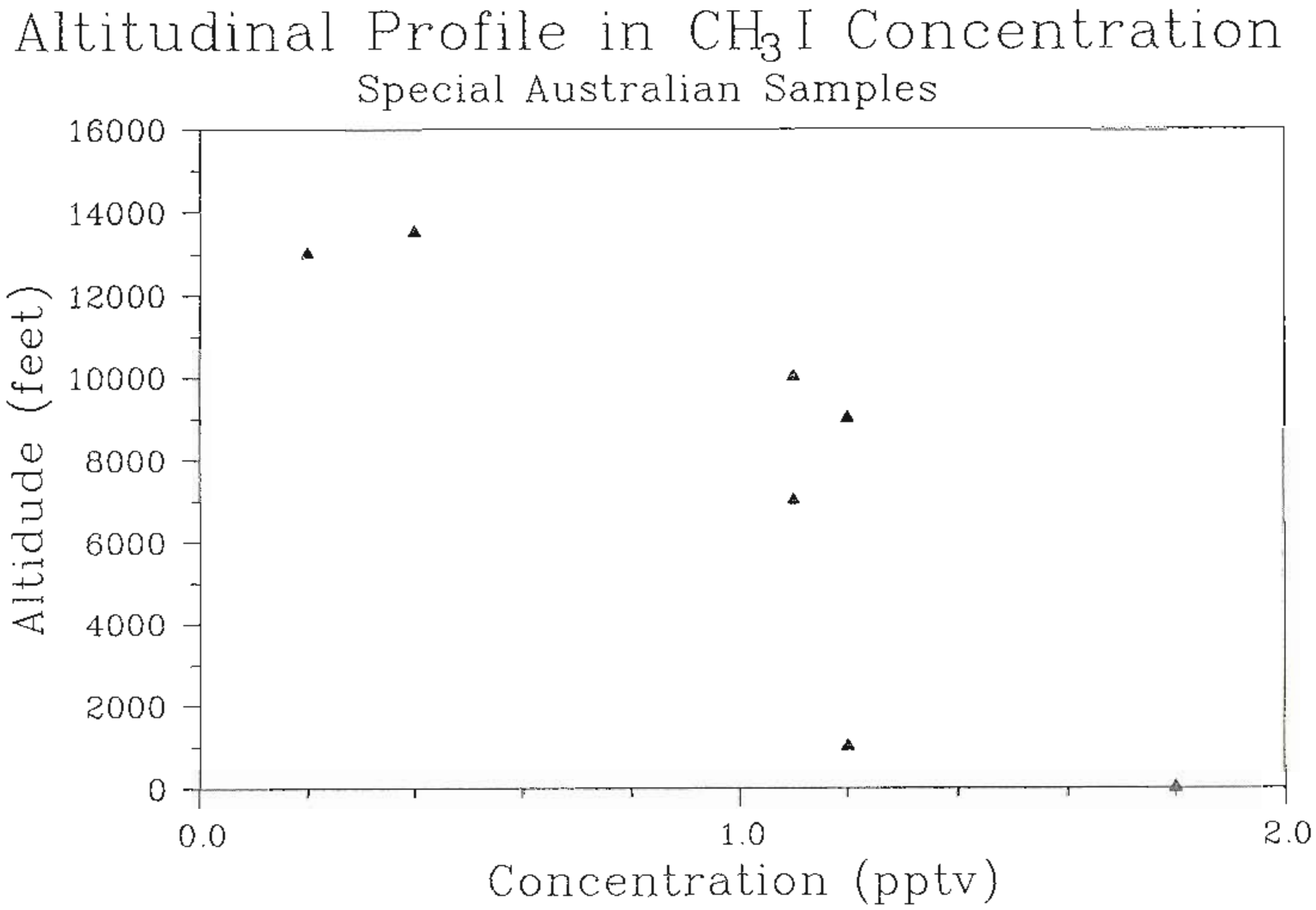

Altitudinal Profile in CH_3I Concentration
Special Australian Samples
Altidude (feet)
16000
14000
12000
10000
8000
6000
4000
2000
0
0.0
1.0
2.0
Concentration (pptv)

Figure 5.4

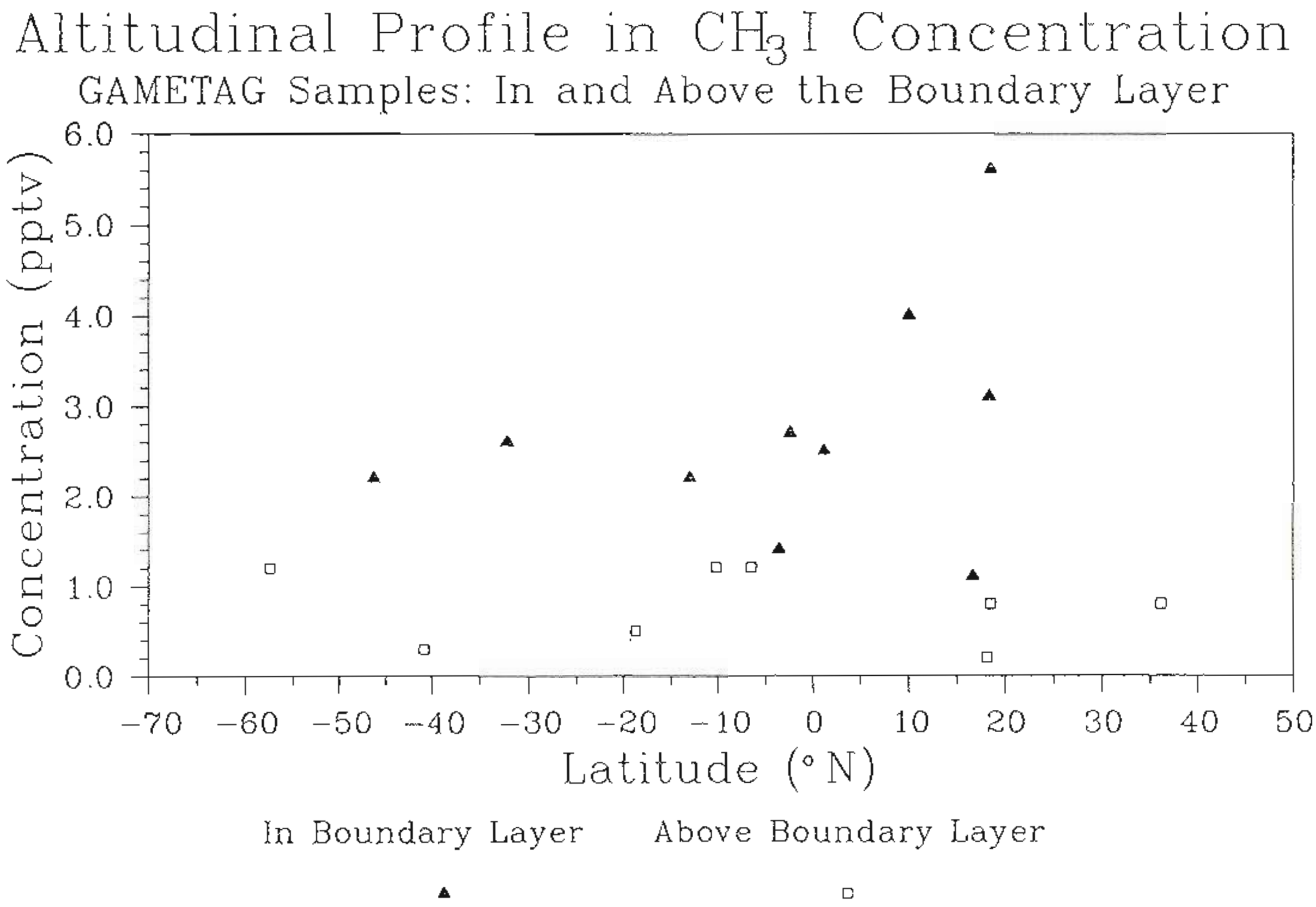

Altitudinal Profile in CH3I Concentration
GAMETAG Samples: In and Above the Boundary Layer
Concentration (pptv)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−70
−60
−50
−40
−30
−20
−10
0
10
20
30
40
50
Latitude (° N)
In Boundary Layer ▲
Above Boundary Layer □

Figure 5.5

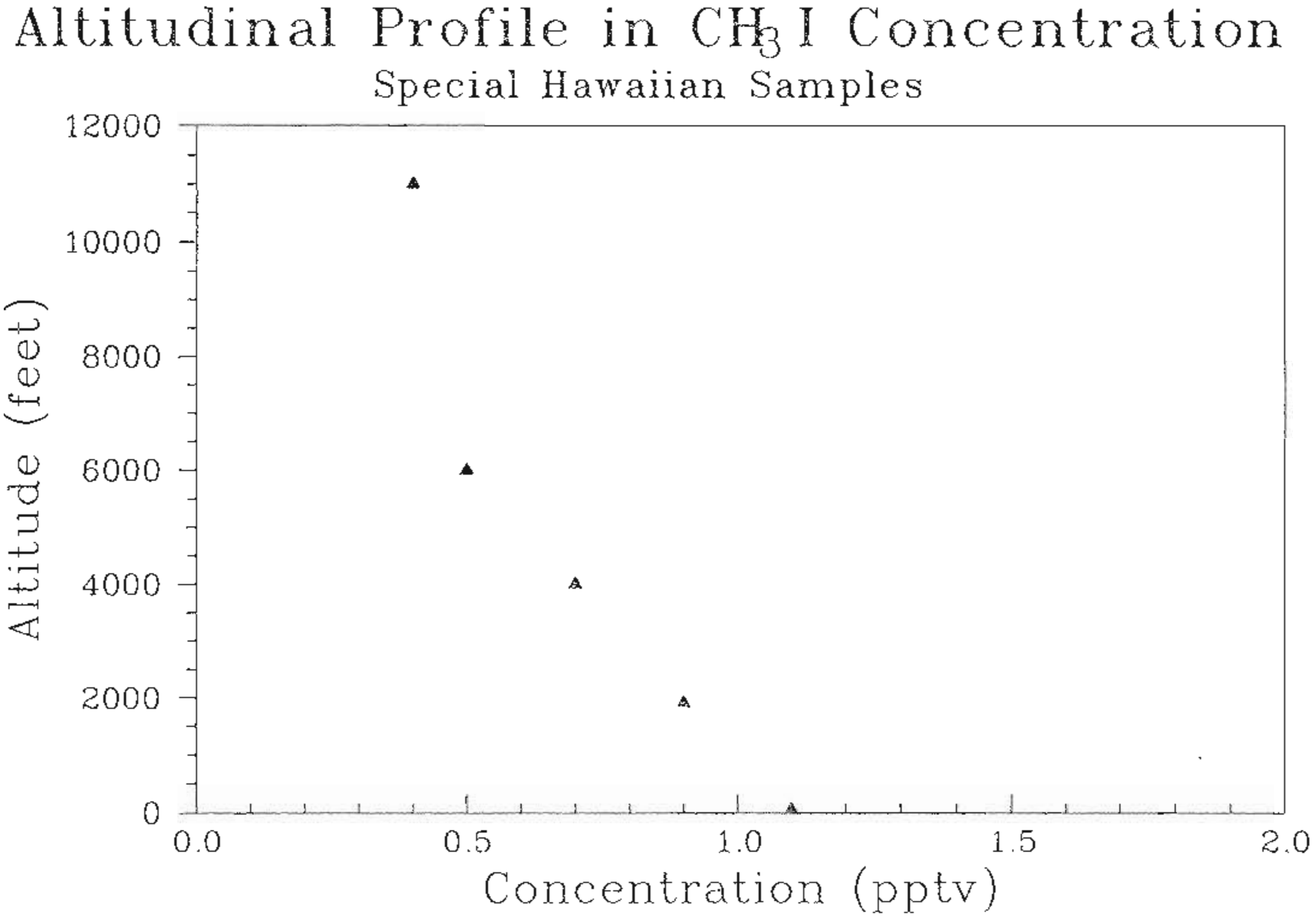

Altitudinal Profile in CH_3I Concentration
Special Hawaiian Samples
Altitude (feet)
12000
10000
8000
6000
4000
2000
0
0.0
0.5
1.0
1.5
2.0
Concentration (pptv)

Figure 5.6

Chapter 6

THE DIFFERENCE IN CH_3I CONCENTRATION BETWEEN CONTINENTIAL AND MARINE AIR MASSES

The monthly average CH_3I concentrations for Cape Meares, Oregon (which has marine air), were compared with CH_3I concentrations from Niwot Ridge, Colorado, and Whiteface Mountain, New York. When the data from all three locations are plotted on the same graph, it can be clearly seen that the marine air has more CH_3I compared to the continental air (Niwot Ridge and Whiteface Mountain). (The number of data points is limited for Niwot Ridge and Whiteface Mountain.) (Table 6.1 and Figure 6.1).

Table 6.1

Niwot Ridge vs. Cape Meares vs. Whiteface Mountain

Month	PNW Cape Meares	Niwot Ridge	Whiteface Mountain
January	1.1 ± 0.4 n = 5	0.6 ± 0.1 n = 5	0.5
February	1.0 ± 0.8 n = 8	--	
March	1.0 ± 0.2 n = 4	--	
April	1.0 ± 0.4 n = 30	--	
May	1.5 ± 0.8 n = 2	1.0 ± 0.1 n = 13	
June	1.4 ± 0.3 n = 6	0.7 ± 0.1 n = 12	
July	1.4 ± 0.2 n = 11	0.6 ± 0.1 n = 8	
August	1.8 ± 0.3 n = 5	0.8 ± 0.1 n = 9	0.6 ± 0.1 n = 8
September	1.6 ± 0.2 n = 5	0.5 ± 0.1 n = 7	1.2 ± 0.4 n = 3
October	1.7 ± 018 n = 17	0.4 ± 0.1 n = 6	0.6 ± 0.1 n = 8
November	1.1 ± 0.3 n = 12	0.4 ± 0.1 n = 6	--
December	1.3 ± 0.4 n = 7	0.5 ± 0.1 n = 7	0.4 ± 0.1 n = 4

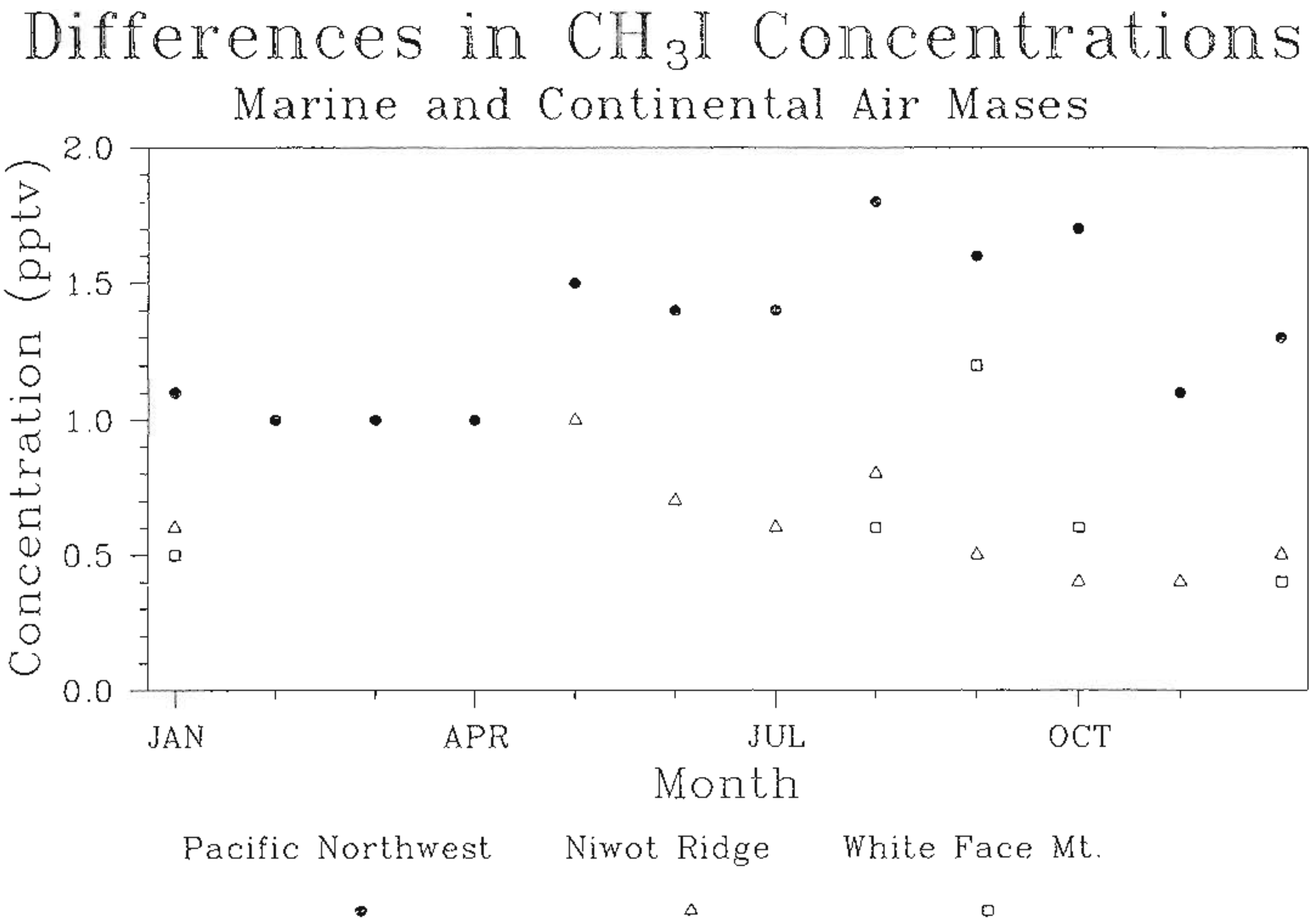

Differences in CH_3I Concentrations
Marine and Continental Air Mases
Concentration (pptv)
2.0
1.5
1.0
0.5
0.0
JAN
APR
JUL
OCT
Month
Pacific Northwest
Niwot Ridge
White Face Mt.

Figure 6.1

Chapter 7

CH_3I IN RAINWATER, SEAWATER, LAKEWATER, SNOW, AND GLACIAL ICE

7.A. CH_3I in Rainwater

Rainwater samples were equilibrated with zero air in glass bottles and the dissolved gases were extracted by a modified McAullife technique (Hoyt, 1982). The headspace over the rainwater was analyzed by temperature-programmed electron capture gas chromatography, TP/EC/GC. Rainwater was collected at two locations: at the Oregon Graduate Center and in Hillsboro, Oregon. The majority of the samples were collected at OGC. Total number of rainwater samples was 50. The headspace concentrations varied from 1 pptv to 426 pptv. On some days rainwater was collected at both locations, but there was no apparent correlation between the concentrations observed. More studies need to be done to understand why the same rainstorm contains different levels of CH_3I at different locations (Table 7.1).

Though several headspace samples collected at OGC showed CH_3I concentrations over 100 pptv (a total of 9), 3 samples collected in Hillsboro showed the highest concentrations: 426, 324, and 292 pptv.

Rainwater samples have been collected at all times of the day and night, but there is no definite pattern, i.e., to say that samples collected at any particular time of day showed high or low levels of CH_3I.

7.B. CH_3I in Seawater and Related Samples

Seawater samples were obtained from the Oregon coast, Puget Sound, Point Lobos (California), Florida, and from open ocean cruises on the Pacific Ocean, with the majority of the samples coming from the Oregon coast (Table 7.2).

Typically, seawater samples collected from the Oregon coast during the summer months had about 40 pptv of CH_3I in the headspace over the water (with a calculated equilibrium concentration in air of about 7 pptv), and during the winter months the CH_3I concentration dropped to less than half the summer value -- to about 15 pptv (with a calculated equilibrium concentration in air of about 2.5 pptv). This may be due to decreasing biological activity in seawater during the winter months.

Seawater samples collected on Pacific cruises showed CH_3I headspace concentrations of about 80 pptv (with a calculated equilibrium concentration of about 14 pptv). Similar concentrations were observed in the samples collected offshore at Cape Meares.

Samples of seawater obtained from Puget Sound showed about 250 pptv of CH_3I in the headspace, while Florida samples had about 60 pptv (with calculated equilibrium concentrations of about 43 pptv and 10 pptv respectively).

A special study was done with jellyfish and seaweed to see what levels of CH_3I are present in waters containing these species. The seawater samples with the jellyfish showed about 125 pptv CH_3I with a calculated equilibrium concentration of about 21 pptv. The green seaweed in seawater had about 600 pptv of CH_3I while the red seaweed had about 1200 pptv (with calculated equilibrium concentrations of about 100 pptv and 200 pptv respectively). These studies were done in the laboratory with the seaweed or the jellyfish in the seawater containers. Therefore, the results might be an over-estimation of the equilibrium seawater CH_3I concentrations due to these species. A better study may be done by obtaining seawater samples from areas where there are schools of jellyfish or seaweeds.

7.C. Lakewater Samples from Hagg Lake, Oregon

Date Collected	CH_3I Concentration
08/07/82	2.9 ± 0.4
08/16/82	1.9
08/22/82	3.9
08/23/82	2.6
09/06/82	12.1
09/12/82	13.0
10/03/82	10.1 ± 3.8

Water samples from Hagg Lake were extracted using the McAullife technique. Samples collected in August showed low levels of CH_3I in the headspace (1.9 to 3.9 pptv) compared to the samples collected in September and October (10.1 to 13.0 pptv). Since all these samples represent surface water, it will be interesting to see how the CH_3I concentrations vary with varying weather conditions, especially if there is any rain. We will have to collect rainwater samples from the same area, too, to see whether rainwater contributes to the CH_3I in freshwater lakes and rivers.

7.D. CH_3I in Snow

The majority of the snow samples were collected at Mt. Hood. The rest of the samples were collected in Greenland, Colorado, and at the South Pole. From Table 7.4 (snow samples), it can be seen that, similar to the rainwater samples, the CH_3I concentrations can be quite variable. The variability seems to depend on where the samples were collected, the freshness of the snow, and the depth at which the sample was taken. Especially with the snow samples collected at Mt. Hood the last two points were apparent.

When there hasn't been any new snow, the surface snow showed a lower CH_3I concentration compared to snow below the surface at the same spot. This may be due to the dissociation of CH_3I by UV at higher altitudes and may also be due to degassing of CH_3I from the surface snow.

"Watermelon snow," old surface snow colonized by blue-green algae (red color) obtained at about the 8000-foot level of Mt. Hood, showed low levels of CH_3I.

Snow obtained from the South Pole also showed low levels of CH_3I (but not as low as aged surface snow from Mt. Hood). This may be related to the fact that continental air masses show lower levels of CH_3I than do marine or coastal air masses.

Snow from high altitudes in Colorado and the middle of Greenland also showed relatively low levels of CH_3I.

With all snow samples (except with one old surface snow sample from Mt. Hood) the calculated CH_3I concentration in air that should be in equilibrium with the snow is higher (sometimes as high as a factor of 40) than the CH_3I concentration in the ambient air samples collected with the snow samples, i.e., a large enrichment of CH_3I in snow compared to the ambient air.

With old surface snow samples from Mt. Hood the calculated equilibrium concentration of CH_3I is closer to the ambient concentrations observed. This is also true with the snow samples collected in Greenland and at the South Pole.

7.E. CH_3I in Glacial Ice Samples

The glacial ice samples were obtained from Antarctica. The CH_3I concentration in these samples varied from about 7.8 pptv to about 74.5 pptv. From the limited depth data available for these samples it appears that the deeper samples have lower CH_3I concentrations (Table 7.5).

Table 7.1

Rainwater Samples

Date	Location (Comments)	CH_3I concentration (pptv) Headspace	Rainwater	Equilibrium (Air-Calculated)	Ambient (Observed)
04/11/81	Hillsboro (night)	5.7 ± 2.4	33.0 ± 13.7	4.6 ± 1.9	
04/20/81	OGC	4.9	28.2	3.9	
06/15/81	OGC	220.7	1271.7	178.0	1.4 ± 0.4
07/03/81	OGC (day)	21.4	123.3	17.3	1.0
07/03/81	OGC	133.4	768.8	107.6	1.0
07/29/81	OGC (night)	5.6	32.2	4.5	1.4
08/09/81	OGC (t-storm)	5.2 ± 3.6	30.1 ± 20.6	4.2 ± 2.9	1.1
08/09/81	Hillsboro	358.7 ± 94.7	2066.7 ± 545.7	289.3 ± 76.4	
08/10/81	OGC	4.3	24.9	3.5	1.3
08/10/81	Hillsboro	15.9	91.7	12.8	
08/11/81	OGC	24.1	139.0	19.5	1.2
08/12/81	OGC (day)	5.4	31.1	4.4	1.0
08/12/81	Hillsboro (day)	20.6	118.7	16.6	
08/30/81	Hillsboro (night)	6.2	35.8	5.0	
09/03/81	OGC (morning)	9.1	52.6	7.4	
09/03/81	OGC (night)	94.5	544.6	76.2	
09/09/81	OGC (morning)	1.5 ± 0.2	8.5 ± 1.0	1.2 ± 0.1	1.4
08/11/81	OGC (evening)	104.1	600.0	84.0	0.8

Table 7.1 (continued)

Date	Location (Comments)	Headspace	Rainwater	Equilibrium (Air-Calculated)	Ambient (Observed)
09/19/81	OGC (day)	53.8 ± 32.2	309.9 ± 185.3	43.4 ± 25.9	
09/20/81	OGC (day)	123.7	712.5	99.8	
09/26/81	Hillsboro (evening)	324.3	1868.8	261.6	1.8
10/06/81	OGC	193.1	1112.9	155.8	
10/21/81	OGC (day)	1.5 ± 0.3	8.5 ± 1.9	1.2 ± 0.3	1.2
10/22/81	OGC (day)	1.2 ± 0.3	7.0 ± 1.6	1.0 ± 0.2	0.5
10/22/81	OGC (squall)	19.9 ± 4.6	114.9 ± 27.0	16.1 ± 3.8	1.0
10/26/81	OGC	3.1	17.9	2.5	1.1
10/29/81	OGC	1.2 ± 0.3	7.1 ± 2.0	1.0 ± 0.3	0.6
12/02/81	OGC	120.4 ± 94.1	693.9 ± 542.1	97.2 ± 75.9	
12/03/81	OGC	100.6 ± 26.5	579.8 ± 152.4	81.2 ± 21.3	
11/18-19/82	OGC	120.3 ± 71.8	693.1 ± 413.5	97.0 ± 57.9	
11/28/82	OGC	71.2	410.3	57.4	
12/17/82	OGC	179.3	1033.4	144.7	

Table 7.2

Seawater & Related Samples

				CH_3I Concentration (pptv)		
	Date	Location	Comments	Headspace	Seawater	Equilibrium (Air-Calculated)
	06/29/81	Cape Meares		11.0 ± 3.7	54.8 ± 18.3	9.3 ± 3.1
	07/01/81	Cape Meares		5.8 ± 0.6	29.0 ± 2.8	4.9 ± 0.5
Anal.	07/29/81	NOAA Cruise		14.6 ± 1.5	72.9 ± 7.6	12.4 ± 1.3
	08/09/81	Cape Meares		9.7	48.7	8.3
	08/16/81	off Oregon coast		16.9 ± 4.7	84.7 ± 23.5	14.4 ± 4.0
Anal.	08/18/81	Seattle area		50.9 ± 6.0	245.6 ± 29.8	43.3 ± 5.1
Anal.	11/02/81	Gammon cruise		17.0 ± 3.0	85.1 ± 15.0	14.5 ± 2.5
	May 1982	NOAA Cruise		17.5 ± 2.5	87.4 ± 12.6	14.9 ± 2.1
	07/25/82	Cannon Beach	control	9.1 ± 1.4	45.7 ± 7.0	7.8 ± 1.2
	07/25/82	Jellyfish		24.8 ± 9.0	123.8 ± 45.1	21.1 ± 7.7
	07/25/82	Green seaweed		121.2	606.1	103.0
	07/25/82	Red seaweed		239.9	1200.0	203.9
	08/02/82	Cape Meares		8.5 ± 0.4	42.7 ± 1.9	7.3 ± 0.3
	08/03/82	Cape Meares		9.5 ± 0.1	47.4 ± 0.4	8.1 ± 0.1
	08/09/82	Lincoln City surf		8.2 ± 0.7	41.1 ± 3.7	7.0 ± 0.6
	08/10/82	Cape Meares		8.3 ± 0.3	41.4 ± 1.3	7.0 ± 0.2
	08/22/82	Cannon Beach		8.1 ± 1.8	40.6 ± 8.9	6.9 ± 1.5

Table 7.2 (continued)

				CH_3I Concentration (pptv)		
	Date	Location	Comments	Headspace	Seawater	Equilibrium (Air-Calculated)
	08/25/82	Arcadia		7.3 ±	36.5 ± 1.7	6.2 ± 0.3
	08/15/82	Florida		12.3 ±	61.3 ± 16.8	10.4 ± 2.9
	09/01/82	Cape Meares		5.5 ±	27.4 ± 2.9	4.7 ± 0.5
	09/15/82	Cape Meares		8.3 ±	41.6 ± 0.4	7.1 ± 0.1
	09/29/82	Cape Meares		5.4 ±	26.9 ± 1.9	4.6 ± 0.3
	12/22/82	Cape Meares		3.9	19.7	3.3
Anal.	01/6-7/82	Point Lobos, California		14.5 ±	72.5 ± 23.3	12.3 ± 4.0
	01/12/83	Cape Meares		3.0 ±	15.0 ± 3.0	2.6 ± 0.5
	01/12/83	Cape Lookout		2.6 ±	12.9 ± 1.5	2.2 ± 0.3

Table 7.3

Snow and Related Samples

Date	Location (Comments)	CH$_3$I concentration (pptv) Headspace	Snow	Equilibrium (Air-Calculated)	Ambient (Observed)
04/05/81	Mt. Hood	110.9 ± 11.6	639.2 ± 66.7	46.0 ± 4.8	1.1
05/13/81	Mt. Hood	9.6 ± 1.2	55.3 ± 7.0	4.0 ± 0.5	1.7 ± 1.1
08/10/81	Mt. Hood (watermelon snow)	1.4	8.0	0.6	
08/10/81	Mt. Hood	5.3 ± 2.7	30.7 ± 15.6	2.2 ± 1.1	
12/12/81	Mt. Hood	18.3 ± 3.8	105.2 ± 21.8	7.6 ± 1.6	
01/10/82	Mt. Hood	12.2 ± 2.0	70.3 ± 11.5	5.1 ± 0.8	
01/17/82	Mt. Hood	24.8 ± 1.6	142.7 ± 8.9	10.3 ± 0.6	3.7
01/24/82	Mt. Hood	12.1 ± 2.2	69.8 ± 12.7	5.0 ± 0.9	1.1
01/31/82	Mt. Hood	102.2 9.0	588.6 51.8	42.4 3.7	2.6
02/10/82	Mt. Hood (surface snow)	19.6	112.8	8.1	
02/10/82	Mt. Hood (1 ft. deep)	54.4	313.2	22.6	
02/10/82	Mt. Hood (snow bank)	9.2	53.0	3.8	
02/14-15/82	Colorado	9.2 ± 4.0	53.1 ± 23.2	3.8 ± 1.7	0.8 ± 0.4
08/31/82	Mt. Hood (surface snow)	0.5 ± 0.1	3.1 ± 0.4	0.2 ± 0.0	0.5 ± 0.0

Table 7.4

Glacial Ice Samples
(Antarctica)

			CH_3I Concentration (pptv)	
Date Analyzed	Sample #	Depth (m)	Headspace	In Ice
04/21/81	J-9 #57	84	4.8	27.5
04/21/81	J-9 #27	45.5	7.1	40.9
04/22/81	B-16	101	4.4	25.2
04/29/81	#181		3.2	18.6
11/11/82	#74 (Bottle #37)		1.4	7.8
11/11/82	B-411 (Bottle #9)		2.8	16.2
11/11/82	Bottle #15		2.9	16.7
01/25/83	Bottle #37		2.9	16.8
01/25/83	Bottle #39		12.8	73.5
01/28/83	Bottle #15		3.6	21.0
02/01/83	Bottle #5		1.9	10.8

Chapter 8

CONCLUSIONS

A temperature-programmed electron capture gas chromatographic (TP-EC-GC) method using a packed column was developed that enabled atmospheric methyl iodide (CH_3I) to be accurately measured. Prior to this method CH_3I was measured by isothermal electron capture gas chromatography with uncertain results due to poor resolution of the CH_3I peak from $C_2Cl_3F_3$ (F-113). Also the detection limit of the isothermal method was sensitive only to 5 to 10 pptv of CH_3I in the direct analysis of 3 to 8 mL samples. Increased sensitivity to measure 0.05 pptv of CH_3I was achieved by the TP-EC-GC method using 200 mL samples. The analysis of this large volume of air was possible by first concentrating it in a freezeout loop and then cryofocusing the contents of the freezeout loop on the head of the column prior to analysis.

In addition to CH_3I and $C_2Cl_3F_3$ (F-113), CCl_3F (F-11), $CHCl_3$, CH_3CCl_3, CCl_4, C_2HCl_3 (TCE), and C_2Cl_4 (PCE) were accurately measured by the TP-EC-GC method.

At 1.6 pptv the precision for CH_3I was ±5%, and the reproducibility was within ±10% over a period of 1½ years.

The data obtained by the TP-EC-GC method were very consistent and were able to establish that CH_3I is present in the atmosphere in minute concentrations. Typical background concentrations are less than 3 pptv. This is shown in summary in Table 8.1

Table 8.1

Station	Latitude	Range (pptv) (Monthly Avg.)	n	Comments
Pt. Barrow, Alaska	70°N	< 1.5	139	
Cape Meares, Oregon	45°N	1.0-1.8	115	
Mauna Loa, Hawaii (11,000 ft.)	20°N	< 1.0	119	Undetected few times
Cape Kumukahi, Hawaii	20°N	1.7-4.0	107	
Marshall Islands	7°N	2.0-4.0	23	For only a few months
Samoa	15°S	1.0-2.0	110	
Tasmania	40°S	∿ 1.0	5	For only a few months
South Pole	90°S	< 0.75	21	Only in summer; undetected few times

Air samples were also obtained from coastal regions with high biological activity in the seawater. These samples had CH_3I concentrations higher than air samples obtained from the background stations in Table 8.1 Such sampling areas have been designated as "hot spots" because of the high CH_3I concentrations. The CH_3I concentrations observed at these "hot spots" are shown in Table 8.2

The majority of the samples were collected at coastal regions within the boundary layer, except those collected at Mauna Loa (11,000 feet) and at the south pole (∿9000 ft.).

Table 8.2

"Hot Spot" Station	Range (pptv)	Median (pptv)	n
Cape Point, South Africa	4-180	18	42
Irafoss, Iceland	1-31	6	15
Off Peruvian coast	4-10	7	6

The data record of 18 months indicates a seasonal cycle at Cape Meares and at Cape Kumukahi with CH_3I concentration higher in summer than in winter. The data from Mauna Loa indicate that the cycle is reversed with CH_3I concentration lower in summer than in winter. This is shown in Table 8.3:

Table 8.3

Station	Summer CH_3I (pptv)	n	Winter CH_3I (pptv)	n
Cape Meares	1.6 ± 0.2	21	1.0 ± 0.6	19
Cape Kumukahi	2.9 ± 1.4	30	1.8 ± 0.6	30
Mauna Loa	0.4 ± 0.3	29	0.9 ± 0.4	33

Summarizing the data from the 1591 samples analyzed over a period of 1½ years, it can be concluded that CH_3I is ubiquitous in the atmosphere and apparently biological in origin. The background CH_3I concentration in the equatorial region is about 3 pptv, dropping to 0.75 pptv at Pt. Barrow and to less than 0.5 pptv at the south pole. These results indicate an "equatorial bulge." All stations except Mauna Loa from Table 8.1 were considered in this data analysis of the latitudinal distribution of CH_3I.

Data from five aircraft flights showed that the CH_3I concentration drops off rapidly with increasing altitude. The data from the "GAMETAG" flights and comparison of data from Mauna Loa station versus Cape Kumukahi station indicate the CH_3I concentration above the boundary layer is less than half that in the boundary layer. This is seen in Table 8.4:

Table 8.4

	Above Boundary Layer CH_3I (pptv)	n	In Boundary Layer CH_3I (pptv)	n
GAMETAG flights	0.8 ± 0.4	8	2.7 ± 1.3	10
Hawaii stations	0.60± 0.05 (Mauna Loa)	119	2.15± 0.10 (Cape Kumukahi)	107

The observed altitude profile may be explained by the short lifetime of about 5 days (Lovelock, 1973; Zafiriou, 1974) and an oceanic surface source.

Model calculations of Chameides and Davis (1980) indicated significant effects on tropospheric photochemistry at 10 pptv of CH_3I. Therefore, as regards the troposphere, my data suggest that CH_3I will not play any significant role in tropospheric photochemical models. However, within the boundary layer in the vicinity of localized "hot spots" the data suggest that CH_3I may play a very significant role in the photochemical cycles indicated in Chameides and Davis' model.

Data for snow and rainwater samples indicate that precipitation can be supersaturated with CH_3I (relative to calculated CH_3I concentration in precipitation in equilibrium with observed atmospheric CH_3I at the time the samples were collected). Levels of supersaturation of up to a factor of 42 for snow and up to a factor of 145 for rainwater were observed.

CH_3I with its short lifetime may be used as a tracer for marine air masses, especially to study vertical transport since its sources are at the surface and its destruction due to solar radiation is rapid.

Based on the experience in using the TP-EC-GC method with a packed column, the need for the development of electron capture gas chromatographic techniques with even better resolution and greater sensitivity to measure the wide variety of organo-halogen compounds in the atmosphere was recognized. The use of different types of capillary columns and the addition of different dopant gases to the electron capture detector to optimize selective sensitivities to these organo-halogen compounds are being considered as exciting research topics for the future.

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VITA

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Rohith has been married to Lalani since 1979 and they have a son, Navindra, aged 4 years.