GLOBAL DISTRIBUTION OF ORGANO-BROMINE GASES

Rohith Gunawardena
B.Sc., University of Sri Lanka (Colombo), 1978
M.S., Oregon Graduate Center, 1985

A dissertation submitted to the faculty
of the Oregon Graduate Center
in partial fulfillment of the
requirements for the degree
Doctor of Philosophy
in
Atmospheric Sciences

April 1989

The dissertation "Global Distribution of Organo-Bromine Gases" by Rohith Gunawardena has been examined and approved by the following Examination Committee:

Reinhold A. Rasmussen, Dissertation Advisor
Professor

M. Aslam K. Khalil
Professor

James J. Huntzicker
Professor

Joann Sanders-Loehr
Professor

DEDICATION

I dedicate this dissertation to my parents.

ACKNOWLEDGEMENTS

I would like to thank all those who helped me during this work. I am grateful to my advisor Dr. Rei Rasmussen for giving me the opportunity to work on this project and for his guidance and support. I would like thank Bob Dalluge for his help with installing and maintaining the gas chromatographic equipment. I would like to thank Paul Turner and Jim Mohan for their help with computer work. I would also like to thank Dr. Aslam Khalil and Marty Shearer for their help with the Model calculations. I thank Edie Taylor, Don Stearns, Steve Crawford, Bob Watkins and all other friends for their help and support during this work.

I am grateful to the members of my examination committee, Drs. Rei Rasmussen, Aslam Khalil, Jim Huntzicker and Joann Sanders-Loehr, for examining my dissertation and for their helpful comments.

Finally, I would like to thank my wife, Lalani, for standing by me all these years.

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ABSTRACT

Global Distribution of Trace Organo-Bromine Gases

Rohith Gunawardena, Ph.D.
Oregon Graduate Center, 1989

Dissertation Advisor : Professor Reinhold A. Rasmussen

Both man-made and natural trace organo-bromine gases are present in the atmosphere in minute quantities - in the order of a few parts per trillion by volume. The man-made species $CBrF_3$ and $CBrClF_2$ are believed to be an important source of bromine to the stratosphere where they act as catalysts in the chlorofluorocarbon-ozone-depletion hypothesis.

A high resolution capillary column EC-GC method with an O_2 doped detector was developed, System V, to measure these and related organo-bromine gases in the atmosphere. It was developed from a packed column EC-GC method, System I, that was used to measure CH_3I at sub pptv levels but could measure only one organo-bromine gas, $CBrClF_2$. The development work to improve upon System I involved testing and matching different types of columns, carrier gases, make-up gases to the detector and detector temperatures to obtain operating conditions with optimum resolution, very high sensitivity and sufficiently stable baseline to measure atmospheric organo-bromine gases. During this development work, nine organo-bromine gases were identified in clean background air. The precision of analysis of the each system used was sufficient to determine the distributions and time course behavior of the species studied.

During the course of this study, samples collected weekly at 11 remote stations around the world spanning latitudes from 82°N down to 42°S were analyzed for these organo-bromine gases. In addition, samples collected for 10 years at Cape Meares - Oregon, Cape Matatula - American Samoa, Cape Grim - Tasmania and at the South Pole during the austral summer months were analyzed for long term trends of $CBrF_3$ and $CBrClF_2$. Significant altitudinal differences, interhemispheric gradients and seasonal cycles were observed for certain gases. Long-term trends were observed for $CBrF_3$ and $CBrClF_2$. $CBrF_3$ showed an exponential increase. From 1979 to 1987, its northern and southern hemispheric concentrations have increased at rates of 21% and 18% per year. $CBrClF_2$ showed a linear increase. Between 1985 and 1987, its northern and southern hemispheric concentrations have increased at rates of 16% and 19% per year. Model calculations indicated that the lifetimes of $CBrF_3$ and $CBrClF_2$ are about 80 and 20 years, respectively.

1 INTRODUCTION

Organo-bromine gases have been observed in the atmosphere in minute concentrations [Lovelock (1975), Harsch and Rasmussen (1977), Fabian et al. (1981), Singh et al. (1983), Khalil and Rasmussen (1984), Rasmussen and Khalil (1984), Berg et al. (1984), Hov et al. (1984), Khalil and Rasmussen (1985), Lal et al. (1985), Class et al. (1986), Khalil et al. (1987), Cicerone et al. (1988) and Singh et al. (1988)]. These observations do not provide systematic data on the behavior these gases in the atmosphere. When this study began, only a little was known about the spatial and temporal distribution of these gases over the globe. Even less was known about their sources and sinks in the atmosphere.

Some of these organo-bromine gases are purely anthropogenic, $CBrF_3$ and $CBrClF_2$ [Fabian et al. (1981), Khalil and Rasmussen (1985), Lal et al. (1985) and Singh et al. (1988)]. The natural species are believed to be $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ [Burreson et al. (1975), Rasmussen and Khalil (1984), Berg et al. (1984), Khalil and Rasmussen (1985), Gschwend et al. (1985) and Class et al. (1986)]. Some others are both anthropogenic as well as natural in origin: CH_3Br, and CH_2Br-CH_2Br [Lovelock (1975), Harsch and Rasmussen (1977), Fabian et al. (1981), Singh et al. (1983), Khalil and Rasmussen (1984), Hov et al. (1984), Rasmussen and Khalil (1984), Khalil and Rasmussen (1985) and Wei Min Hao (1986)].

1.1 Importance of Organo-Bromine Gases in the Atmosphere

Organo-bromine gases are believed to be the source of bromine to the stratosphere. In the chlorofluorocarbon - ozone depletion hypothesis, the man-made species, $CBrF_3$ and $CBrClF_2$, are believed to play a dominant role [Wofsy et al. (1975), Prather et al. (1984) and McElroy et al.(1986)]. These two gases are used in increasing amounts as high technology fire extinguishing chemicals [Khalil and Rasmussen (1985) and Anderson (1987)]. In regards to their green house effect, long-lived gases like $CBrF_3$ may be important in the future if their growth rates continue to increase indefinitely as $CBrF_3$ molecules in concert with the other chlorofluorocarbons absorb the Earths' infra red radiation at a different wave length than the major green house gases like CO_2 and H_2O [Watson et al. (1985)].

Wofsy et al. (1975) suggested that bromine is a better catalyst for initiating the O_3 degradation cycle than either nitric oxide or chlorine. Originally they suggested that a small bromine concentration of about 10 pptv in the stratosphere could reduce the global budget of ozone by about 0.3%. The proposed catalytic destruction of ozone by bromine could take either of two paths.

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + O \rightarrow Br + O_2$$

$$\overline{}$$

$$O + O_3 \rightarrow 2O_2 \tag{1}$$

or

$$2\{Br + O_3 \rightarrow BrO + O_2\}$$

$$BrO + BrO \rightarrow 2Br + 2O_2$$

$$O_3 + O_3 \rightarrow 3O_2 \qquad (2)$$

Subsequently, Prather et al. (1984) suggested ozone could be further depressed by accumulation of industrial bromocarbons (an additional 1% at current level of Br in the atmosphere). Their work suggested that the long life-times of $CBrF_3$ and $CBrClF_2$ would allow their steady state concentrations to increase to about 10 and 2.5 pptv respectively if their emission levels remained at their 1983 levels. If the use of these bromocarbons were to grow approximately six fold to 20×10^9 grams per year, the stratospheric abundance of bromine would rise to about 100 pptv. In their model the effects of chlorine and bromine are nearly additive. In conjunction with the present levels of chlorine and oxides of nitrogen, an increase in bromine from 20 to 100 pptv would cause a 4% reduction in the column density of ozone.

Total ozone has been measured at the British Antarctic Survey stations since 1957. Beginning in 1979 the values for total ozone were observed to have decreased considerably during October (early austral spring) [Farman et al. (1985) and McElroy et al. (1986)]. This phenomenon has been recognized as the "Ozone Hole" over Antarctica. The original suggestion was that this is due to the synergistic interaction of chlorine and bromine in the rate-limiting step in the ozone destruction cycle as described by the following equations.

$$Br + O_3 \rightarrow BrO + O_2 \quad (3)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (4)$$

$$BrO + ClO \rightarrow Br + Cl + O_2 \quad (5)$$

$$O_3 + O_3 \rightarrow 3O_2 \quad (6)$$

If it is assumed that Cl and Br are present in the form of reactive oxides, ClO and BrO, only concentrations of 3 ppbv and 25 pptv respectively are needed to reduce the column abundance of O_3 by 2% per day over Antarctica during the spring Ozone Hole [McElroy et al. (1986)]. The organo-bromine gases provide a source of bromine to the stratosphere [Wofsy et al. (1975), Prather et al. (1984) and McElroy et al. (1986)]. Therefore, to understand the role bromine plays in the atmosphere, it is necessary to determine global distribution of the organo-bromine gases.

Scientifically, the determination of the global distribution of the organo-bromine gases is important since we have so little information about their latitudinal distribution, seasonal variations, long-term trends, sources (anthropogenic and natural) and sinks.

The determination of the global distribution of organo-bromine gases was undertaken as an analytical challenge because of their extremely low concentration in the atmosphere [in the order of a few parts per trillion by volume (pptv) or less] and the presence of a great number of other organo-halogen gases.

1.2 Observations and Measurements of Organo-Bromine Gases in the Atmosphere

Lovelock (1975) with his invention of the electron capture detector was the first to measure an organo-bromine compound in the environment. He observed CH_3Br at a level of 2.5×10^{-9} ml of gas per ml of sea water on the English coast. Since then, CH_3Br has been observed by several investigators [Harsch and Rasmussen (1977), Fabian et al. (1981), Singh et al. (1983), Khalil and Rasmussen (1984), Rasmussen and Khalil (1984), Berg et al. (1984), Hov et al. (1984), Khalil and Rasmussen (1985), and Wei Min Hao (1986)].

Harsch and Rasmussen (1977) measured CH_3Br in urban air and found concentrations up to 220 pptv. They also measured CH_3Br in auto exhaust and found an automobile burning leaded gasoline contained 18,000 to 55,000 pptv CH_3Br in the exhaust. An automobile burning unleaded fuel had only 1,000 to 1,300 pptv CH_3Br in the exhaust. They suggested that auto exhaust is a significant source of CH_3Br in urban air and that the trend towards unleaded gasoline should decrease CH_3Br in urban air substantially. Wei Min Hao (1986) observed CH_3Br at concentrations similar to those observed by Harsch and Rasmussen (1977) in exhaust gases of automobiles burning leaded gasoline and concluded that automobiles contribute only a very small fraction (0.2%) to the global source of CH_3Br.

The CH_3Br measurements of Singh et al. (1983) and Khalil and Rasmussen (1985) indicate a higher concentration in the Northern hemisphere than in the Southern hemisphere (by about 25% to 35%). The concentrations observed by Khalil and Rasmussen were 10 pptv and 8 pptv for the Northern and Southern hemispheres respectively. The concentrations observed by Singh et al. were about a factor of 2.5 higher than those observed by Khalil and Rasmussen. The above observations were made on samples collected during two ocean cruises {one on the Atlantic [Singh et al. (1983)] and the other on the Pacific [Khalil and Rasmussen (1985)]}. The measurements of CH_3Br in the Arctic by Rasmussen and Khalil (1984), Hov et al. (1984) and

Berg et al. (1984) are in agreement - with concentrations in 10 to 15 pptv range. The only measurements of CH_3Br at the South Pole were made by Khalil and Rasmussen (1985). Their measurements indicated 7.5 pptv of CH_3Br at the South Pole.

The only stratospheric measurements of CH_3Br were made by Fabian et al. (1981) with a concentration of 1.2 pptv at 14.4 km and below the detection limit of 0.1 pptv at 20 km. Their samples were collected from balloon flights.

Gas chromatographic measurements of a number of organo-bromine gases have been done on samples collected in the Arctic (at Point Barrow, Alaska) - of $CBrClF_2$, CH_3Br, CH_2BrCl, CH_2Br_2 and CH_2Br-CH_2Br. The seasonal variations were reported by Rasmussen and Khalil (1984). The concentrations in and out of Arctic Haze layers were also determined. The concentration of CH_2BrCl and CH_2Br_2 during Spring (2.9 and 5.4 pptv respectively) were higher than during rest of the seasons (by 21% and 13% respectively). $CBrClF_2$ concentrations observed during the winter (1.2 pptv) was 9% higher than during the other seasons. The CH_3Br and CH_2Br-CH_2Br concentrations reported by Rasmussen and Khalil during this study were not considered to be significantly higher during the other seasons (at 10.6 and 1.5 pptv respectively). The measurements made by Rasmussen and Khalil in and out of the Arctic Haze layers indicated higher concentrations in-Haze for CH_2Br-CH_2Br (1.2 pptv), CH_2BrCl (2.3 pptv) and CH_2Br_2 (4.2 pptv) than out of the Haze (where the concentrations were 0.4, 2.0 and 2.5 pptv respectively). CH_3Br and $CBrClF_2$ had in-Haze concentrations of 10.5 and 1.1 pptv respectively but did not show any significant difference from the out-of-Haze concentrations (of 10.8 and 1.1 pptv respectively).

The measurements of CH_2Br_2 and CH_2Br-CH_2Br in the Arctic by Berg et al. (1984) had large variabilities with the concentrations 15±12 and 11±10 pptv respectively. $CHBr_3$ had a similar variability, 15±13 pptv. Their measurements indicated $CHBr_3$ to be the dominant contributor of gaseous bromine to the Arctic troposphere with 38±10%. Stratospheric samples, taken during a tropopause folding event by them, showed a total concentration of the four brominated species high enough to support a total stratospheric bromine concentration of 249 pptv.

In addition to measuring CH_3Br, Rasmussen and Khalil (1985) also measured $CBrF_3$, $CBrClF_2$, CH_2BrCl, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$ at the South Pole from October to December of 1984. The concentrations observed were 1, 1.1, 2.5, 0.7, 1 and 1 pptv respectively. They also observed a long-term increase in the $CBrClF_2$ concentration at the South Pole from 1979 through 1984. They estimated the concentration of $CBrClF_2$ in the Antarctic atmosphere to be increasing at the rate of 23% per year (or about 5.0×10^{10} grams per year). They suggested the presence of $CBrClF_2$ in the atmosphere is entirely due to anthropogenic activities, mainly as a high technology fire extinguishing compound.

Lal et al. (1985) measured $CBrClF_2$ at different altitudes (at 44° North) ranging from the ground level up to 25 km. They observed that the $CBrClF_2$ concentration dropped by two orders of magnitude at 25 km from the ground level concentration of about 1 pptv. They also observed from balloon flights in southern France that the $CBrClF_2$ concentration was increasing in the atmosphere at the rate of about 20% per year (from September 1982 to October 1984). Fabian et al. (1981), from their balloon flights measured $CBrF_3$ in the stratosphere. The concentration of $CBrF_3$ dropped from 1.0 pptv at 10 km to 0.06 pptv at 25.9 km.

Class et al. (1986) measured the organo-bromine gases $CHBrCl_2$, CH_2Br_2, $CHBr_2Cl$ and $CHBr_3$ - using EC-GC techniques with different capillary columns and combinations of capillary columns - in air samples collected in Europe and over the Atlantic ocean. They observed high concentrations of CH_2Br_2 and $CHBr_3$ in air samples collected at beaches with high algal populations as compared to samples collected at locations with no significant algal populations. The concentration range for CH_2Br_2 was 0.8 to 50 pptv and for $CHBr_3$ it was 0.6 to 460 pptv. $CHBr_2Cl$ concentrations observed were within 0.06 and 10 pptv and $CHBrCl_2$ concentrations were always 1 pptv or less. The concentrations of CH_2Br_2 and $CHBr_3$ observed by them above the marine boundary layer were less than one pptv.

Gschwend et al. (1985), in their identification of organo-bromine gases that were emitted from marine macroalgae, used a gas chromatograph mass spectrometer (GC-MS) system. They identified CH_2Br_2, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ and CH_3-CH_2-CH_2Br as the major organo-bromine gases emitted by some marine macroalgae. They estimated emissions of the organo-bromine gases per gram of dry weight of the alga per day. The major emissions were; 14,000 ng of $CHBr_3$, 4,300 ng of $CHBr_2Cl$ and 2,100 ng CH_2Br_2. The minor emissions were of 33 ng of $CHBrCl_2$ and 20 ng of CH_3-CH_2-CH_2Br. They observed that higher emissions of polybromomethanes from two brown algae, *Ascophyllum nodosum* and *Fucus vesiculosis*, occurred in October and November. They suggested that the macroalgae are a major source of volatile organo-bromine to the atmosphere. Burreson et al. (1975) found several bromine containing haloforms in the essential oil of the alga *Asparagopsis taxiformis* (Rhodophyta) - $CHBr_3$ (the major constituent), $CHBr_2Cl$, $CHBrClI$, $CHBr_2I$ and $CHBrI_2$.

Singh et al. (1988) measured $CBrF_3$ and $CBrClF_2$ in air samples collected at different altitudes at Hydrabad, India (17 ° N) and at Gap, France (44 ° N). $CBrF_3$ was analyzed using EC-GC and GC-MS techniques. $CBrClF_2$ was analyzed using EC-GC. They used sample sizes between 200 and 600 ml in their analyses. The $CBrF_3$ concentration decreased from 1.2 pptv at an altitude of 10 km to 0.05 pptv at 27 km. The $CBrClF_2$ concentration decreased from 1.96 pptv at an altitude of 10 km to 0.06 pptv at 22 km. The estimated 1987 northern hemisphere tropospheric concentrations were 1.3 pptv for $CBrF_3$ and 1.96 pptv for $CBrClF_2$. The annual growth rates were estimated to be 4.5% for $CBrF_3$ and 12% for $CBrClF_2$. Their estimates of 1987 global release rates were 1.2 kilo tons (kt) for $CBrF_3$ and 2.2 kt for $CBrClF_2$.

Barrie et al.(1988) measured ground level O_3, $CHBr_3$ (ground level and at different altitudes) and filtrable Br at Alert in the Canadian Arctic. Their measurements showed disappearance of O_3 with the polar sunrise. These disappearances of O_3 occurred when there were strong surface inversions. They also observed a strong inverse correlation between the ground level O_3 and the filtrable Br in April 1986. Highest levels of $CHBr_3$ were observed below the inversion layer. Their measurements indicated a seasonal variation of the $CHBr_3$ concentration with the highest levels in the late summer - early fall period and a rapid decrease and the lowest concentrations in early spring during the polar sunrise. They suggested $CHBr_3$ as the major source of the Br in the lower Arctic troposphere.

Cicerone et al.(1988) measured gaseous CH_3Br and $CHBr_3$ at five stations (Point Barrow in Alaska, Mauna Loa and Cape Kumukahi in Hawaii, Matatula in Samoa and Kaitorete in New Zealand). They analyzed air samples collected weekly in stainless canisters from 1984 through 1987 using GC-MS techniques. Their measurements showed the two southern hemispheric stations consistently had lower CH_3Br concentrations but the differences were not statistically significant. Typically the CH_3Br concentrations were 10 to 11 pptv. Their measurements showed increasing trend in the CH_3Br concentration at all stations at rates between 0.02 and 0.08 pptv per month. Seasonal cycles were observed in the $CHBr_3$ concentration at Point Barrow and Cape Kumukahi with maxima in December through February and minima in June through August. At Point Barrow the average $CHBr_3$ concentration was 6.3 pptv and at Cape Kumukahi it was 3.1 pptv. They did not observe increasing trend in the $CHBr_3$ concentration at any station.

Most measurements of individual organo-bromine gases that have been made by the various researchers [Lovelock (1975), Harsch and Rasmussen (1977), Singh et al. (1983), Khalil and Rasmussen (1984), Rasmussen and Khalil (1984), Khalil and Rasmussen (1985), Lal et al. (1985) and Class et al. (1986)] were done using EC-GC techniques. The work by Berg et al. (1984), Hov et al. (1984) and Gschwend et al. (1985) were done by GC-MS techniques.

The difficulties most researchers had in measuring atmospheric organo-bromine gases were due to the lack of analytical systems sensitive enough to study very low concentrations, at the pptv level of these gases as seen in the atmosphere. Class et al. (1986), because of the poor sensitivity of their detection system, had to use large sample volumes (up to 20 liters) for their measurements using purge and trap techniques for sample enrichment.

1.3 Residence Times for Some Bromine Species

Various investigators have estimated the residence times of the different forms of bromine in the atmosphere [Rahn et al. (1976), Kritz and Rancher (1980), Singh et al. (1983), Khalil and Rasmussen (1984), Prather et al. (1984) and Gammon et al. (1985)]. These range between 7.25

days in the case of gaseous inorganic bromine and 110 years for $CBrF_3$. As seen in Table 1.3.1, gaseous inorganic bromine and particulate bromine have shorter residence times (of the order of a few days) than the gaseous organic bromine (of the order of a few to several years). Gaseous bromine dominates over particulate bromine by a factor of 3.9 to 18.5 [Rahn et al. (1976), Cicerone et al. (1981) and Berg et al. (1983)]. It was also seen that, of the gaseous forms, organic bromine component was a factor of 5.5 higher than inorganic bromine [Rahn et al. (1976)].

It was apparent that, of the three forms of bromine in the atmosphere, the organic form was the most important because of the higher proportion of bromine in that form (organic : inorganic : particulate ratio was about 10 : 2 : 1) and the much higher residence times of the organic bromine as compared to the other forms. The high residence times of the organo-bromine gases were important because they allow the organo-bromine gases to be transported into the stratosphere where they can act as a source of bromine to the chlorofluorocarbon - ozone depletion scheme of reactions.

Seasonal cycles of the organo-bromine gases had not been studied on a global scale. Long term trends had been studied only in the case of $CBrClF_2$ though another purely anthropogenic organo-bromine compound, $CBrF_3$, with a long lifetime have been observed in the atmosphere. Altitudinal profiles have been studied only of $CBrF_3$, $CBrClF_2$ and CH_3Br. It was seen that even the organo-bromine gases that have been identified in the atmosphere have not been studied completely. The residence times for some bromine species are summarized in Table 1.3.1.

Table 1.3.1

The residence times for some of the bromine species

Investigator	Bromine Species	Lifetime
Rahn et al. (1976)	Particulate Br Inorganic gaseous Br Organic gaseous Br Total gaseous Br	10 days 8 days 25 days 24 days
Kritz & Rancher (1980)	Gaseous inorganic Br	7.25 days
Singh et al. (1983)	CH_3Br (from oceanic source)	1.2 years
Khalil & Rasmussen (1984)	CH_3Br	1.4 years
Prather et al. (1984)	$CBrF_3$ $CBrClF_2$	110 years 25 years
Gammon et al. (1985)	$CBrF_3$ $CBrClF_2$ CH_3Br CH_2Br-CH_2Br	110 years 25 years 2.3 years ~1 year
Fabian (1986)	$CBrF_3$ CH_3Br	62 - 112 years 1.7 years

1.4 ANNUAL GLOBAL INPUTS OF SOME BROMINE SPECIES

Several investigators have estimated the annual global input of some of these organo-bromine gases (see Table 1.4.1). Gschwend et al. (1985) estimated annual global inputs of organo-bromides to the atmosphere. They estimated the rates of release of different organo-bromides per gram of dry marine algae per day. Then from the global algal biomass estimates they calculated the annual inputs of organo-bromides to the atmosphere (from marine macroalgae). The contribution from industrial products were estimated from fumigants, gasoline additives and flame retardants. They also estimated the contribution that chlorination of water makes to the global budget of organo-bromides. Their estimate of global input for organo-bromides was 16.6×10^{10} grams bromine per year.

Singh et al. (1983) estimated the oceanic source of global CH_3Br to be 30.0×10^{10} grams per year. The global emissions of CH_3Br as estimated by Khalil and Rasmussen (1984) was 9.0×10^{10} grams per year, which was lower than the estimate for the oceanic source alone for CH_3Br as estimated by Singh et al. (1983).

Wei Min Hao (1986) in his study of the emission of CH_3Br from automobiles using leaded gasoline estimated that automobiles contribute only a small fraction of about 0.2% ($5.3 \pm 4.9 \times 10^7$ grams) to the annual global source of CH_3Br.

Anderson (1975) estimated the volcanic emissions of bromine (mostly as HBr) to be 5.0×10^{10} grams bromine per year. The estimated annual global inputs of some bromine containing compounds are summarized in Table 1.4.1.

TABLE 1.4.1

Estimated annual global inputs of bromine containing gases

Investigator Source	Bromine (1.0×10^{10} g/year)
Gschwend et al. (1985)	
Macroalgae	1.0
Industrial Products	
CH_3Br (fumigant)	5.0
CHBr=CHBr (gasoline additive, fumigant)	10.0
$CBrF_3$ (flame retardant)	0.1
Chlorination of Water	0.5
Total global input	16.6
Singh et al. (1983)	
Global oceanic source for CH_3Br	30.0
Khalil and Rasmussen (1984)	
Global emissions of CH_3Br	9.0
Khalil and Rasmussen (1985)	
Global emissions of $CBrClF_2$	0.5
Lal et al. (1985)	
Global emission of $CBrClF_2$	0.36
Wei Min Hao (1986)	
Global emissions of CH_3Br from automobiles	$5.3 \pm 4.9 \times 10^{-3}$

1.5 The need for studying atmospheric trace organo-bromine gases

Four reasons can be given for studying the global distribution of trace organo-bromine gases.

1. Measuring very low concentrations of organo-bromine gases in the atmosphere - an analytical challenge.
2. No systematic studies of these organo-bromine gases on a global scale.
3. The importance of the man made organo-bromine gases to the stratospheric chemistry presently and in the future (in the chlorofluorocarbon-ozone depletion hypothesis).
4. The possible contribution by long lived organo-bromine gases to the energy balance of the earth's atmosphere.

2 EXPERIMENTAL METHOD

Introduction

This section on the experimental method discusses of the different configurations of the temperature-programmed electron capture gas-chromatographic systems (TP-EC-GC) used in the course of this study from 1981 to 1988. The methods used to collect and store the air samples are also discussed. Each gas-chromatographic system used a Perkin-Elmer 3920 B gas chromatograph equipped with an ^{63}Ni electron capture detector. The temperature program of the oven used liquid nitrogen for sub-ambient operation. The chromatograms, peak height and peak area information were recorded by a Hewlett-Packard 3388 A integrator.

2.1 The Development of the Experimental Method

The original TP-EC-GC system used a packed column. It had limited sensitivity and resolution. The system was primarily used to measure atmospheric CH_3I at low pptv concentrations. From this low resolution packed column TP-EC-GC system a conventional high resolution capillary column Cap-EC-GC system evolved. The capillary column system required a make-up gas to the detector for proper operation. Therefore, it was possible to use different types of make-up gases to improve the sensitivity of the detector to species with low electron capture efficiencies. This was done without affecting the resolution of the chromatographic peaks. The final Cap-EC-GC system (V) was tuned for very high sensitivity to measure weakly absorbing organo-bromine gases in clean background air samples through the use of an O_2 doped N_2 make-up gas.

2.1.1 System I

TP-EC-GC (SP-2100 Packed Column with Ar/CH_4 Carrier Gas)

The TP-EC-GC system used a packed column of dimensions 10 feet long by 1/4 inch OD. Column material was 10% SP-2100 (methyl-silicone) on 100/120 mesh Supelcoport. Ar(95%)/CH_4(5%) carrier gas was used at a flow rate of 50 ml per minute. The temperature of the GC oven was programmed to start at 10°C with a 4-minute initial hold and to increase to 80°C at the rate of 16°C per minute. The run time for each analysis was 20 minutes. The sub-ambient initial temperature was obtained with liquid N_2 coolant. The detector was operated at 350°C with a standing current of 3.0 nano amperes. With System I eleven gases were measured of which only one ($CBrClF_2$) contained bromine (Figure 2.1.1.1).

System I was used from 1981 to 1983 for my MS thesis work [Gunawardena (1985)] to measure atmospheric CH_3I. Typically the CH_3I concentrations were between 1 and 3 pptv. At the conditions this system was operated, it had sufficient resolution and sensitivity to measure CCl_2F_2 [F-12], CCl_3F [F-11], CH_3I, CCl_2F-$CClF_2$ [F-113], $CHCl_3$, CH_3-CCl_3, CCl_4, $CHCl=CCl_2$ [TCE] and $CCl_2=CCl_2$ [PCE]. $CClF_2$-$CClF_2$ [F-114] was also observed but not measured due to lack of a calibration standard. CH_3Br was observed in a few samples that were analyzed by the TP-EC-GC method but was not in the calibration tank used. There was an unidentified peak in all the chromatograms with a retention time that was between F-114 and CH_3Br. This peak was later identified as $CBrClF_2$ [BCF]. The standard used for the CH_3I work had this compound in it and was later calibrated for the ambient level of $CBrClF_2$. The data were recovered for the period 1981 to 1983 by measuring the peak heights by hand. The only organo-bromine data I was able to recover from the TP-EC-GC chromatograms were those of

$CBrClF_2$. These data provided an important part of the long term BCF data set for seven sampling stations; Point Barrow - Alaska, Cape Meares - Oregon, Mauna Loa and Cape Kumukahi - Hawaii, Cape Matatula - American Samoa, Cape Grim - Tasmania and the South Pole.

Based on my experience with the TP-EC-GC system it was apparent that a more sensitive system with higher resolution was needed to measure other trace organo-halogen gases in the atmosphere. The result was a TP-EC-GC system with a capillary column, - a Cap-EC-GC system.

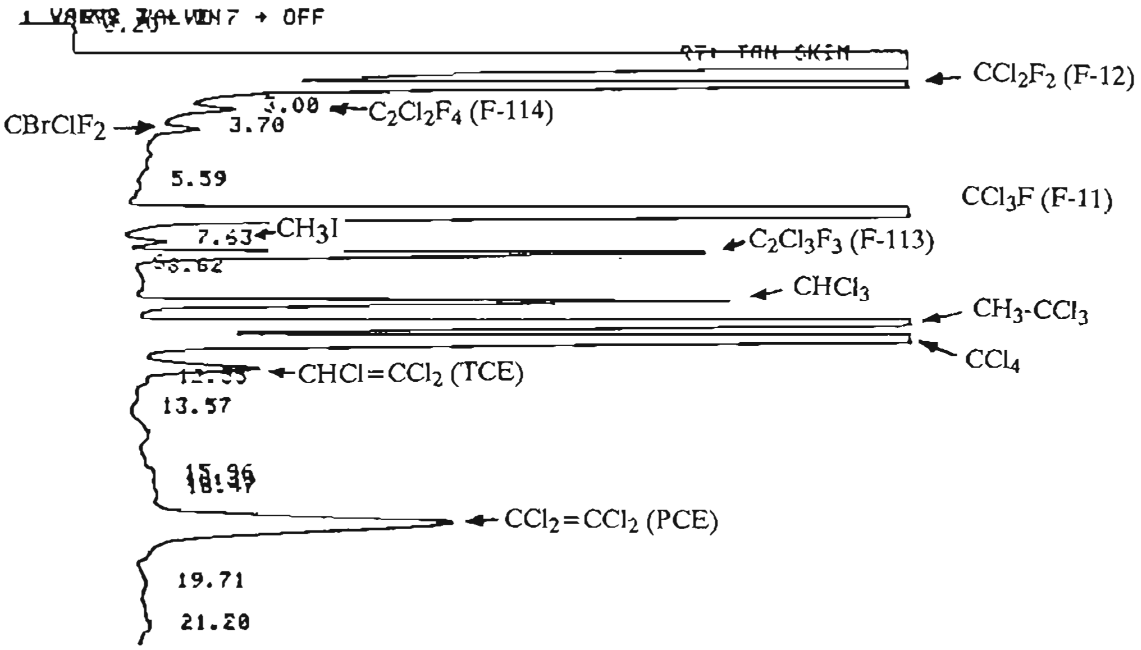


Figure 3.1.1.1 : A typical chromatogram from System I
Packed GC column with Ar/CH_4 carrier gas
Detector temperature 350°C
One organo-bromine gas measured
$CBrClF_2$

2.1.2 System II

CAP-EC-GC (SE-30 Capillary Column with Ar/CH_4 Make-Up Gas)

The first EC-GC system in our laboratory with a capillary column used a J & W Scientific SE-30 (methyl silicone) column, length 30 m, diameter of 0.25 mm and a film thickness 0.25 μm. The standing current (3.0 nano amperes) was the same as used for the TP-EC-GC system. The detector temperature was lowered to 325°C from 350°C. The carrier gas used was Zero grade He and operated at a pressure of 20 psig. The make-up gas to the detector was Ar(95%)/CH_4(5%) operated at a flow rate of 50 ml per minute. The temperature program started at -60°C with an initial hold time of 2.25 minutes, increasing to 150°C at a rate of 8°C per minute. System II was used to measure 17 gases (Figure 2.1.2.1). This system was used from January 1983 to February 1984.

With System II, it was possible to load a larger sample (500 ml) than with System I (100 or 200 ml) and have a stable baseline. With the higher resolution and the ability to load a larger sample volume, it was possible to measure three organo-bromine gases, CH_3Br, CH_2Br_2 and CH_2Br-CH_2Br (EDB) not measured with the packed column. In Figure 2.1.2.1 the four organo-bromine gases measured are labelled on the left margin.

During this phase of the development work, the effect of the make-up gas flow rate on the ECD response to $CBrClF_2$ [BCF], CH_3Br, CH_2Br_2 and CH_2Br-CH_2Br [EDB] was investigated. The results (Table 2.1.2.1) showed that decreasing the make-up gas flow rate increased the response of the ECD to the four gases. This was suspected due to the increased residence time of the molecules in the detector.

TABLE 2.1.2.1

The effect of the Ar/CH_4 make-up gas flow rate on the ECD response

Compound	Relative response (peak height)		
	50 ml per min.	31 ml per min.	11 ml per min.
$CBrClF_2$ (BCF)	727	989	2387
CH_3Br	114	175	437
CH_2Br_2	206	283	439
CH_2Br-CH_2Br (EDB)	29	33	34

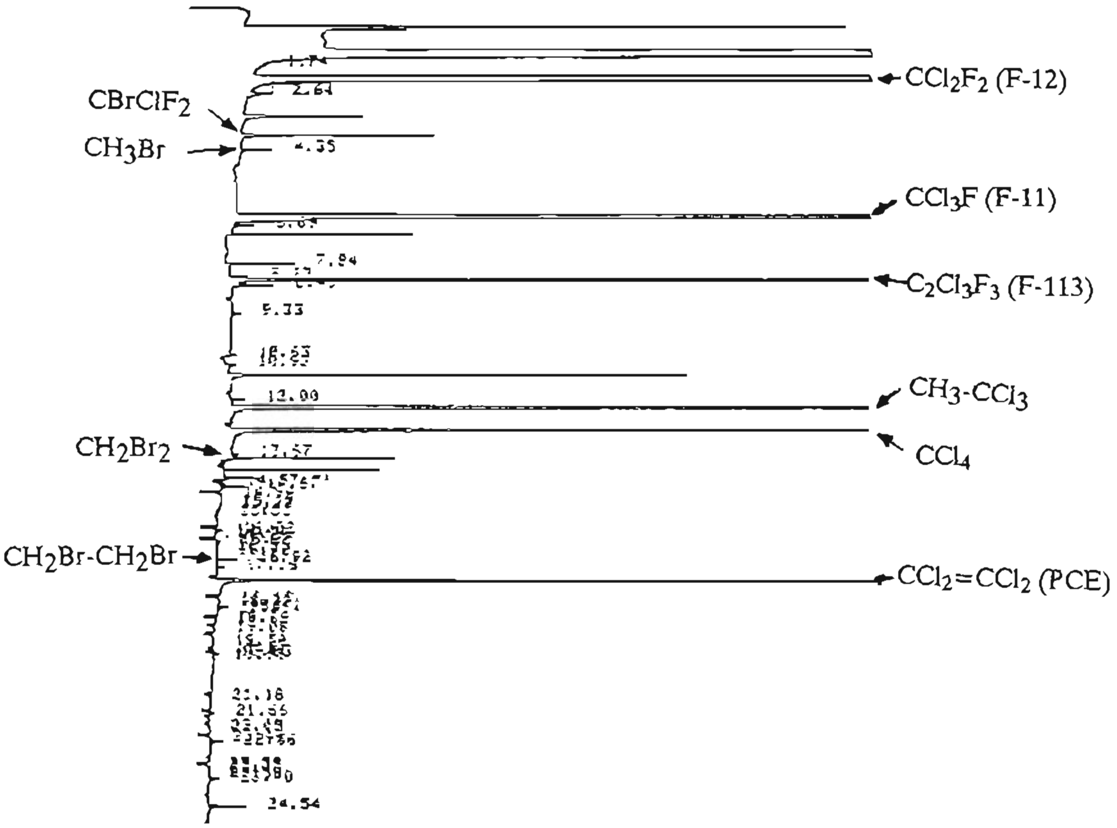


Figure 3.1.2.1 : A typical chromatogram from System II
SE-30 capillary column with Ar/CH_4 make-up gas
Detector temperature 325°C
Four organo-bromine gases measured
$CBrClF_2$, CH_3Br, CH_2Br_2 and CH_2Br-CH_2Br

2.1.3 System III

CAP-EC-GC (SE-30 Capillary Column with N_2 Make-Up Gas and Detector Temperature of 250°C)

With Cap-EC-GC systems it was possible to change the make-up gas without affecting the resolution of the chromatographic peaks while changing the response of the ECD to different gases. In System III, N_2 was substituted for Ar/CH_4 as the make-up gas to the detector. The make-up gas flow rate was 50 ml per minute. Introduction of N_2 make-up gas increased the sensitivity of the ECD so three other organo-bromine gases CH_2BrCl, $CHBr_2Cl$ and $CHBr_3$ could be measured. A total of twenty two gases were measured with this method. Figure 2.1.3.1 shows a typical chromatogram from System III with the seven organo-bromine gases measured labelled on the left margin. This system was used from February 1984 to September 1984.

During this phase of the development work, the effect of temperature on the sensitivity of the electron capture detector to different organo-bromine gases was investigated. The results showed that the sensitivity increased with increased detector temperature for $CBrClF_2$ [BCF], CH_3Br, CH_2BrCl and CH_2Br_2. For $CHBr_3$ the sensitivity decreased with increasing detector temperature. There were no such changes in the detector response for $CHBr_2Cl$ and $CH_2Br\text{-}CH_2Br$ [EDB]. (Table 2.1.3.1 shows the effect of temperature on ECD response to these seven organo-bromine gases.) The detailed effect of temperature on the ECD response to $CBrClF_2$, CH_3Br, CH_2BrCl, CH_2Br_2 and $CHBr_3$ are plotted in Figures 2.1.3.2, 2.1.3.3, 2.1.3.4, 2.1.3.5 and 2.1.3.6 respectively. In conclusion, a detector temperature of 250°C and a standing current of 2.0 nano amperes were selected for use with the N_2 make-up gas because they provided a stable baseline and sufficient sensitivity to measure seven organo-bromine gases.

TABLE 2.1.3.1

Effect of the detector temperature on ECD response to seven organo-bromine gases

Compound	Detector temperature (°C)						
	350	325	300	275	250	225	200
	Relative response (peak height)						
$CBrClF_2$	518	542	465	414	396	370	397
CH_3Br	90	90	65	*	53	*	27
CH_2BrCl	12	14	12	9	8	5	6
CH_2Br_2	167	170	157	141	132	116	115
$CHBr_2Cl$	**	14	22	15	21	17	26
$CH_2Br\text{-}CH_2Br$	22	27	35	26	25	23	27
$CHBr_3$	**	23	38	52	114	130	162

* Baseline interference

** Not observed at this detector temperature

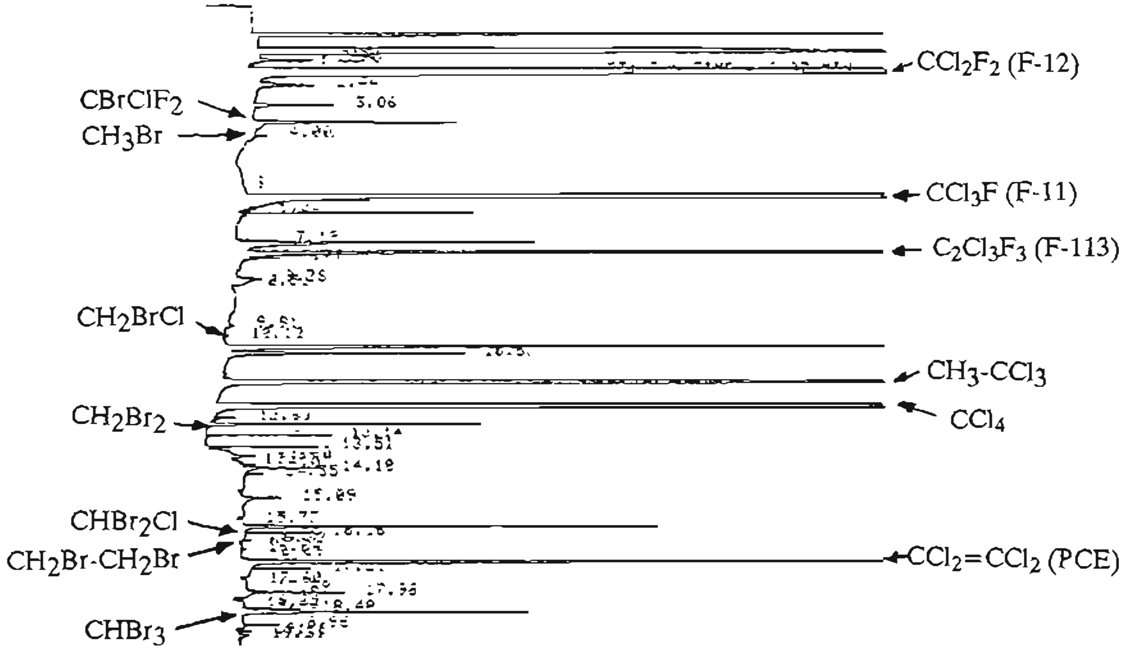


Figure 3.1.3.6 : A typical chromatogram from System III
SE-30 capillary column with N_2 make-up gas
Detector temperature 250°C
Seven organo-bromine gases measured
$CBrClF_2$, CH_3Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$,
CH_2Br-CH_2Br and $CHBr_3$

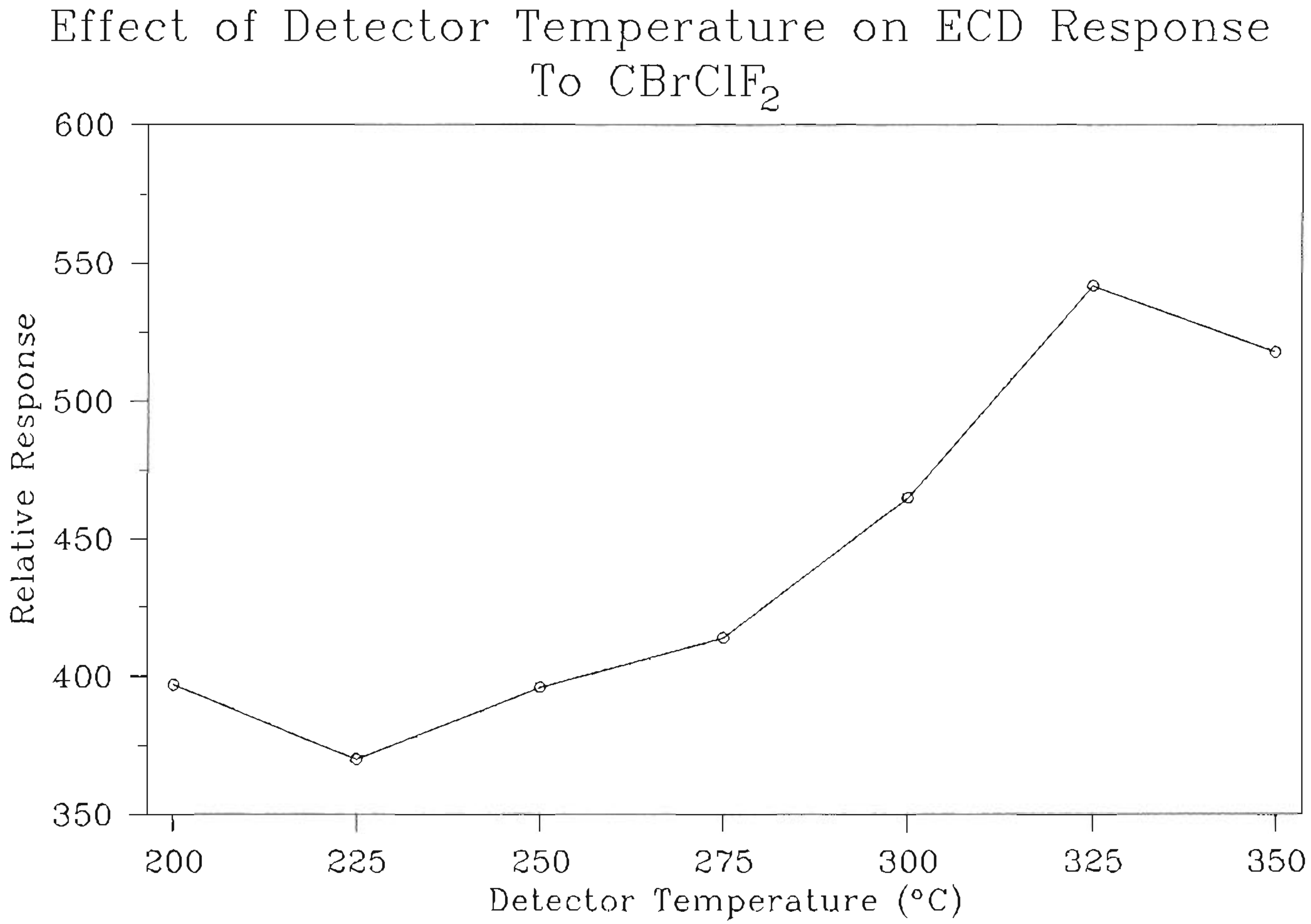


Figure 2.1.3.2 : The effect of detector temperature on the ECD response to $CBrClF_2$

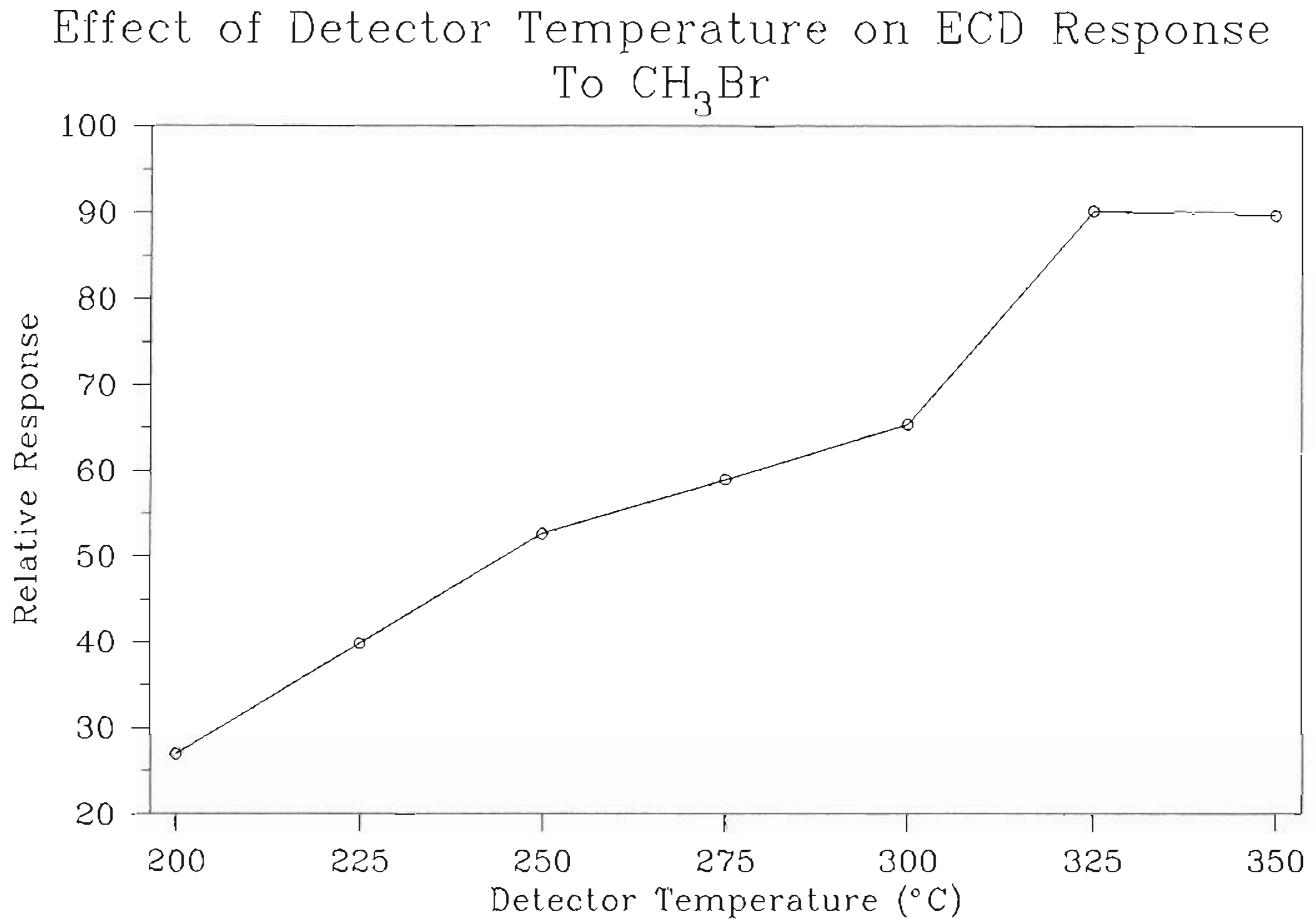


Figure 2.1.3.3 : The effect of detector temperature on the ECD response to CH_3Br

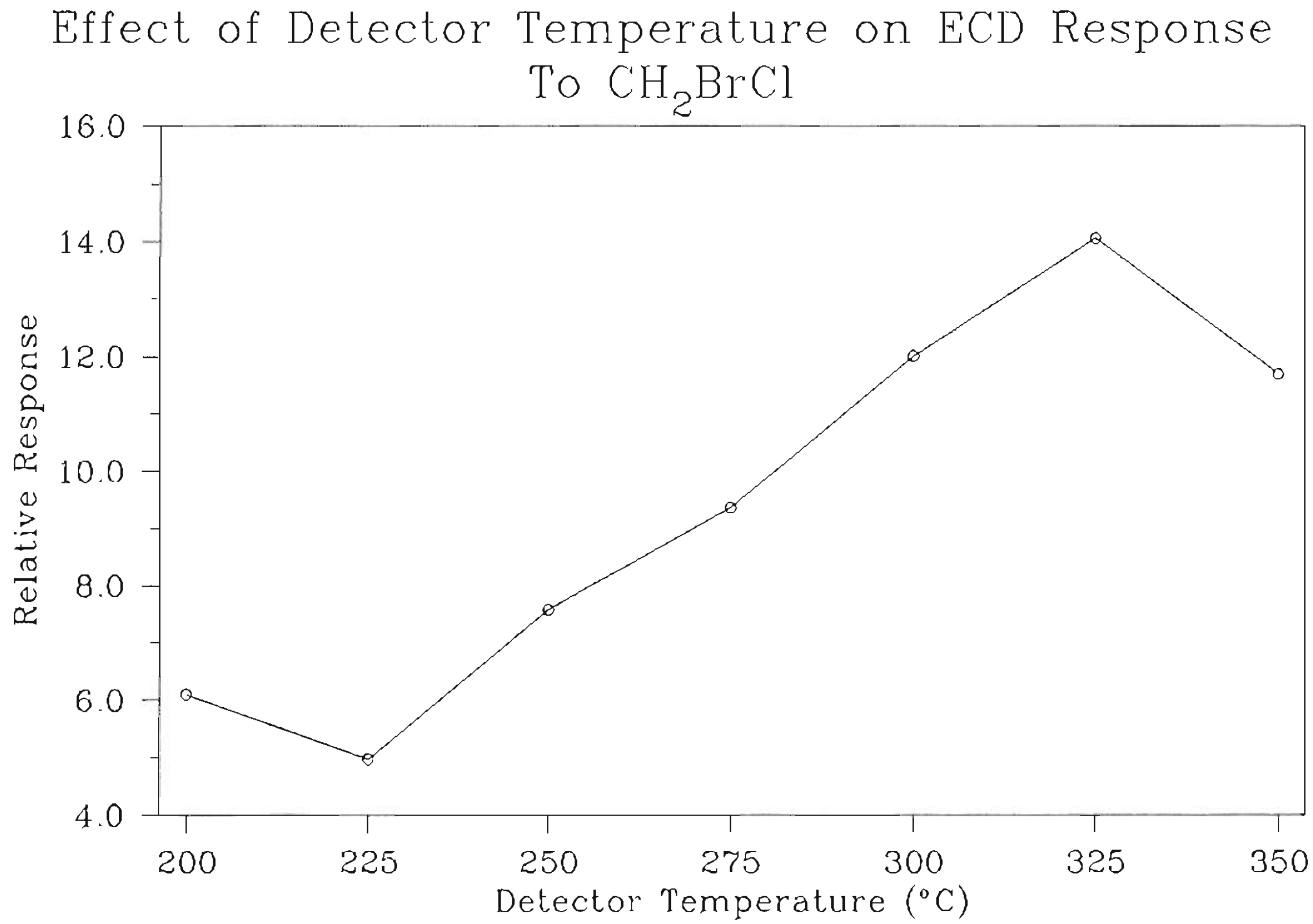


Figure 2.1.3.4 : The effect of detector temperature on the ECD response to CH_2BrCl

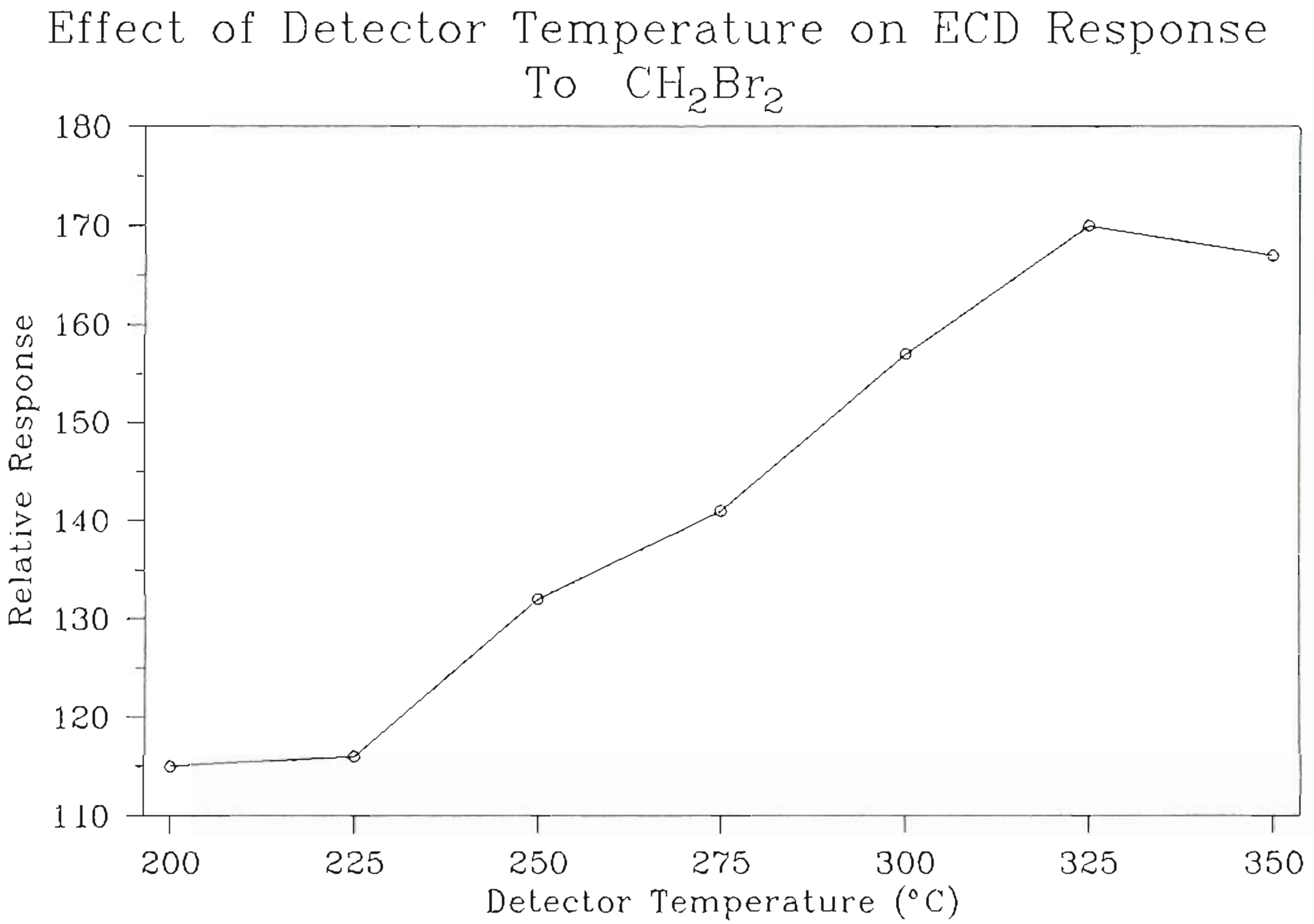


Figure 2.1.3.5 : The effect of detector temperature on the ECD response to CH_2Br_2

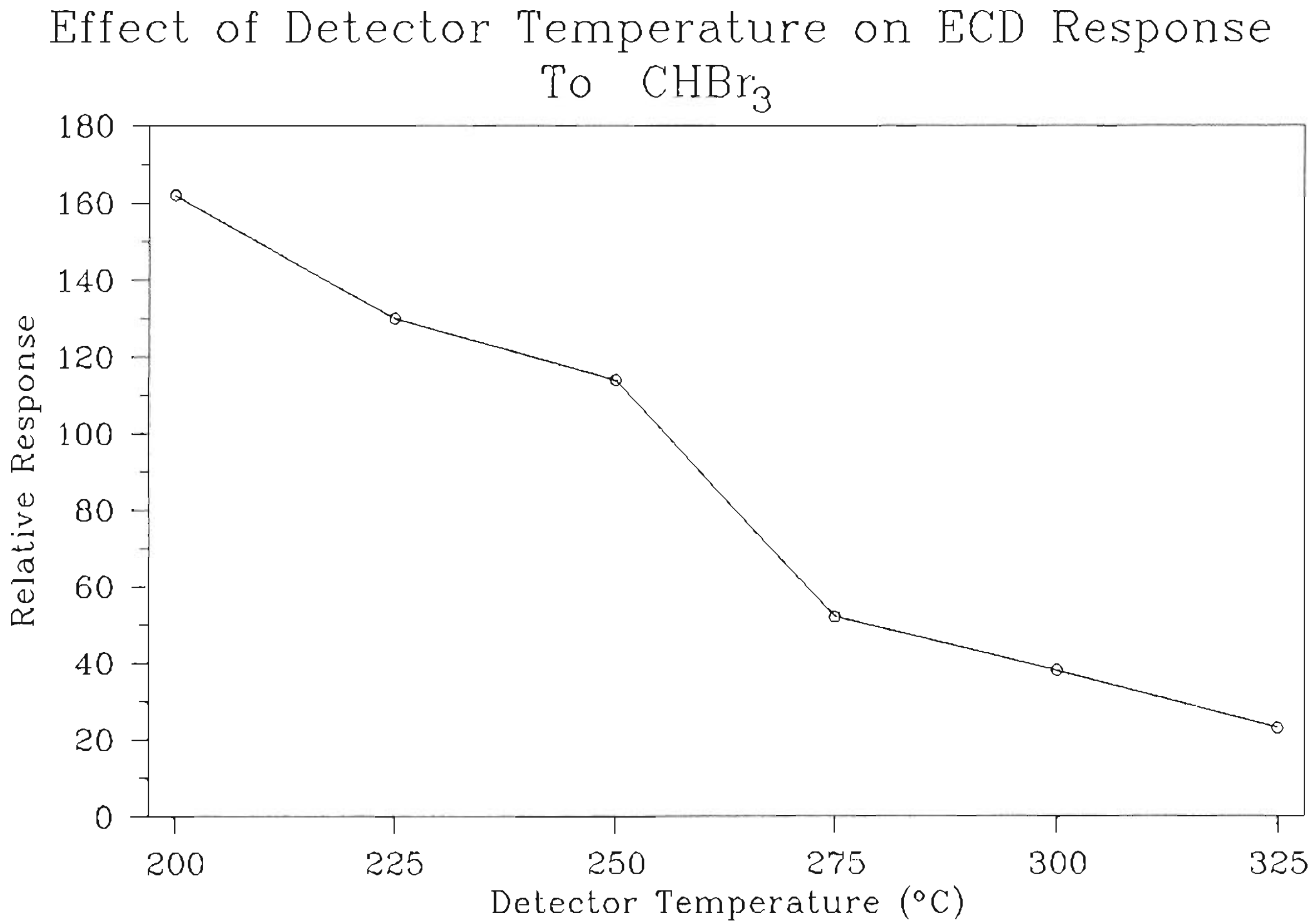


Figure 2.1.3.6 : The effect of detector temperature on the ECD response to $CHBr_3$

2.1.4 System IV

CAP-EC-GC (SE-30 Capillary Column with O_2 Doped N_2 Make-Up Gas)

In System IV, an O_2 doped N_2 was substituted for N_2 as the make-up gas to the detector. The make-up gas flow rate was 50 ml per minute. Introduction of O_2 doped N_2 make-up gas increased the sensitivity of the detector selectively so CH_3-CH_2Br could be measured in ambient air samples without the loss of sensitivity to the other gases. A total of twenty five organo-balogen gases were measured with this system of which eight contained bromine. Figure 2.2.4.1 shows a typical chromatogram from System IV with the organo-bromine gases labelled on the left margin. This system was used from September 1984 to April 1985.

During this step in the development work, O_2(0.292%)/N_2 was tested as a make-up gas to the detector. Studies by Grimsrud and Miller (1978) and Rasmussen et al. (1980) had shown that doping the N_2 carrier gas with O_2 increased the response of the ECD to weakly absorbing gases such as CH_3Cl. In the present work, O_2 greatly enhanced the ECD response to all gases (compared to pure N_2 make-up gas) but did not give a stable baseline. Therefore, O_2(0.14%)/N_2 was tested as the make-up gas. At this level a stable baseline was obtained. Of the three make-up gases N_2, O_2(0.14%)/N_2 and O_2(0.292%)/N_2, the smallest ECD response to organo-bromine gases was with N_2 and the largest response was with O_2(0.292%)/N_2. With an O_2 doped N_2 make-up gas, the relative increase in ECD response was greater to weakly absorbing gases than to strong absorbers. To obtain a stable baseline with the O_2 doped N_2 make-up gas, the standing current was lowered from 2.0 to 0.5 nano amperes and the detector temperature was raised from 250°C to 275°C. The effects of O_2 doping on the ECD response to organo-bromine gases are shown in Table 2.1.4.1. The detailed effect of O_2 doping to $CBrClF_2$, CH_3Br,

CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$ are plotted in Figures 2.1.4.2, 2.1.4.3, 2.1.4.4, 2.1.4.5, 2.1.4.6, 2.1.4.7, 2.1.4.8 and 2.1.4.9 respectively. A detector temperature of 275°C, a standing current of 0.5 nano amperes and O_2(0.14%)/N_2 make-up gas were selected for System IV because they provided a stable baseline and the needed increase in sensitivity to measure eight organo-bromine gases.

TABLE 2.1.4.1

The effect of O_2 doping of the N_2 make-up gas on ECD response to organo-bromine gases

Compound	Relative response (peak height)		
	Pure N_2 * 2.0 nano amps. 250°C	O_2(0.14%)/N_2 0.5 nano amps. 275°C	O_2(0.296%)/N_2 0.5 nano amps. 275°C
$CBrClF_2$ (BCF)	3028	5934	10499
CH_3Br	88	1006	3276
CH_3-CH_2Br	**	66	248
CH_2BrCl	31	73	148
CH_2Br_2	495	1439	2574
$CHBr_2Cl$	116	475	879
CH_2Br-CH_2Br (EDB)	37	107	236
$CHBr_3$	624	2328	4412

* The standing current used with N_2 make-up gas was 2.0, it was 0.5 with O_2 doped N_2.

** Peak not observed with N_2 make-up gas.

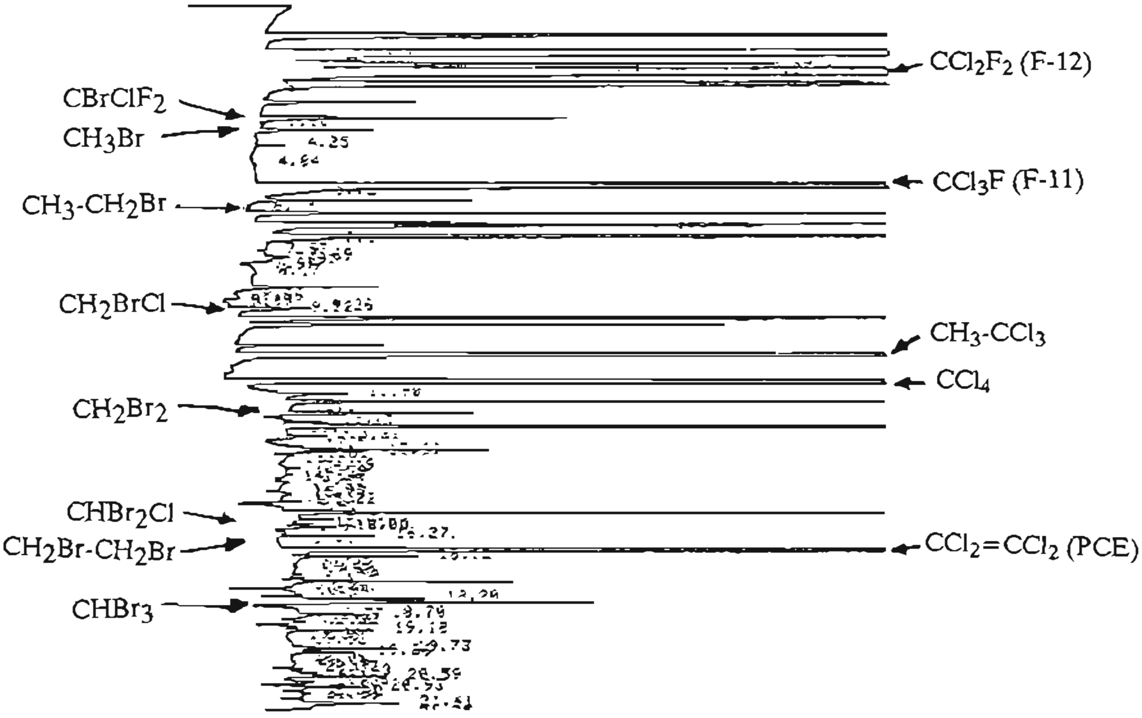


Figure 3.1.4.1 : A typical chromatogram from System IV

SE-30 capillary column with O_2(0.14%)/N_2 make-up gas

Detector temperature 275°C

Eight organo-bromine gases measured

$CBrClF_2$, CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$

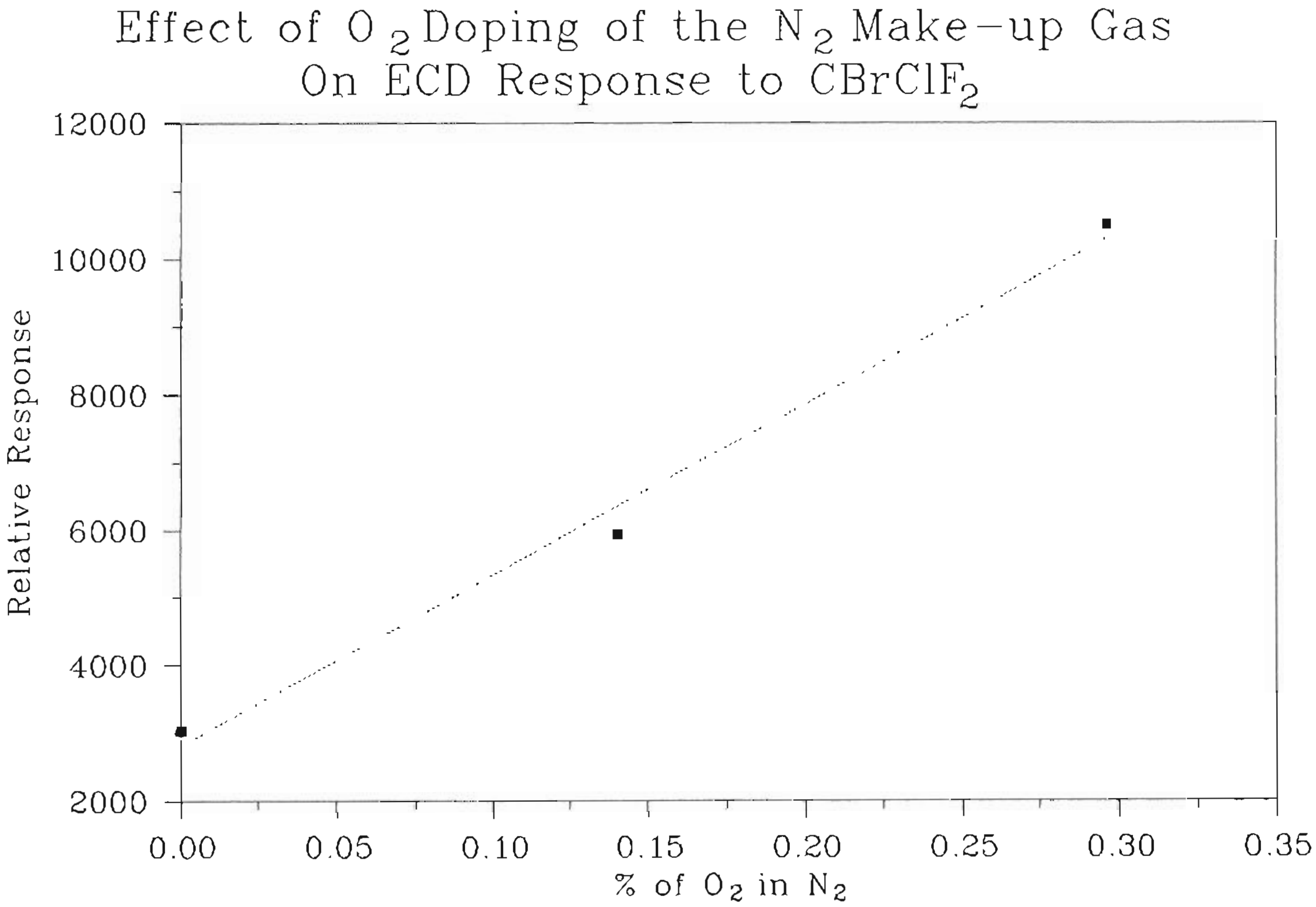


Figure 2.1.4.2 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to $CBrClF_2$

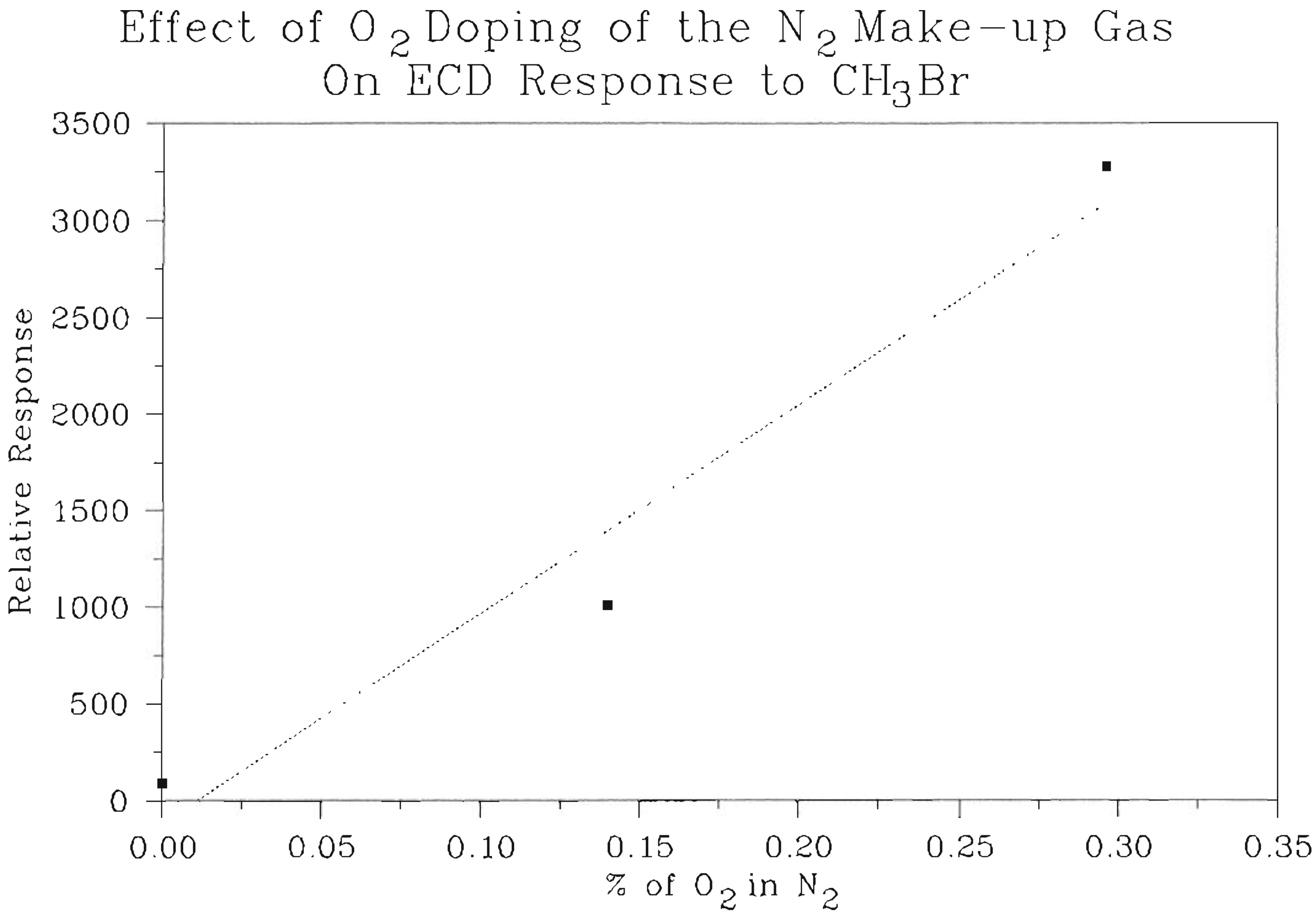


Figure 2.1.4.3 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to CH_3Br

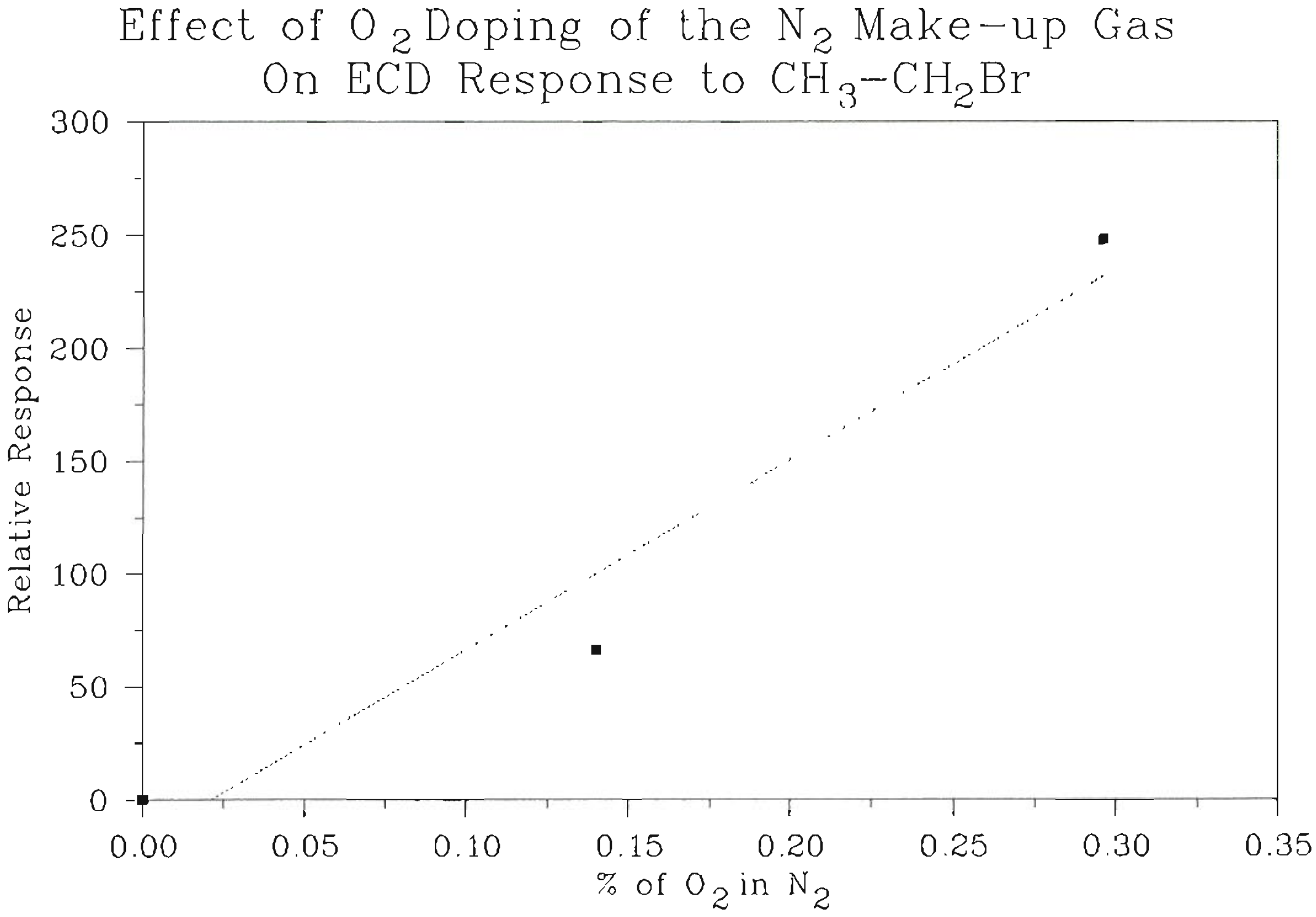


Figure 2.1.4.4 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to CH_3-CH_2Br

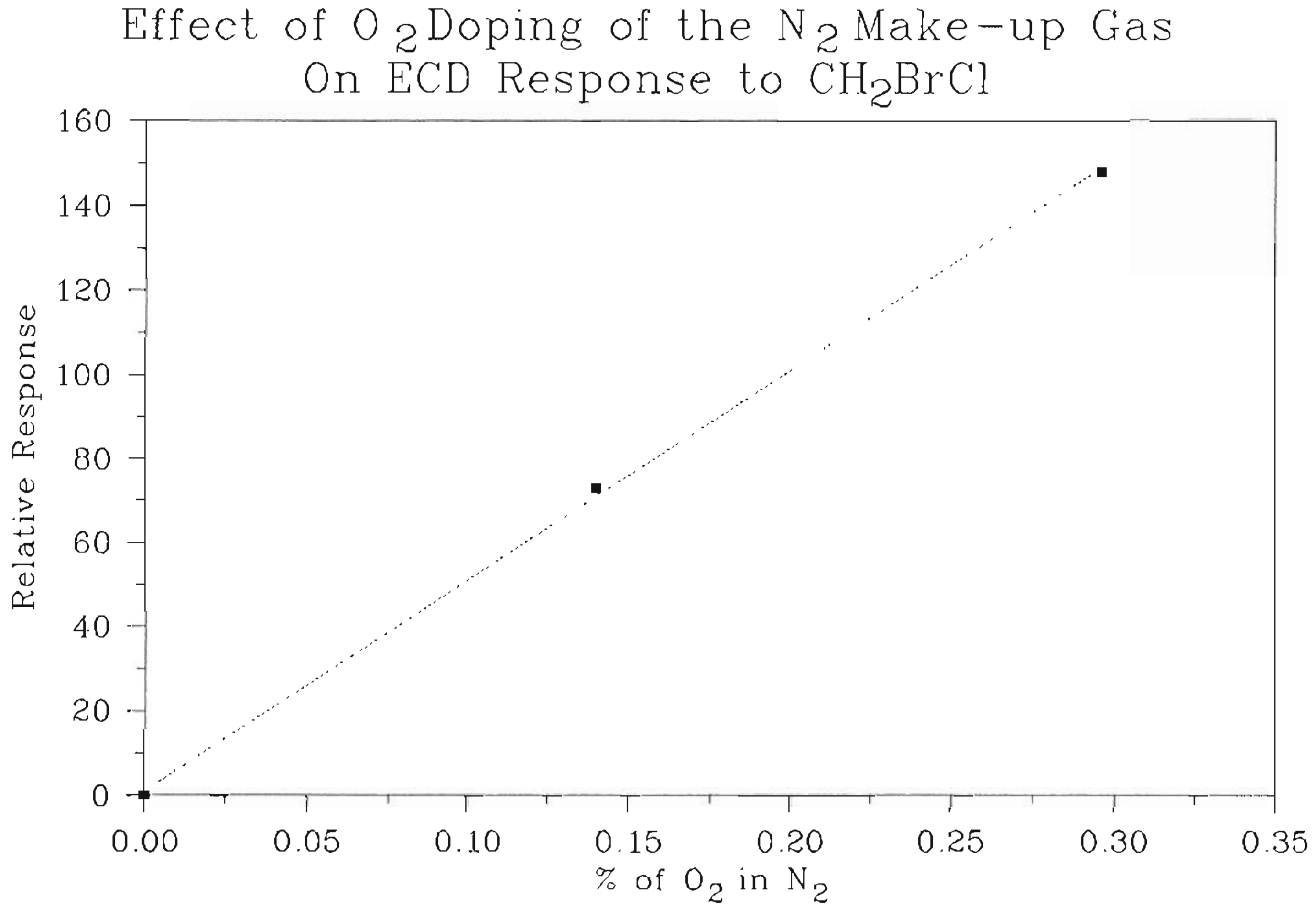


Figure 2.1.4.5 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to CH_2BrCl

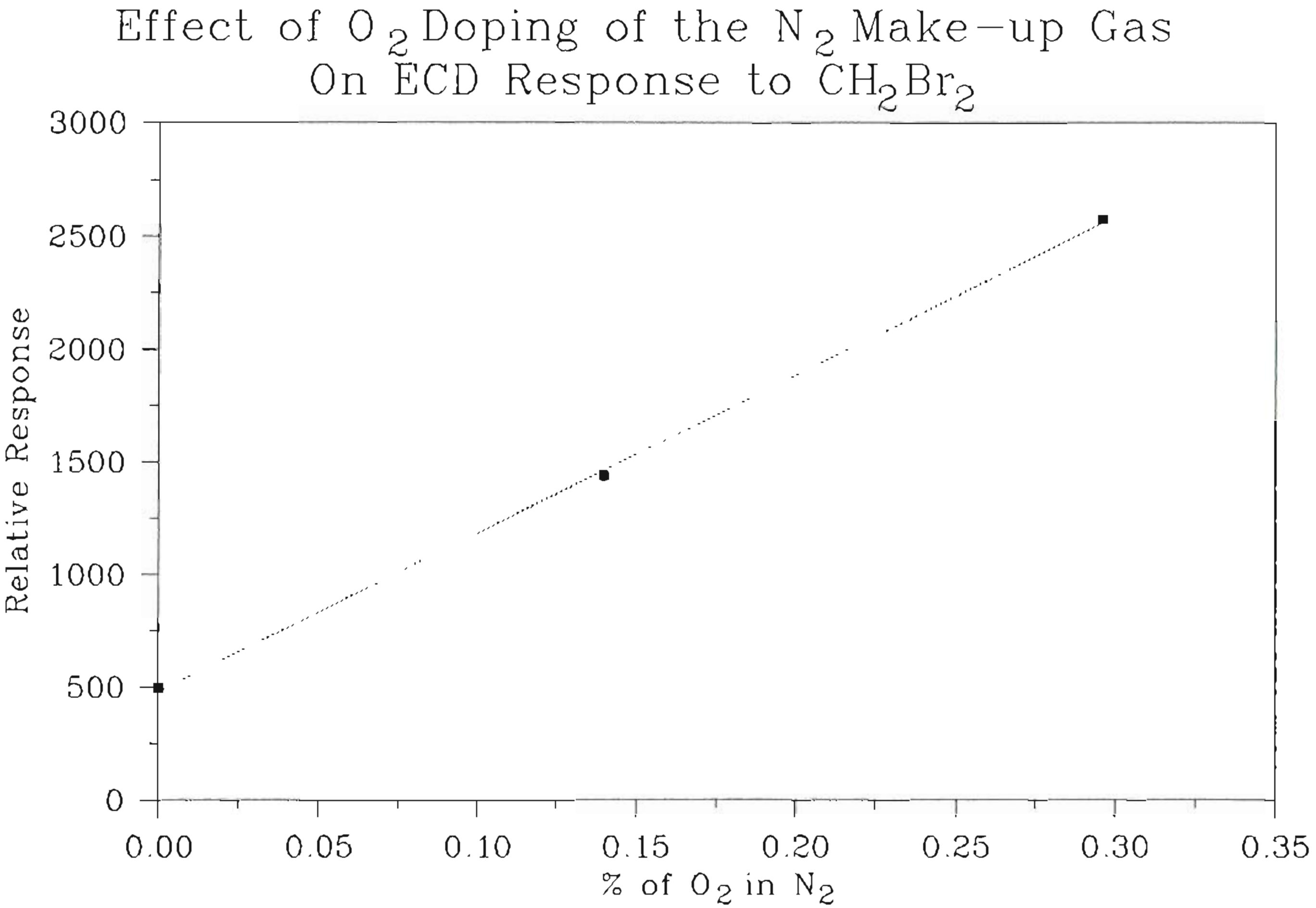


Figure 2.1.4.6 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to CH_2Br_2

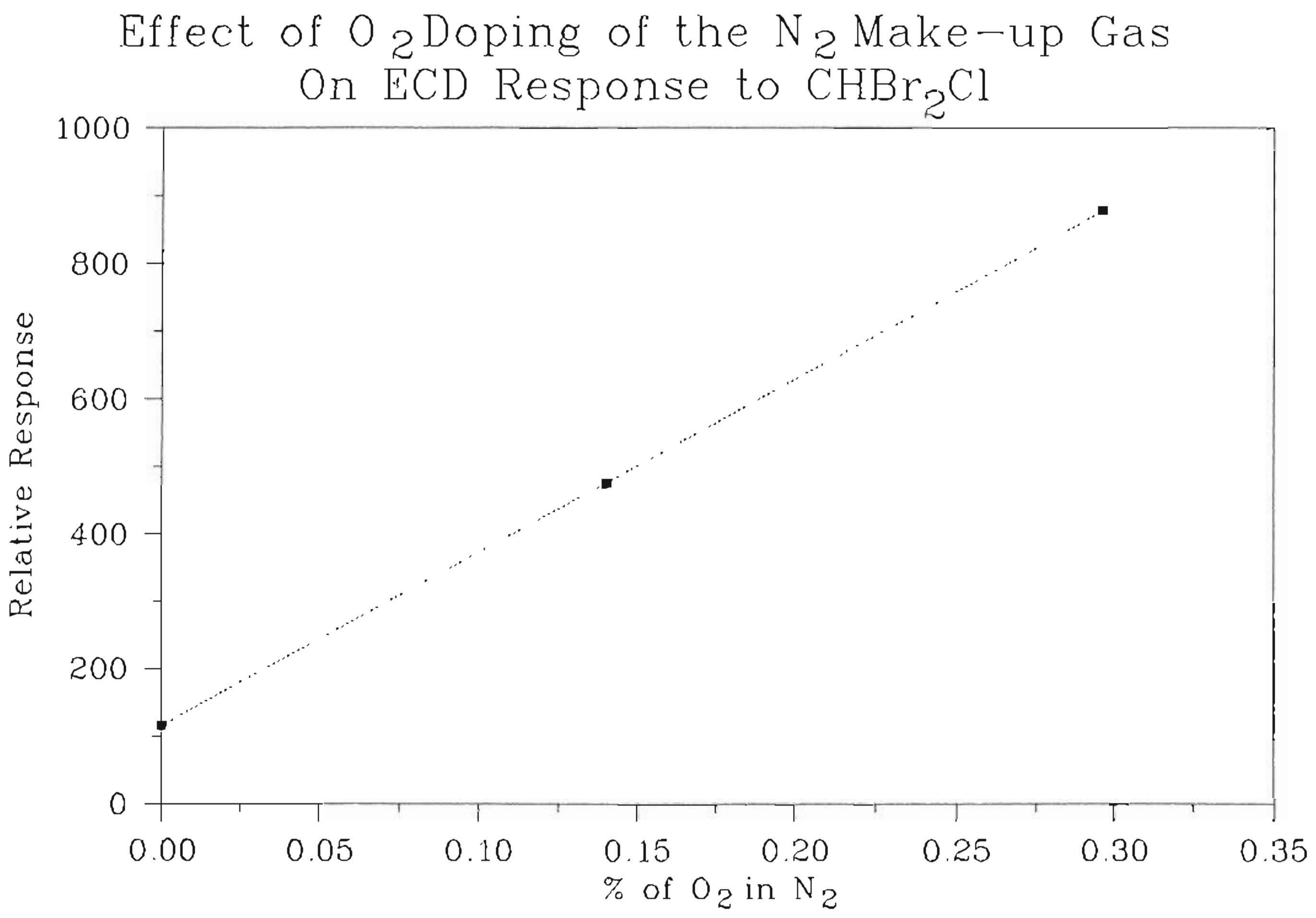


Figure 2.1.4.7 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to $CHBr_2Cl$

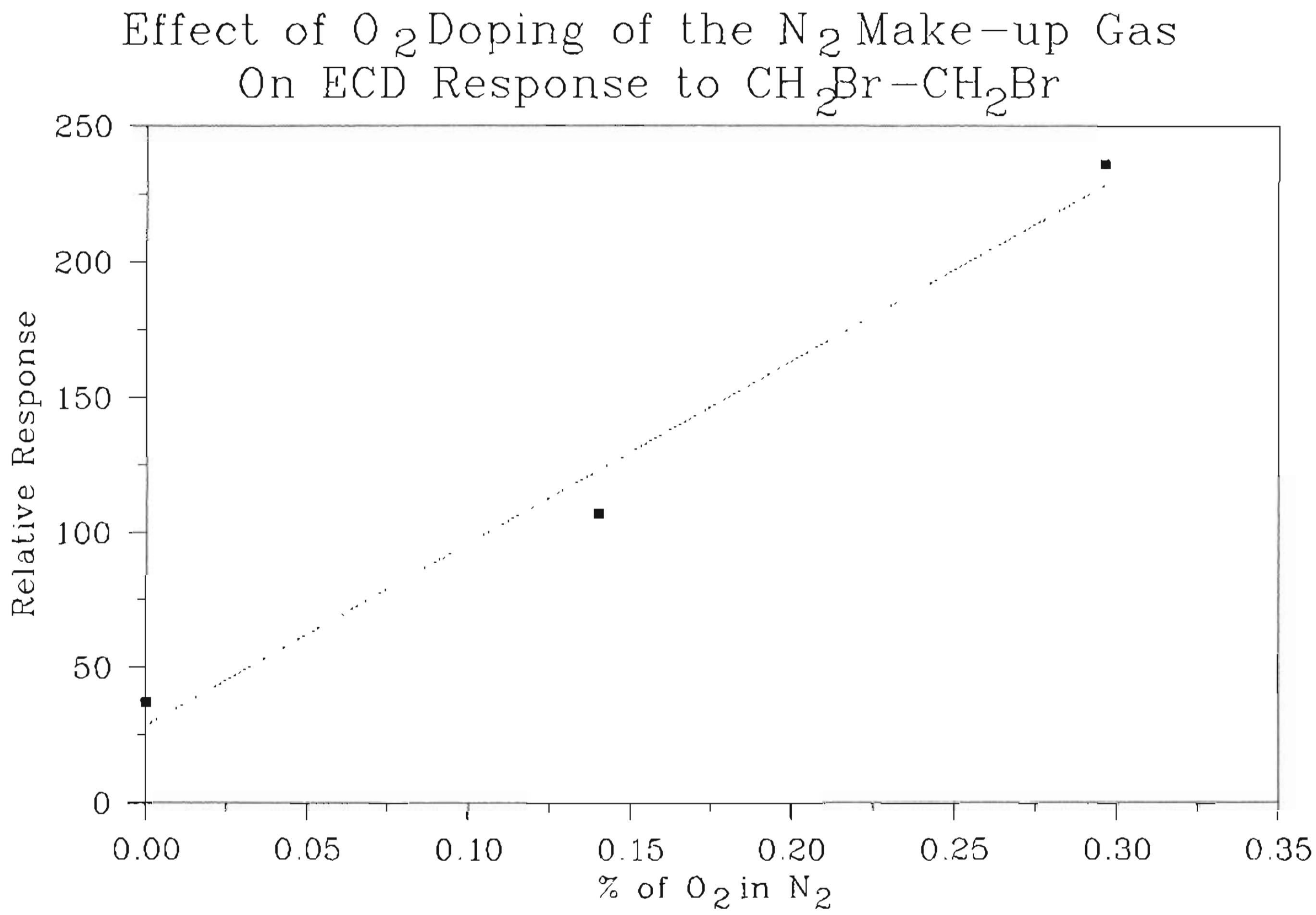


Figure 2.1.4.9 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to CH_2Br-CH_2Br

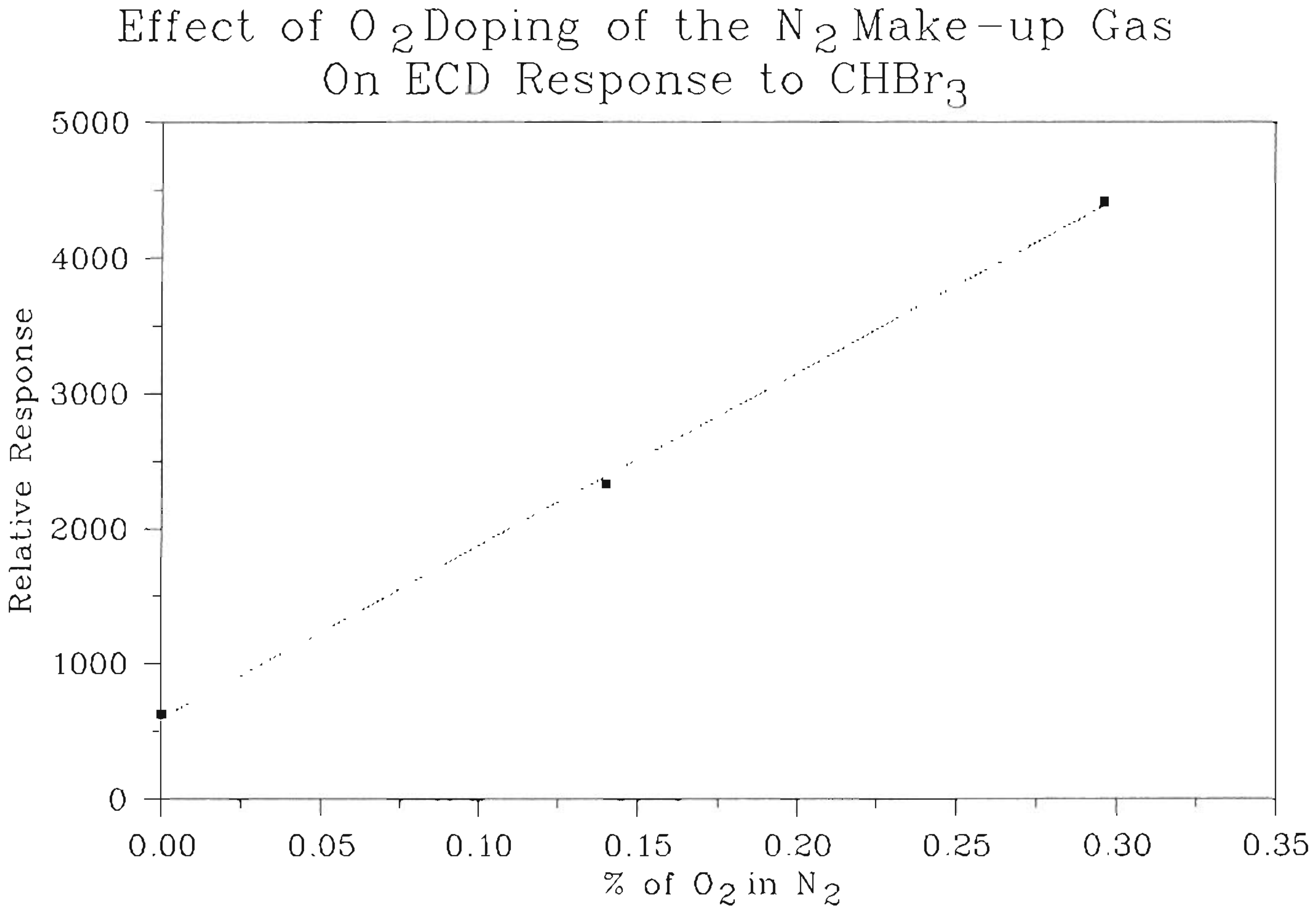


Figure 2.1.4.8 : The effect of O_2 doping of the N_2 make-up gas on the ECD response to $CHBr_3$

2.1.5 System V

CAP-EC-GC (DB-1 Capillary Column with O_2 Doped N_2 Make-Up Gas)

During the final stage of the development work, the SE-30 capillary column used in System IV was replaced with a DB-1 column. This was done because of column degradation. Both columns were from J & W Scientific and had the same column material (methyl silicone) and dimensions (30 m in length and 0.25 mm OD). The only difference was, the SE-30 column had a 0.25 µm coated liquid phase and the DB-1 column had a 1.0 µm bonded phase. The carrier gas was Zero grade He operated at 20 psig and the make-up gas was O_2(0.14%)/N_2 with a flow rate of 50 ml per minute. This was same as with System IV. With the new DB-1 column it was possible to use a lower initial operating temperature of -75°C (as compared to -60°C in System IV). As a result, $CBrF_3$ [F-13B1] could be measured in ambient air samples. A total of twenty seven organo-halogen gases were measured with this system (nine of these contained bromine). System V was used from April 1985 to 1988. Figure 2.1.5.1 shows a typical chromatogram from System V with the nine organo-bromine gases.

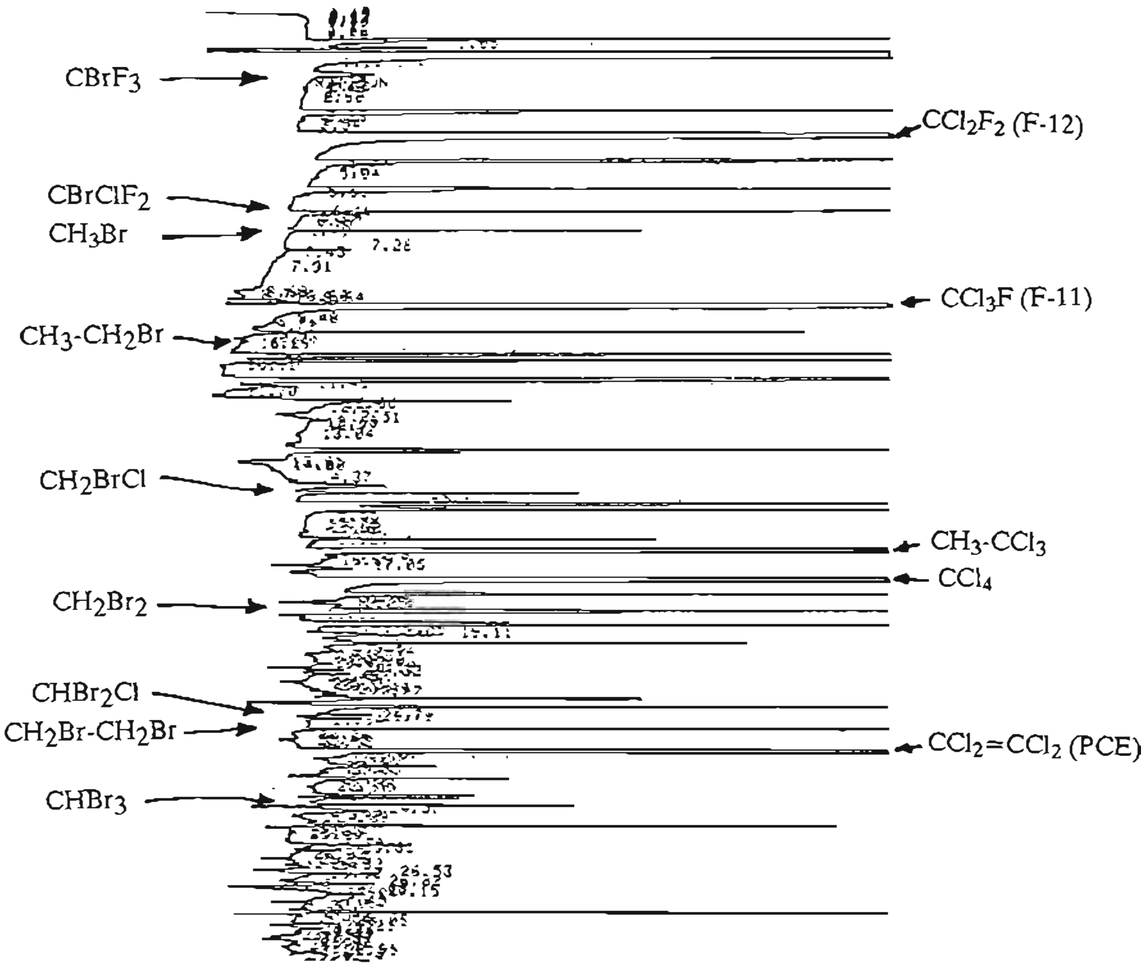


Figure 3.1.5.1 : A typical chromatogram from System V

DB-1 capillary column with O_2(0.14%)/N_2 make-up gas

Detector temperature 275°C

Nine organo-bromine gas measured

$CBrF_3$, $CBrClF_2$, CH_3Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$

2.1.6 A Summary of Equipment and Operating Conditions Used and Gases Measured with Each EC-GC System

The organo-bromine gases measured with each system are listed in Table 2.1.6.1. The basic instrumentation used in this study was common to all the systems. These items are listed in Table 2.1.6.2. Other equipment and operating conditions used with each system are summarized in Table 2.1.6.3.

TABLE 2.1.6.1

Organo-bromine gases measured with each EC-GC system used in this study

Compound	System-1	System-2	System-3	System-4	System-5
$CBrF_3$	No	No	No	No	Measured
$CBrClF_2$	Measured	Measured	Measured	Measured	Measured
CH_3Br	No	Measured	Measured	Measured	Measured
CH_3-CH_2Br	No	No	No	Measured	Measured
CH_2BrCl	No	No	Measured	Measured	Measured
CH_2Br_2	No	Measured	Measured	Measured	Measured
$CHBr_2Cl$	No	No	Measured	Measured	Measured
CH_2Br-CH_2Br	No	Measured	Measured	Measured	Measured
$CHBr_3$	No	No	Measured	Measured	Measured

TABLE 2.1.6.2

Equipment common to all the EC-GC systems used

Gas chromatograph	Perkin-Elmer 3920-B
Detector	Electron Capture with a ^{63}Ni foil (10 milli Curies)
Data recording system	Hewlett-Packard 3388-A Integrator

TABLE 2.1.6.3

Equipment and operating conditions used with each EC-GC system

	System I	System II	System III	System IV	System V
Column type	packed	capillary	capillary	capillary	capillary
Substrate	SP-2100 (methyl silicone)	coated methyl silicone	coated methyl silicone	coated methyl silicone	bonded methyl silicone
Length	10 ft.	30 m	30 m	30 m	30 m
Diameter	1/4 in.	0.25 mm	0.25 mm	0.25 mm	0.25 mm
Film thickness	--	0.25 μm	0.25 μm	0.25 μm	1.0 μm
Carrier gas	Ar(95%) /CH_4	He	He	He	He
Make-up gas	none	Ar(95%) /CH_4	N_2	O_2(0.14%) /N_2	O_2(0.14%) /N_2
Detector temp. (°C)	350	325	250	275	275
Standing current	3.0	3.0	2.0	0.5	0.5
Temp. program					
initial temp. (°C)	10	-60	-60	-60	-75
hold (min.)	2	2.25	2.25	2.25	2.25
rate (°C/min.)	16	8	8	8	8
final temp. (°C)	80	150	150	150	175

2.2 Collection of Samples

Air samples analyzed during the course of this study were collected in internally electropolished stainless steel Type 304 containers equipped with Nupro ^{R} SS-4-H-4 bellows valves. The sample containers had internal volumes of 0.85, 1.6, 3.2, 6 and 34 liters. At each sampling station weekly samples were collected in 0.85 liter cans, except at Cape Meares, Oregon, where 3.2 and 6 liter cans were used. Non-contaminating metal bellows pumps were used to collect these weekly samples. Additional samples were cryogenically collected in 1.6 liter containers at Cape Matatula - Samoa, Cape Grim - Tasmania and at the South Pole. At Cape Meares, large volume samples were collected in 34-liter tanks. The resultant high pressure (300 to 500 psig) samples from 1977 to present form the "Air bank" maintained at the Oregon Graduate Center. The 34-liter tanks filled at Cape Meares were used as calibration standards in the Atmospheric Lifetime Experiment (ALE) program.

2.3 Analysis of Samples

The TP-EC-GC system (System I) was set up as shown in Figure 2.3.1. The Cap-EC-GC systems (System II through System V) were configured as shown in Figure 2.3.2.

The air samples to be analyzed were first dried via a Nafion ^{R} dryer "G" (in Figures 2.3.1 and 2.3.2) to a dew point of -26°C. The sample was then concentrated in an 8-inch by 1/8-inch OD stainless steel U-tube filled with 60/80 mesh glass beads (sample loop "I" in Figures 2.3.1 and 2.3.2) at liquid O_2 temperature. In this preconcentration step the N_2 and most of the O_2 were removed from the sample.

System I

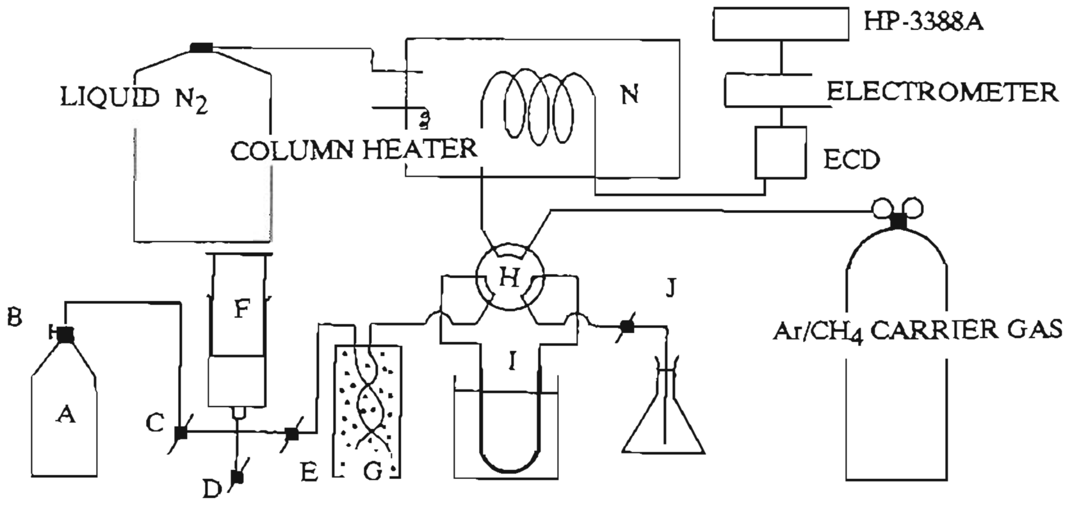
In System I the sample volumes were measured (100 or 200 ml) using a syringe. When the GC oven reached the initial operating temperature of the program, 10°C, the sample was desorbed by immersing the loop "I" in hot water at 70°C and transferred it on to the head of the column.

A sample size of 100 ml was used when analyzing low altitude northern hemispheric samples. A larger sample size of 200 ml was used when analyzing high altitude samples collected at Mauna Loa in Hawaii and southern hemispheric samples. The different size samples were used because the southern hemispheric and high altitude samples generally had low concentrations of the organo-halogen gases measured.

System II through System V

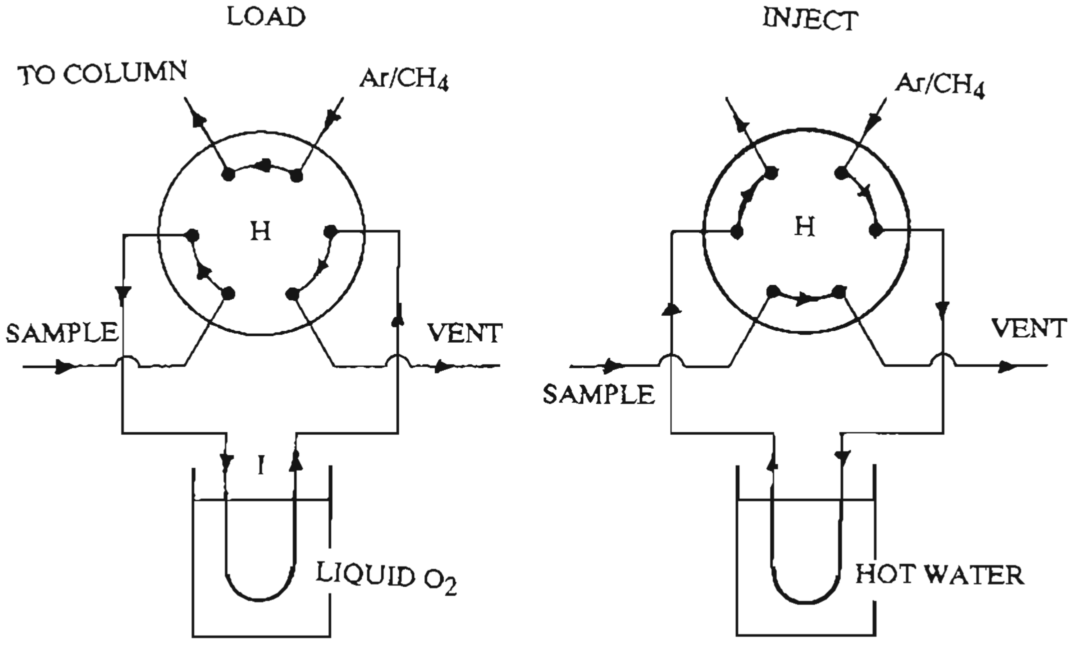
In the Cap-EC-GC systems the sample volume was determined by measuring the pressure difference on gauge "M" in Figure 2.3.2. An increase in pressure of 250 torr was calculated to be equivalent to loading 500 ml of sample. As in System I, the sample was preconcentrated at liquid O_2 temperature in a U-tube filled with glass beads. When the GC oven reached the initial program temperature, -60°C for System II through System IV and -75°C for System V, the trapped sample was transferred on to the head of the column by immersing the sample loop in hot water at 70°C.

SYSTEM I



A - SAMPLE CAN
B - SAMPLE CAN VALVE
C, D, E, J - TOGGLE VALVES
F - SYRINGE

G - NAFION ^{R} DRYER
H - SAMPLE LOAD/INJECT VALVE
I - SAMPLE LOOP
N - PACKED GC COLUMN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INJECT

Figure 2.3.1 : System I

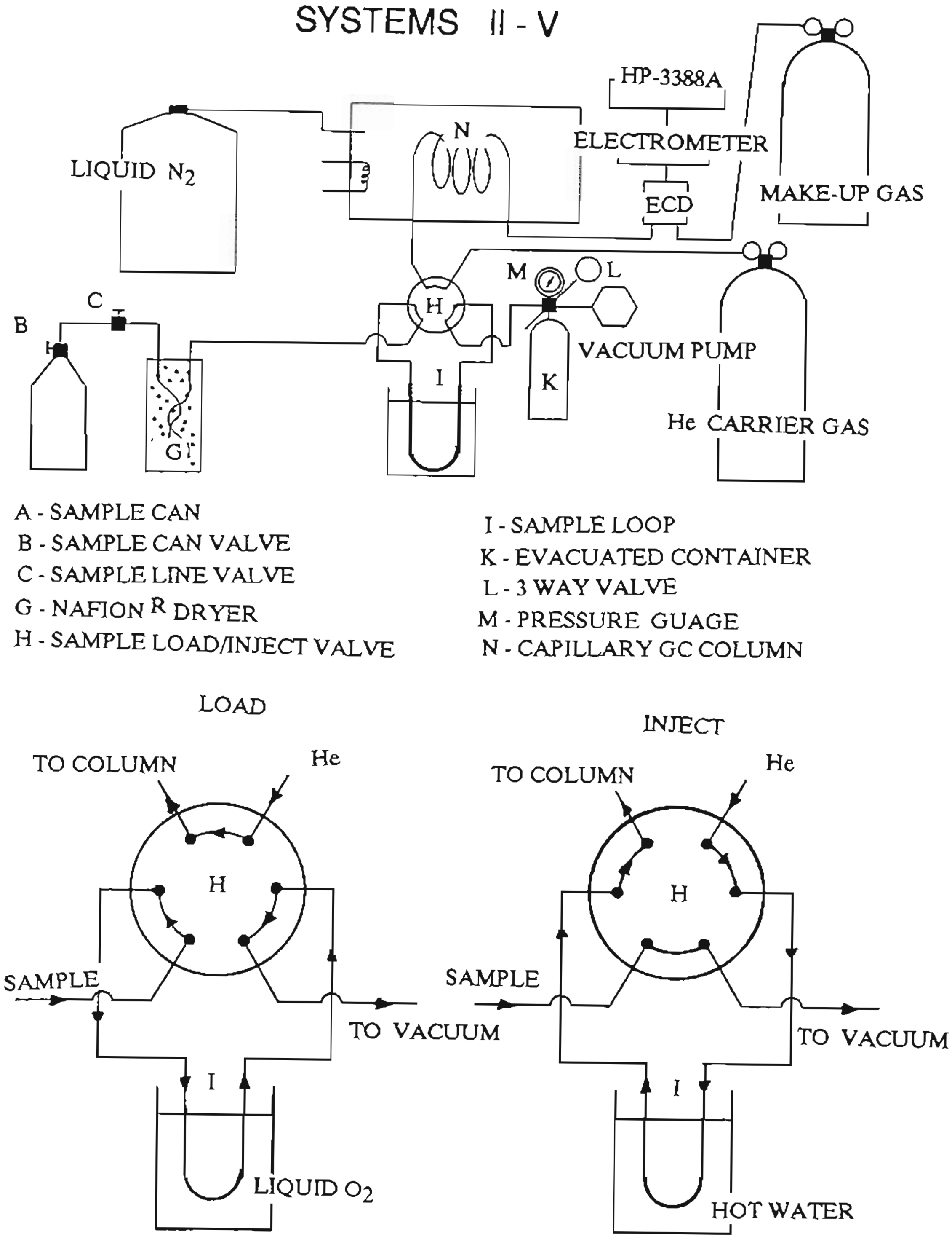

Figure 2.3.2 : Systems II - V

2.4 Linearity of ECD Response to the Organo-Bromine Gases in System V

ALE tanks # 0-026 (collected in 1978) and # R-362 (collected in 1988) were used to test the linearity of the ECD response to the organo-bromine gases selected for study. The two ALE tanks collected 10 years apart were selected for this linearity study because the concentrations of $CBrF_3$ and $CBrClF_2$ in # R-362 were about a factor of 6 higher than in # 0-026. Different volumes (50, 100, 200, 300, 500 and 1000 ml) from these two ALE tanks were analyzed against a standard 500 ml volume of the reference calibration standard. The results (Table 2.4.1) showed that the ECD had a linear response to all gases over the range studied. The relative ECD responses are plotted against the sample size in Figures 2.4.1 ($CBrF_3$), 2.4.2 ($CBrClF_2$), 2.4.3 (CH_3Br), 2.4.4 (CH_3-CH_2Br), 2.4.5 (CH_2BrCl), 2.4.6 (CH_2Br_2), 2.4.7 (CH_2Br-CH_2Br) and 2.4.8 ($CHBr_3$).

Table 2.4.1

Linear correlation coefficients for response versus sample size.

(for sample sizes 50 ml to 1000 ml)

Compound	0-026		R-362	
	R^2	n	R^2	n
1. $CBrF_3$	0.9975	6	0.9944	7
2. $CBrClF_2$	0.9804	7	0.9798	7
3. CH_3Br	0.9940	7	0.9966	7
4. CH_3-CH_2Br	0.9996	5	0.9922	6
5. CH_2BrCl	*		0.9760	6
6. CH_2Br_2	*		0.9752	7
7. CH_2Br-CH_2Br	0.9876	7	*	
8. $CHBr_3$	0.9745	7	0.9846	7

* Baseline interference

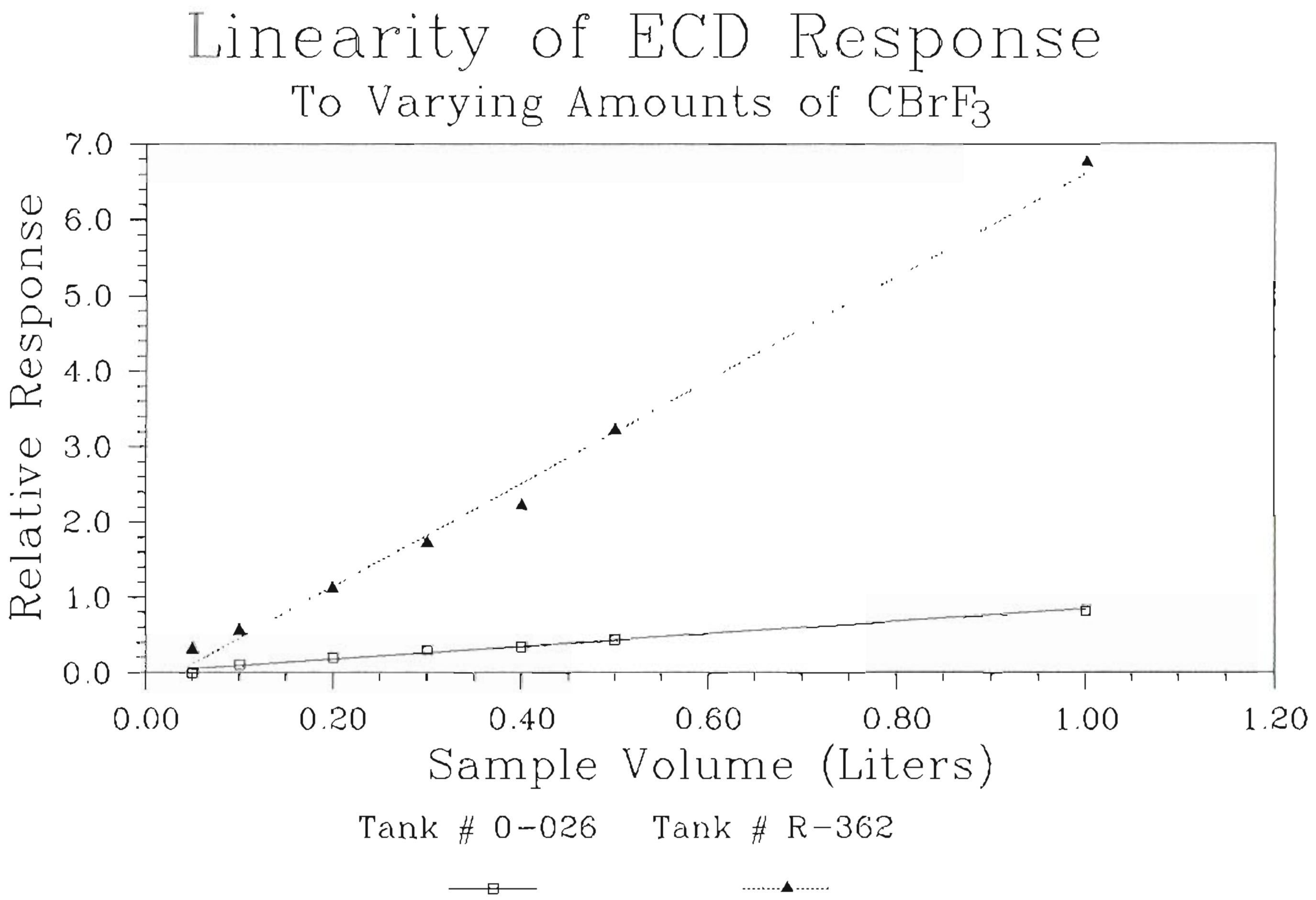

Figure 2.4.1 : Linearity of ECD response to increasing amounts of CBrF$_3$

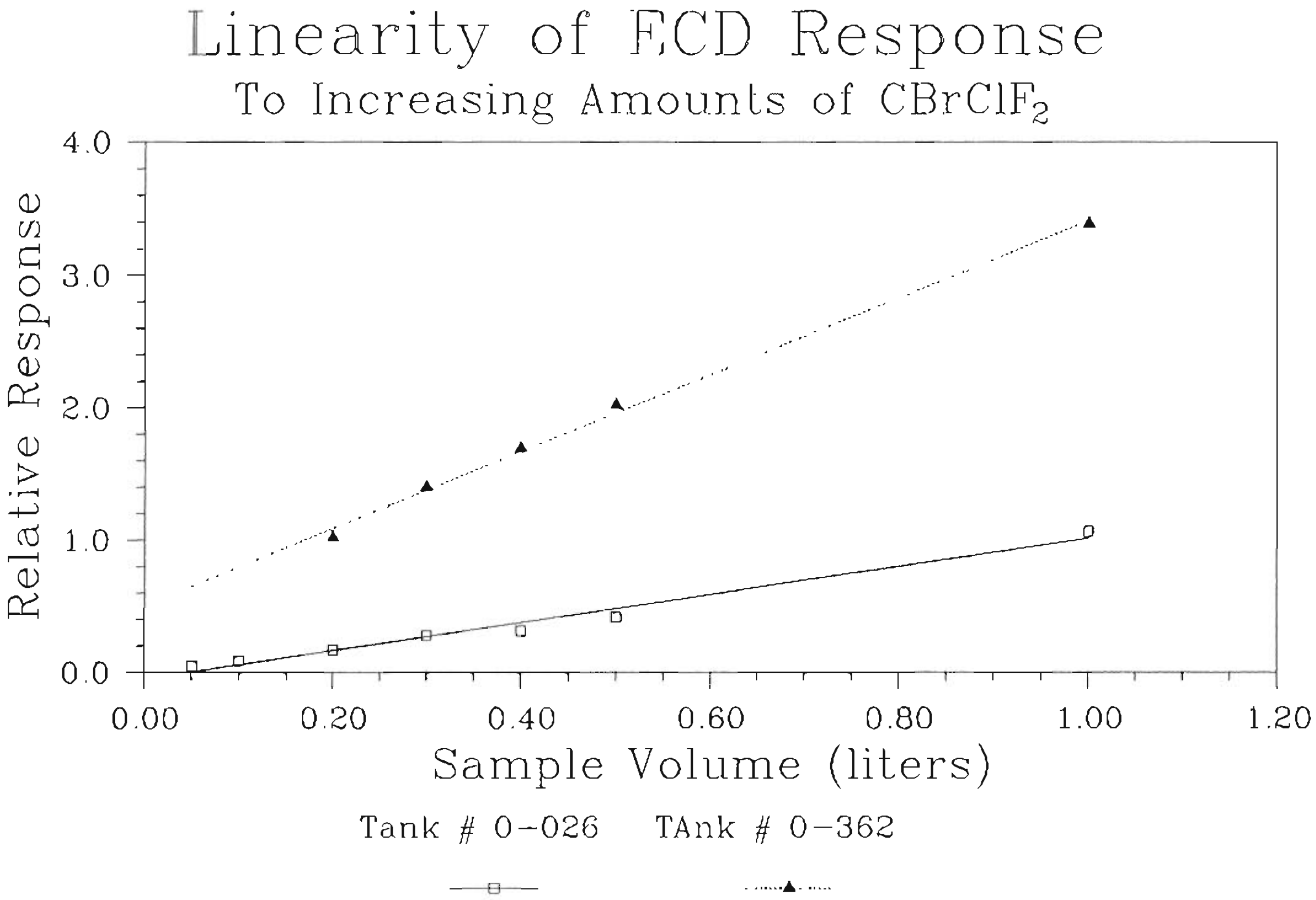

Figure 2.4.2 : Linearity of ECD response to increasing amounts of $CBrClF_2$

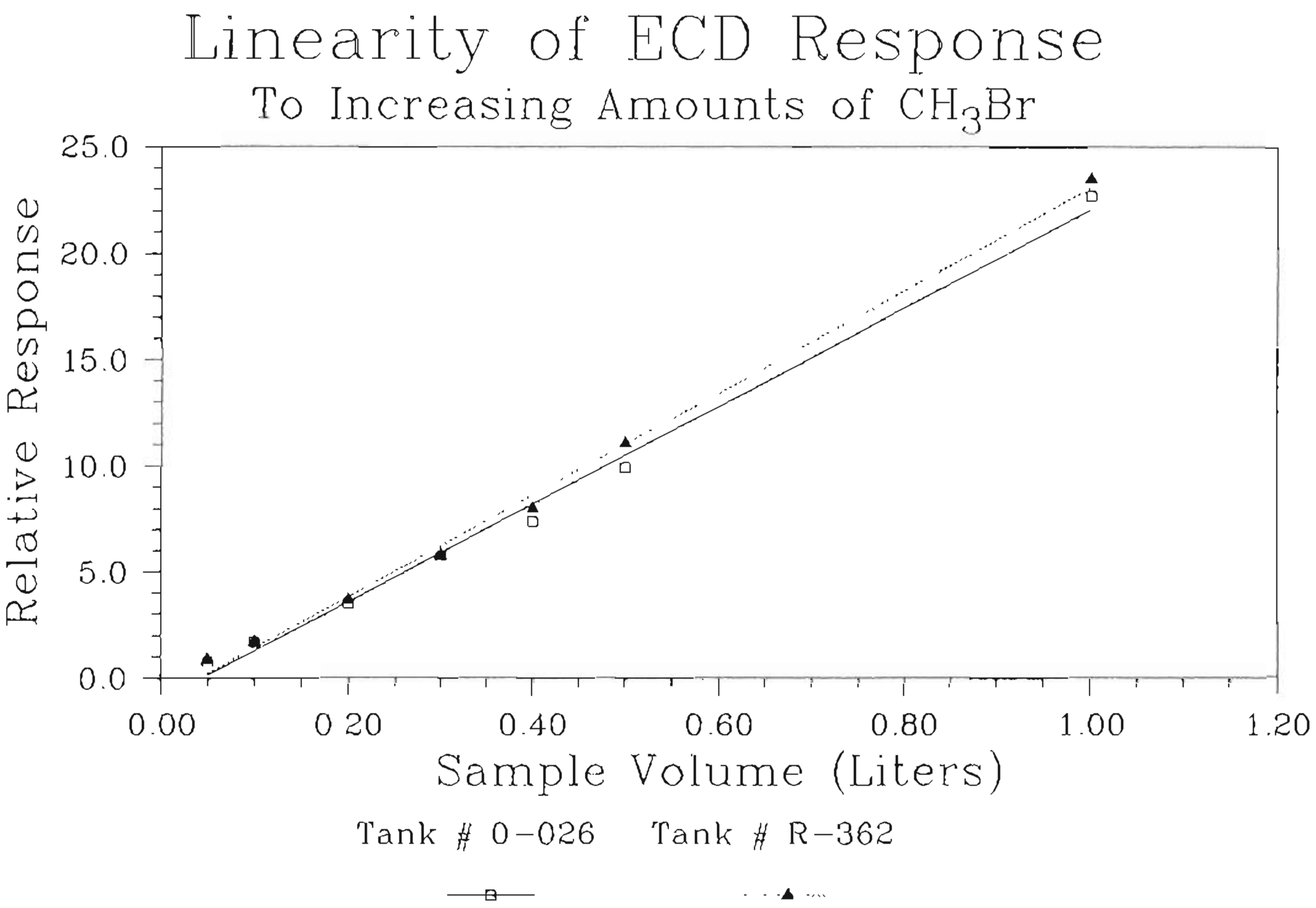

Figure 2.4.3 : Linearity of ECD response to increasing amounts of CH_3Br

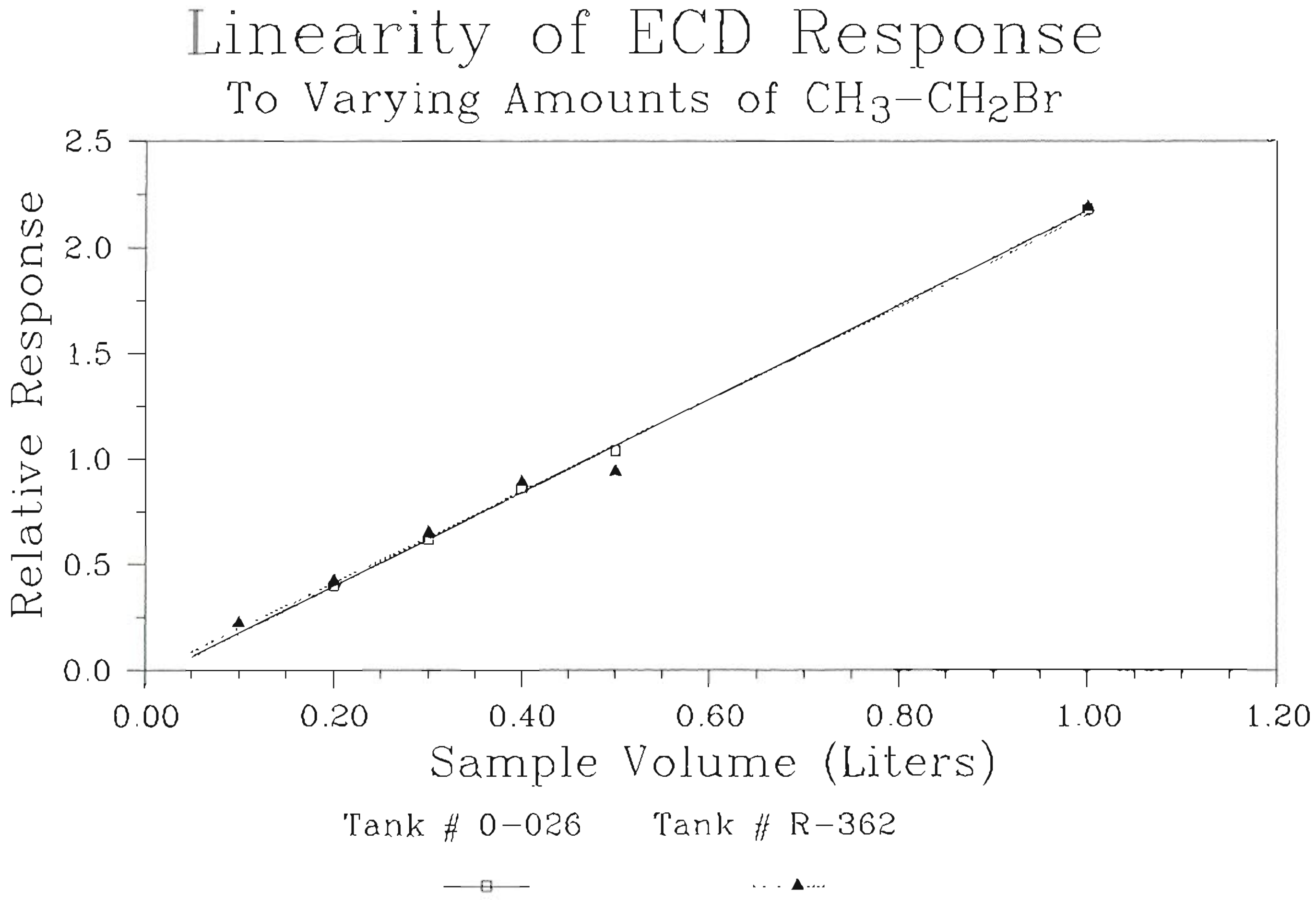

Figure 2.4.4 : Linearity of ECD response to increasing amounts of CH_3-CH_2Br

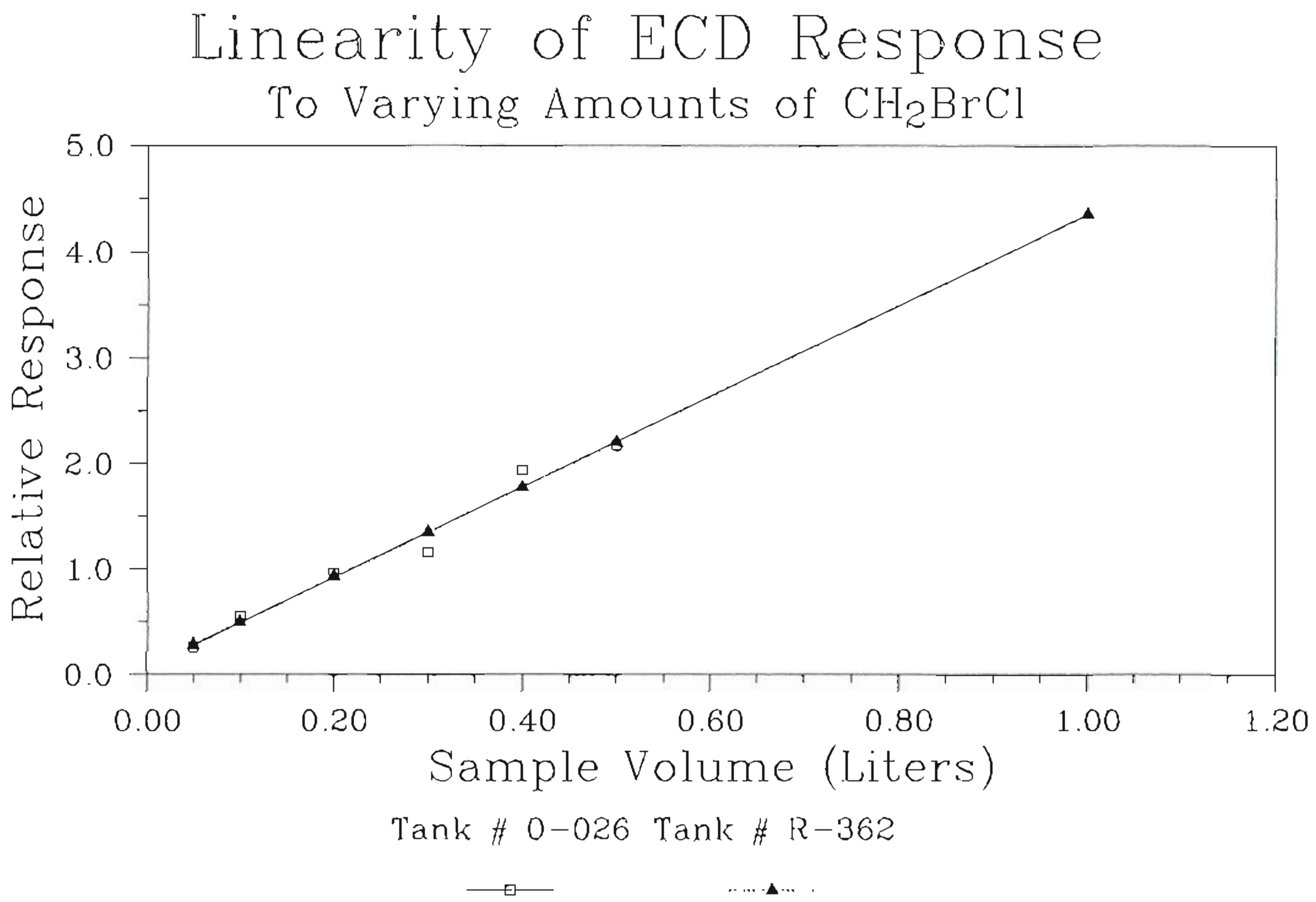

Figure 2.4.5 : Linearity of ECD response to increasing amounts of CH_2BrCl

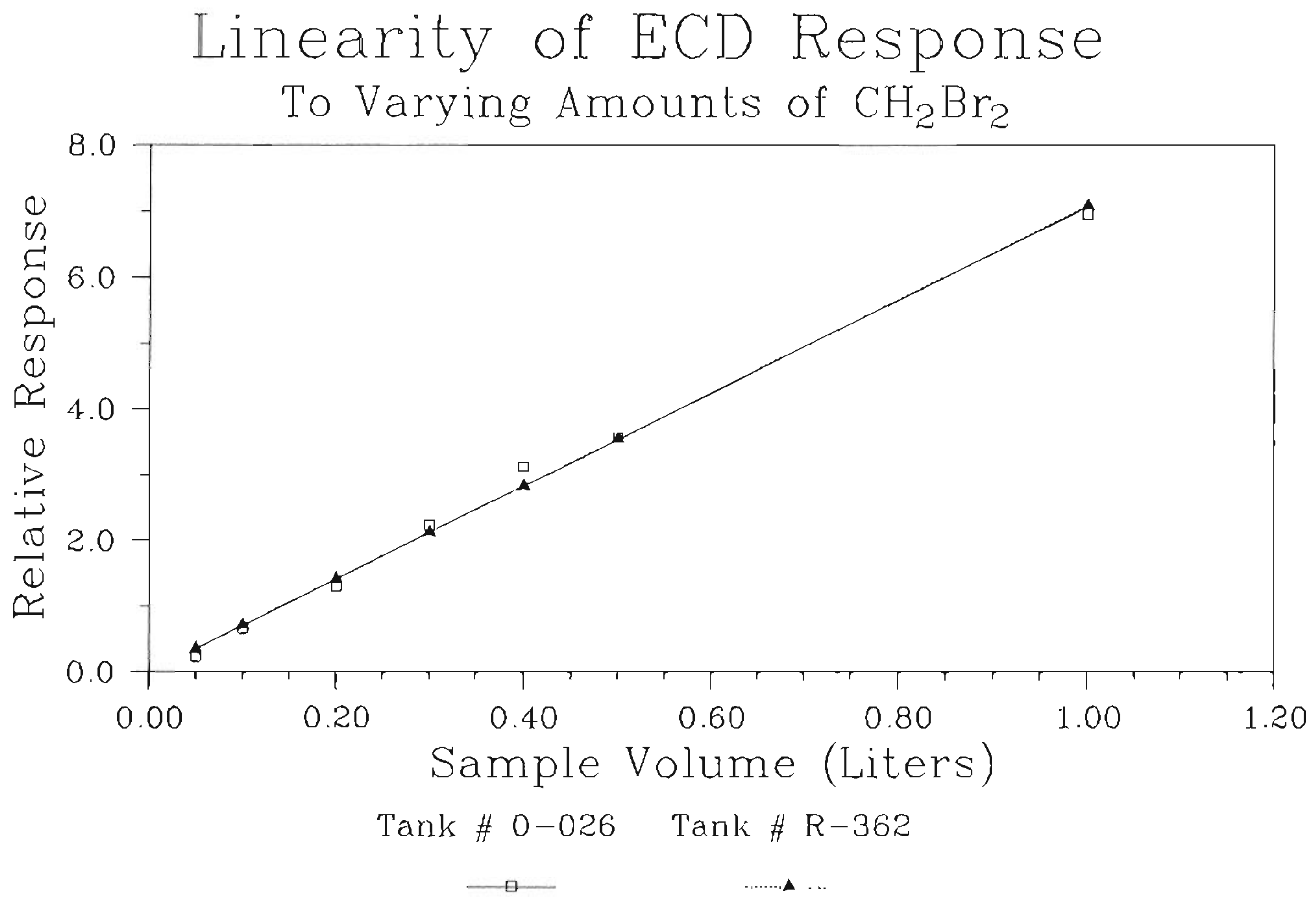

Figure 2.4.6 : Linearity of ECD response to increasing amounts of CH_2Br_2

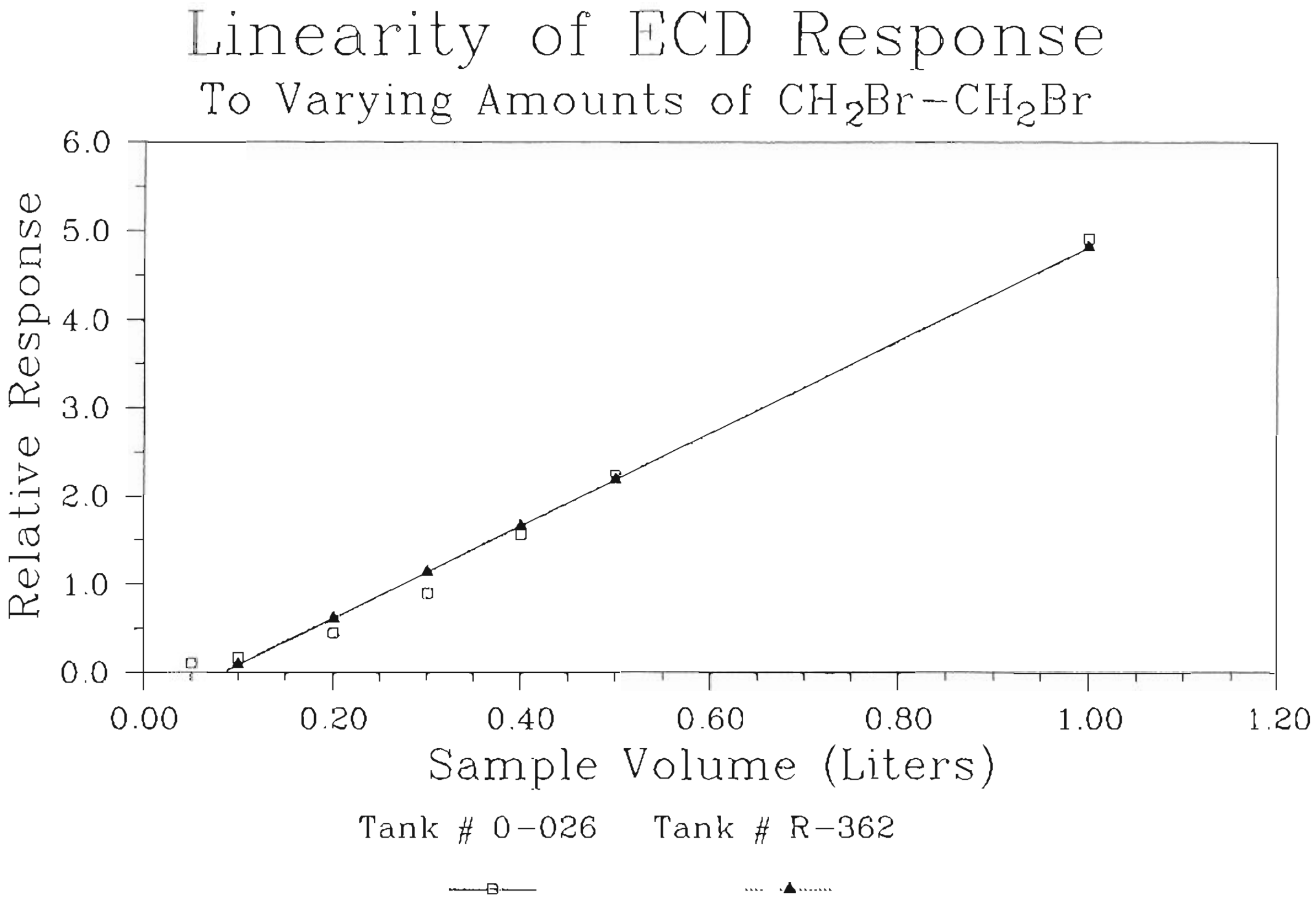

Figure 2.4.7 : Linearity of ECD response to increasing amounts of CH_2Br-CH_2Br

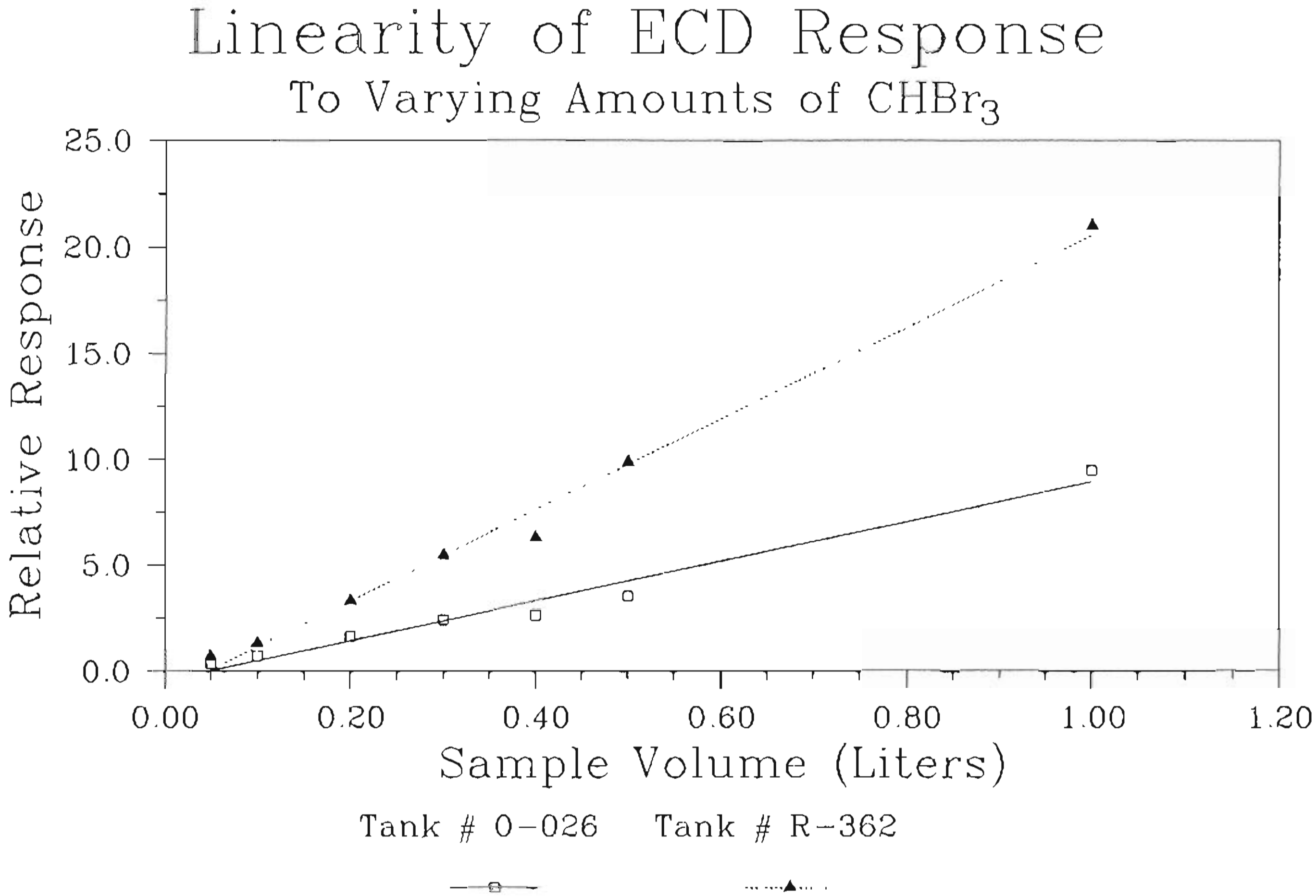

Figure 2.4.8 : Linearity of ECD response to increasing amounts of $CHBr_3$

The minimum detection limit for each organo-bromine compound is listed in Table 2.4.2. These values are for a sample size of 500 ml. It was possible to measure all nine organo-bromine gases in a 500 ml volume of sample with system 5.

TABLE 2.4.2

Lower limit of detection of the organo-bromine gases studied

Compound	Minimum detectable limit * (pptv)
1. $CBrF_3$	0.2
2. $CBrClF_2$	< 0.1
3. CH_3Br	0.5
4. CH_3-CH_2Br	0.2
5. CH_2BrCl	0.2
6. CH_2Br_2	0.2
7. $CHBr_2Cl$	0.2
8. CH_2Br-CH_2Br	0.1
9. $CHBr_3$	0.3

* The minimum detectable limits are for a sample size of 500 ml.

2.5 Precision of Analysis

The precision of analysis for the nine organo-bromine gases were determined for ALE tank # 0-279 on System V. Seven replicate measurements were made on sample volumes of 500 ml each for this study. The results in Table 2.5.1 show that the precision of analysis for each compound was within ±10%. The highest variability was observed for $CBrF_3$ (±9.9%). This may be due to the instability of the oven temperature in the region of -75°C when $CBrF_3$ elutes from the column.

TABLE 2.5.1

Precision of analysis of organo-bromine gases

Compound	Concentration (pptv)	Precision of analysis (n=7)
1. $CBrF_3$	2.5	9.9 %
2. $CBrClF_2$	1.9	0.9 %
3. CH_3Br	11.0	1.8 %
4. CH_3-CH_2Br	1.0	7.0 %
5. CH_2BrCl	1.5	5.7 %
6. CH_2Br_2	3.8	6.0 %
7. $CHBr_2Cl$	1.4	2.7 %
8. CH_2Br-CH_2Br	0.9	7.5 %
9. $CHBr_3$	8.9	3.9 %

* The precision of analysis listed here are for System V and were done with 500 ml samples from ALE tank # 0-279.

2.6 Calibration of Standard Tanks

The $CBrF_3$ {F13B1], $CBrClF_2$ [BCF], CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, and $CHBr_2Cl$ concentrations assigned to the calibration tanks used in my work were prepared by Professor R.A. Rasmussen. A calibration standard from the Environmental Protection Agency was used to determine the concentration of CH_2Br-CH_2Br (EDB) in tank # 0-189. A sample from tank # 0-232 was calibrated for $CHBr_3$ at National Center for Atmospheric Research in Boulder, Colorado. All of the tanks used in this study were cross calibrated against each other. Therefore, these data provide an internally consistent set of concentration values for the organo-bromine gases studied.

The origin of calibration value used for each compound is listed in Table 2.6.1. A total of six tanks were used as calibration standards during the course of this study. The tanks used with each system are listed in Table 2.6.2. The concentration of each organo-bromine compound in these tanks is listed in Table 2.6.3.

TABLE 2.6.1

Origin of calibration value of standard tanks for each compound

Compound	Tank #	pptv	Value given by	Year
1. $CBrF_3$	0-279	1.2	RAR	1985
2. $CBrClF_2$	0-189	1.0	RAR	1983
3. CH_3Br	0-189	12.0	RAR	1983
4. CH_3-CH_2Br	0-279	1.0	RAR	1985
5. CH_2BrCl	0-232	1.0	RAR	1984
6. CH_2Br_2	0-189	4.0	RAR	1983
7. $CHBr_2Cl$	0-279	1.0	RAR	1984
8. CH_2Br-CH_2Br	0-189	4.2	EPA	1987
9. $CHBr_3$	0-232	9.0	NCAR	1985

RAR	Calibration values provided by R.A. Rasmussen.
EPA	Calibrated against a CH_2Br-CH_2Br standard from the EPA.
NCAR	A sample from tank # 0-232 calibrated at NCAR, Boulder, Colorado.

TABLE 2.6.2

Calibration tanks used with each system

System	Calibration tanks used
1	0-108 & 0-116
2	0-189 & 0-232
3	0-232
4	0-232 & 0-279
5	0-279 & 0-278

TABLE 2.6.3

Concentration of organo-bromine gases in the calibration tanks

Compound	Concentrations in calibration tanks (pptv)					
	0-108	0-116	0-189	0-232	0-279	0-278
1. $CBrF_3$	*	*	*	*	1.2	1.3
2. $CBrClF_2$	0.9	0.9	1.0	1.0	1.3	1.4
3. CH_3Br	*	*	12.0	10.6	12.3	15.4
4. CH_3-CH_2Br	*	*	*	*	1.0	0.6
5. CH_2BrCl	*	*	*	1.0	11.4	0.9
6. CH_2Br_2	*	*	4.0	3.9	3.8	4.4
7. $CHBr_2Cl$	*	*	*	*	1.1	1.6
8. CH_2Br-CH_2Br	*	*	3.0	0.7	1.4	0.9
9. $CHBr_3$	*	*	*	9.0	8.9	12.8

* These gases were not measured when these calibration tanks were used

2.7 Stability of Organo-Bromine Gases in Sample Containers

Stability in High Pressure Tanks

The long-term stability of organo-bromine gases in high pressure (100 to 400 psig) ALE tanks was studied over the period of 2 to 5 years. The results in Table 2.7.1 show that the average deviation from the original value were 16% or less. The Halons, $CBrF_3$ [F13B1] and $CBrClF_2$ [BCF], are observed to be very stable in the ALE tanks.

TABLE 2.7.1

Long-term stability of organo-bromine gases in ALE tanks

Compound	Number of tanks studied	Length of test (years)	Deviation from original concentration	
			Average	Largest
1. $CBrF_3$	7	2	-1.9 %	- 8.4 %
2. $CBrClF_2$	6	5	0.5 %	- 8.0 %
3. CH_3Br	9	4	-1.8 %	-11.6 %
4. CH_3-CH_2Br	8	2	-2.7 %	-28.1 %
5. CH_2BrCl	9	3	0.8 %	14.1 %
6. CH_2Br_2	9	4	2.7 %	7.5 %
7. CH_2Br-CH_2Br	7	4	-3.9 %	-31.8 %
8. $CHBr_3$	9	4	-0.3 %	-12.2 %

The stability of $CBrF_3$ was studied in seven ALE tanks. The first set of analyses was made in 1985 and the last set of analyses in 1987. In 1987, the deviations in the $CBrF_3$ concentration were within 5.8% and -8.4% of the initial value. The mean variability at the end of the stability test was -1.9%. The deviation of the $CBrF_3$ concentration in each ALE tank in 1987 is plotted in Figure 2.7.1.

Six ALE tanks were analyzed to test the long-term stability of $CBrClF_2$. The first set of analyses for $CBrClF_2$ was made in 1982. These tanks were analyzed again in 1983, 1984 and in 1987. Over this five-year period, the $CBrClF_2$ concentration in each tank stayed within 7.6% and -8.0% of the initial value. At the end of the stability test the mean variability was 0.5%. The changes of the $CBrClF_2$ concentration in each ALE tank in 1983, 1984 and 1987 are plotted in Figure 2.7.2.

The stability of CH_3Br was determined in nine ALE tanks. The first set of analyses was made in 1983. They were analyzed again in 1984 and 1987. During this four-year period each tank had a CH_3Br concentration that was within 8.7% and -11.6% of the initial value. The mean variability at the end of the stability test was 1.8%. The changes of the CH_3Br concentration in each ALE tank in 1984 and 1987 are plotted in Figure 2.7.3.

Eight ALE tanks were analyzed to test the long-term stability of CH_3-CH_2Br. The first set of analyses was made in 1985. These tanks were analyzed again in 1987. In 1987, the deviations in the CH_3-CH_2Br concentration were within 27.0% and 28.1% of the initial value. The mean variability at the end of the stability test was -2.7%. The change of the CH_3-CH_2Br concentration in each ALE tank in 1987 are plotted in Figure 2.7.4.

Nine ALE tanks were analyzed to test the long-term stability of CH_2BrCl. These tanks were first analyzed in 1984 and in 1987. These analyses showed that CH_2BrCl concentration in each tank stayed within 14.1% and -10.2% of the initial value. The mean variability after three years was 0.8%. The changes of the CH_2BrCl concentration in each ALE tank in 1987 are plotted in Figure 2.7.5.

The stability of CH_2Br_2 was studied in nine ALE tanks. The first set of analyses was made in 1983. They were analyzed again in 1984 and 1987. During this four-year period the CH_2Br_2 concentration was within 7.5% and -5.8% of the initial value. The mean variability at the end of the stability test was 2.7%. The changes of the CH_2Br_2 concentration in each ALE tank in 1984 and 1987 are plotted in Figure 2.7.6.

Seven ALE tanks were analyzed in 1983, 1984 and 1987 to test the long-term stability of $CH_2Br\text{-}CH_2Br$. The results showed that after four years, the $CH_2Br\text{-}CH_2Br$ concentrations in these tanks were within 14.4% and -31.8% of the original values. The mean variability was -3.9%. The changes of the $CH_2Br\text{-}CH_2Br$ concentration in each ALE tank in 1984 and 1987 are plotted in Figure 2.7.7.

The long-term stability of $CHBr_3$ was tested in nine ALE tanks. They were first analyzed in 1984 and again in 1987. The results showed that the $CHBr_3$ concentration in each tank was within 11.5% and -12.2% of the original value and the mean variability was -0.3%. The changes of the $CHBr_3$ concentration in each ALE tank in 1987 are plotted in Figure 2.7.5.

A negative drift in the CH_3Br concentration was observed in one tank. The variations observed in the other eight tanks appear random. A negative drift was observed in the

CH_2Br-CH_2Br concentration of one tank with six tanks showing random differences. With CH_2Br_2, two tanks showed positive drift and one tank showed a negative drift with six tanks showing random variations in the concentration. The differences seen in all six tanks tested for $CBrClF_2$ were random. The long term stability data available for the other gases, $CBrF_3$, CH_3-CH_2Br, CH_2BrCl and $CHBr_3$, were not sufficient to determine any drifts in concentration.

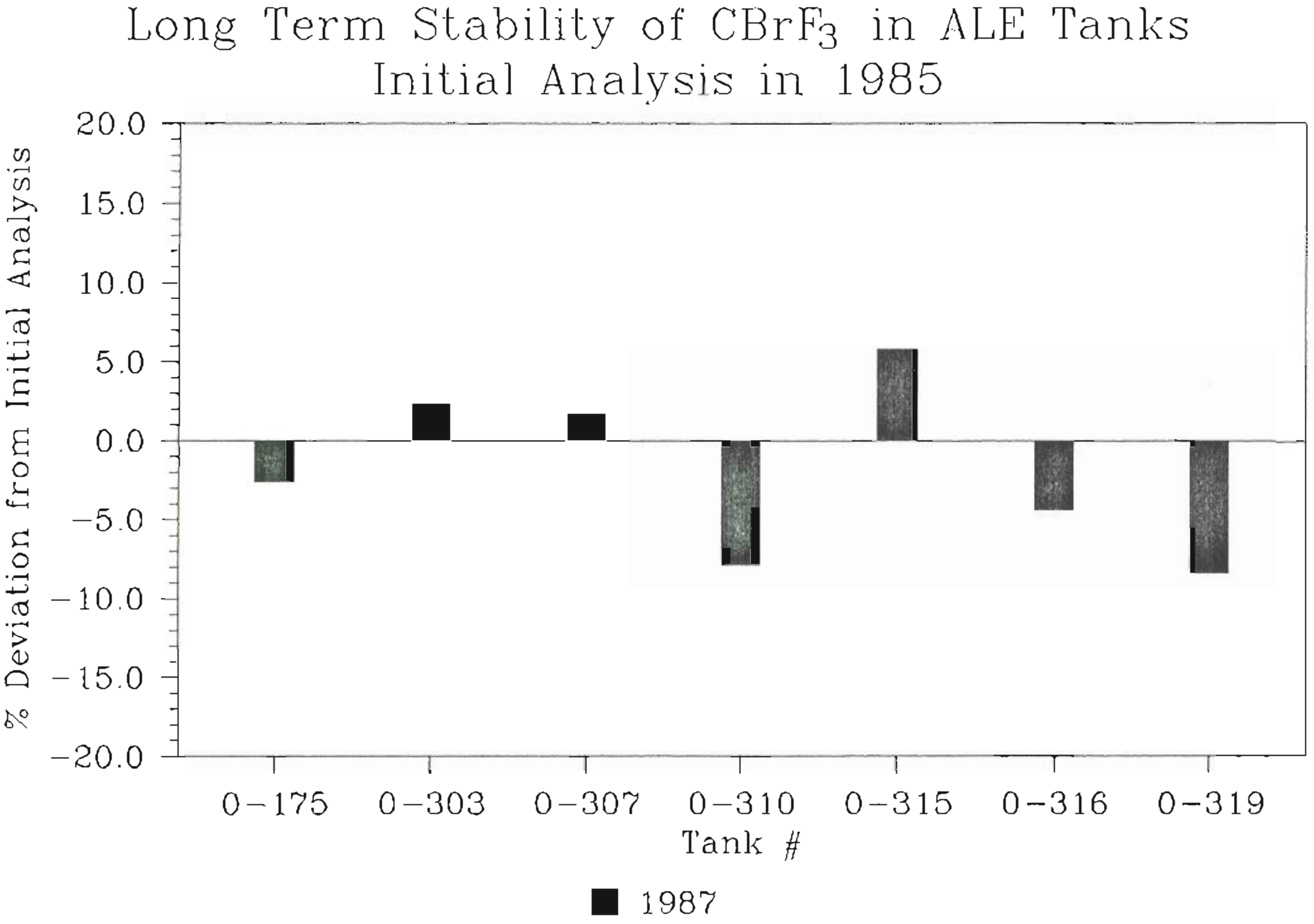

Figure 2.7.1 : Long term stability of $CBrF_3$ in ALE tanks

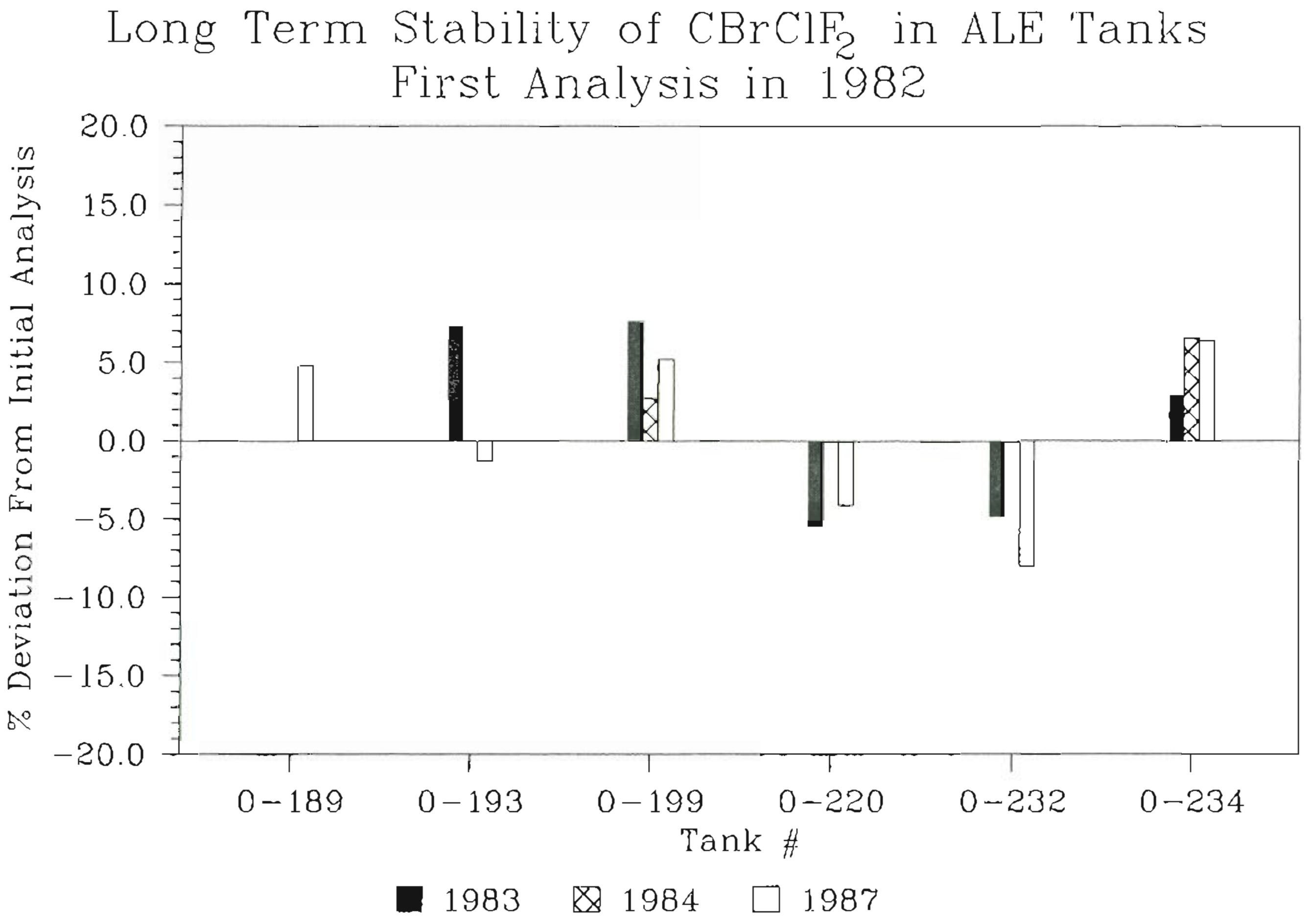

Figure 2.7.2 : Long term stability of $CBrClF_2$ in ALE tanks

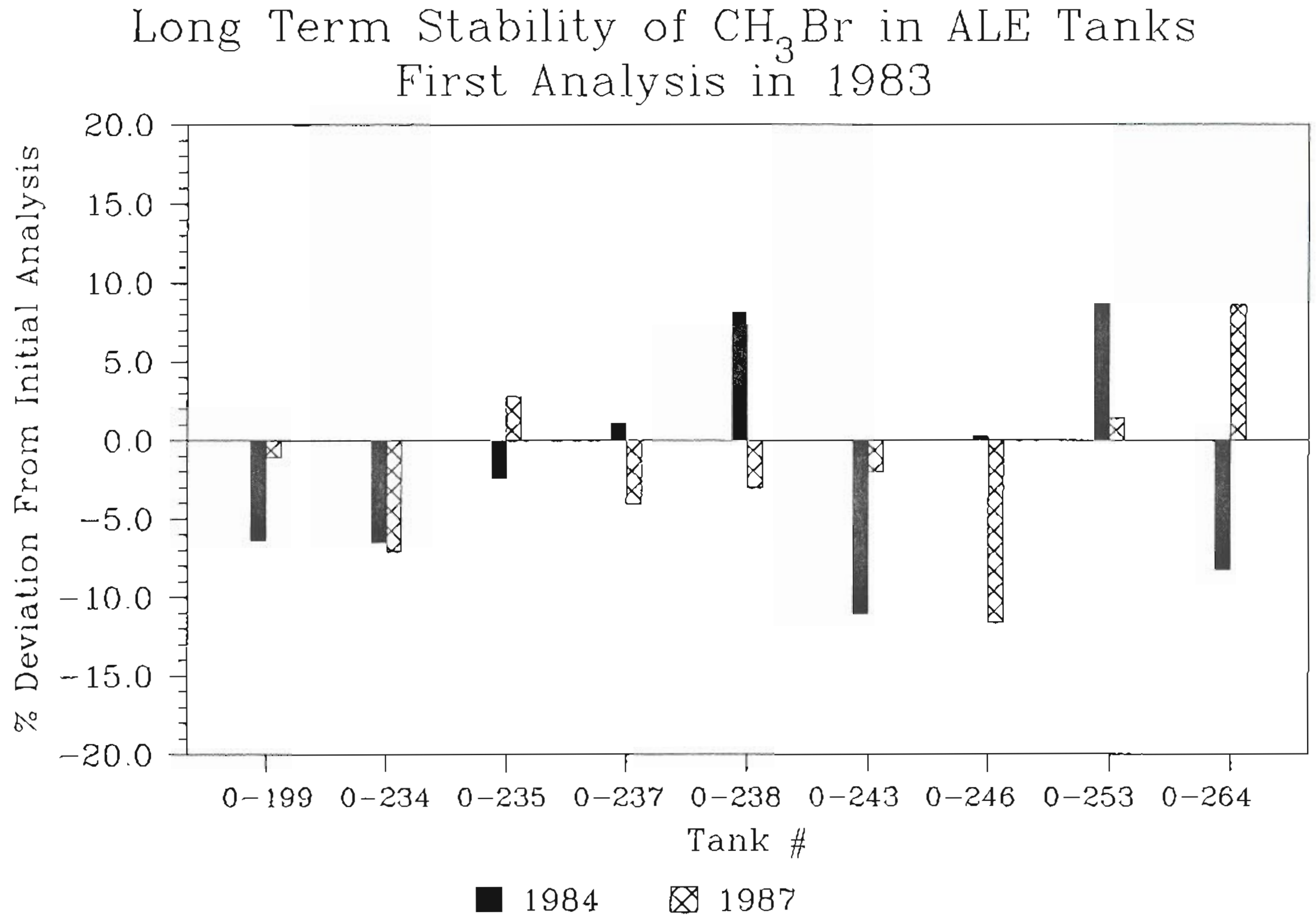

Figure 2.7.3 : Long term stability of CH_3Br in ALE tanks

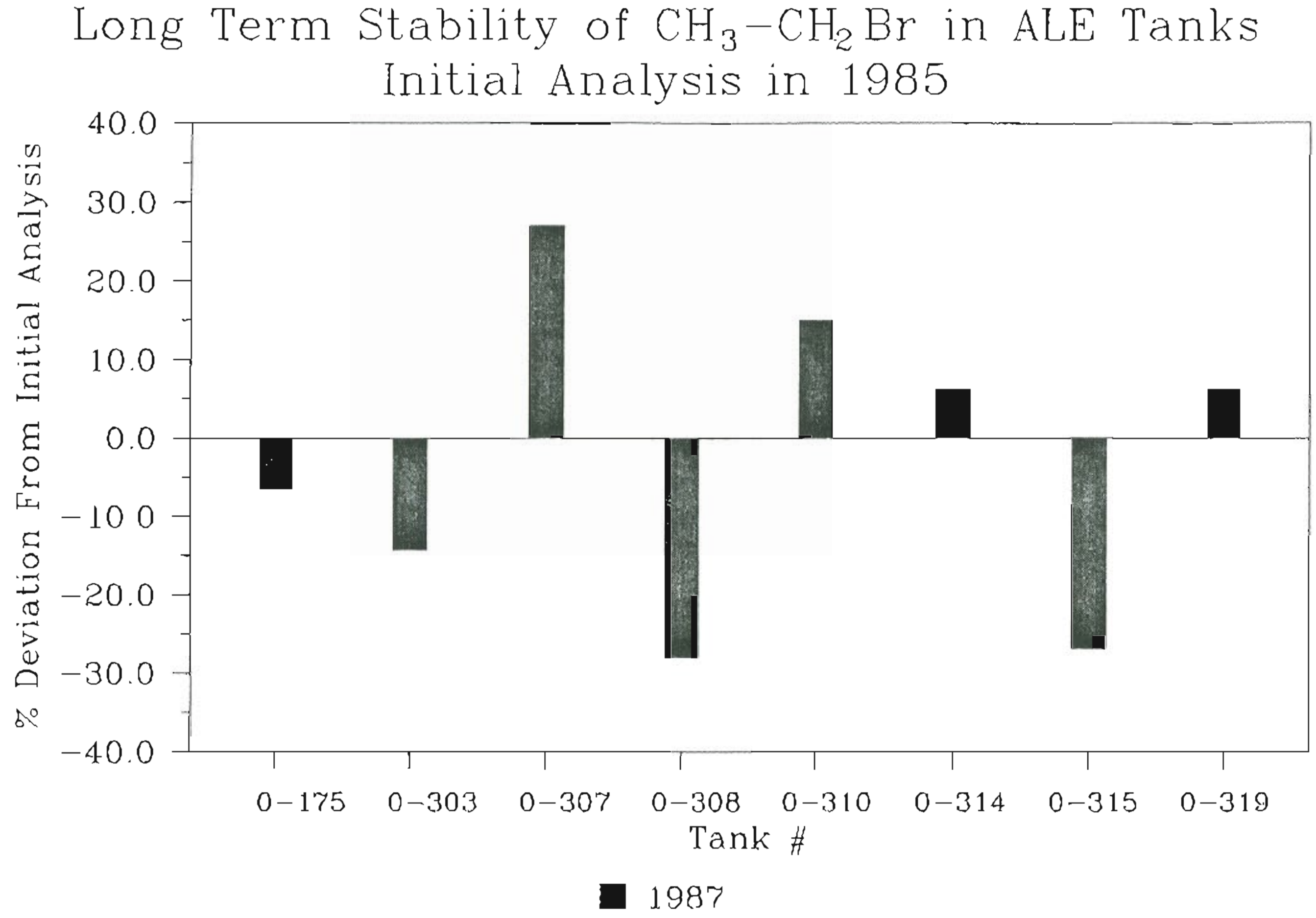

Figure 2.7.4 : Long term stability of CH_3-CH_2Br in ALE tanks

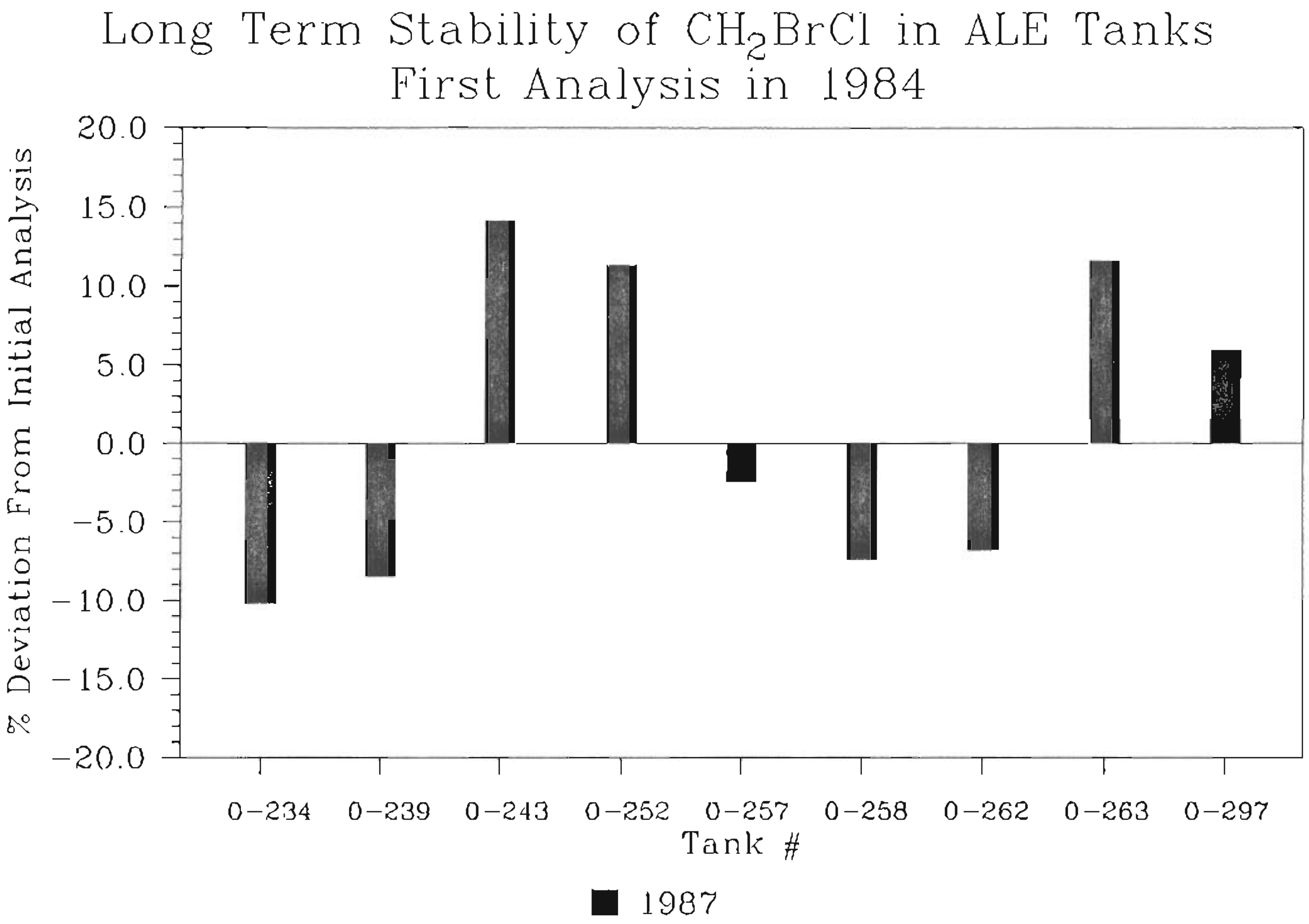

Figure 2.7.5 : Long term stability of CH_2BrCl in ALE tanks

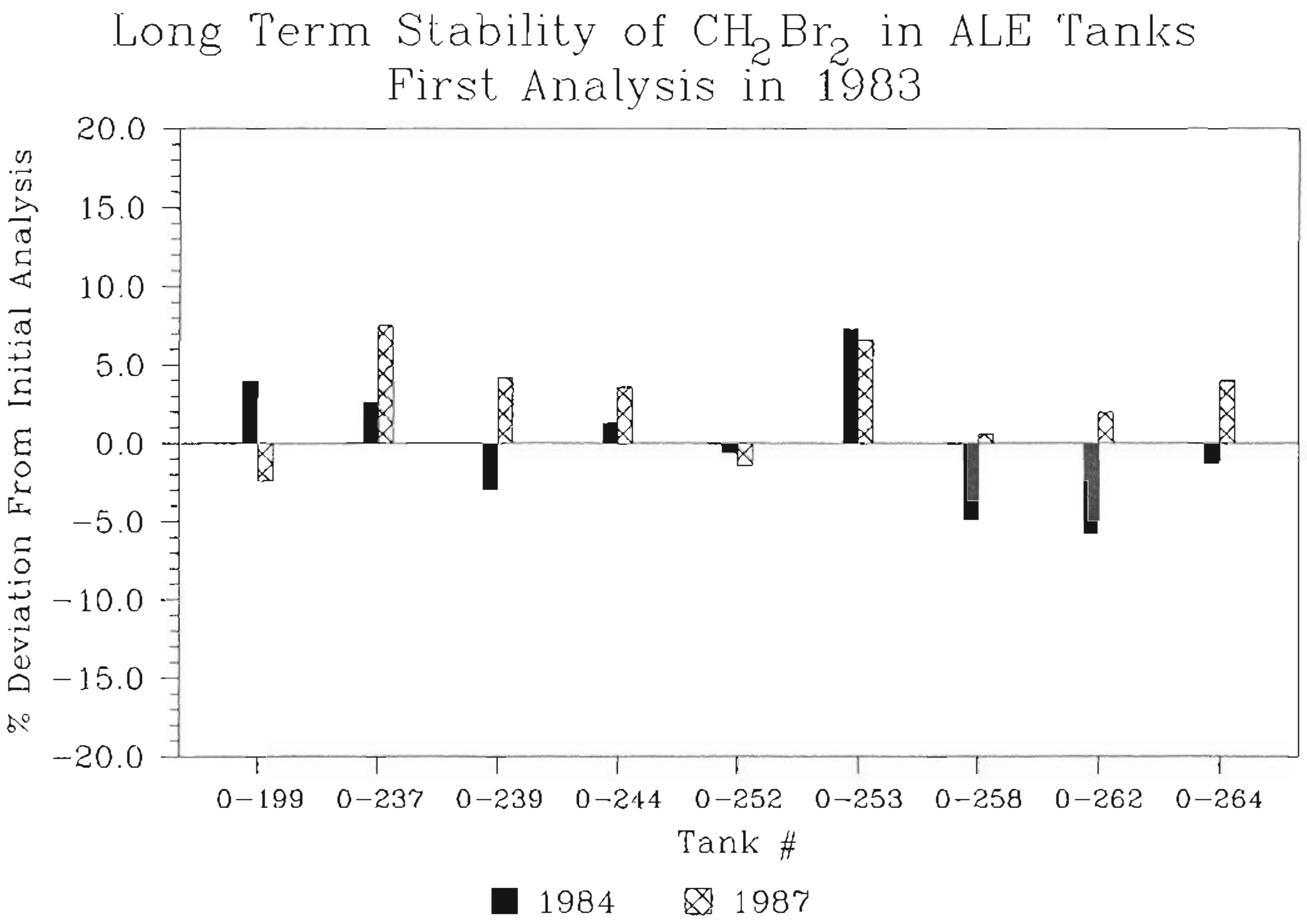

Figure 2.7.6 : Long term stability of CH_2Br_2 in ALE tanks

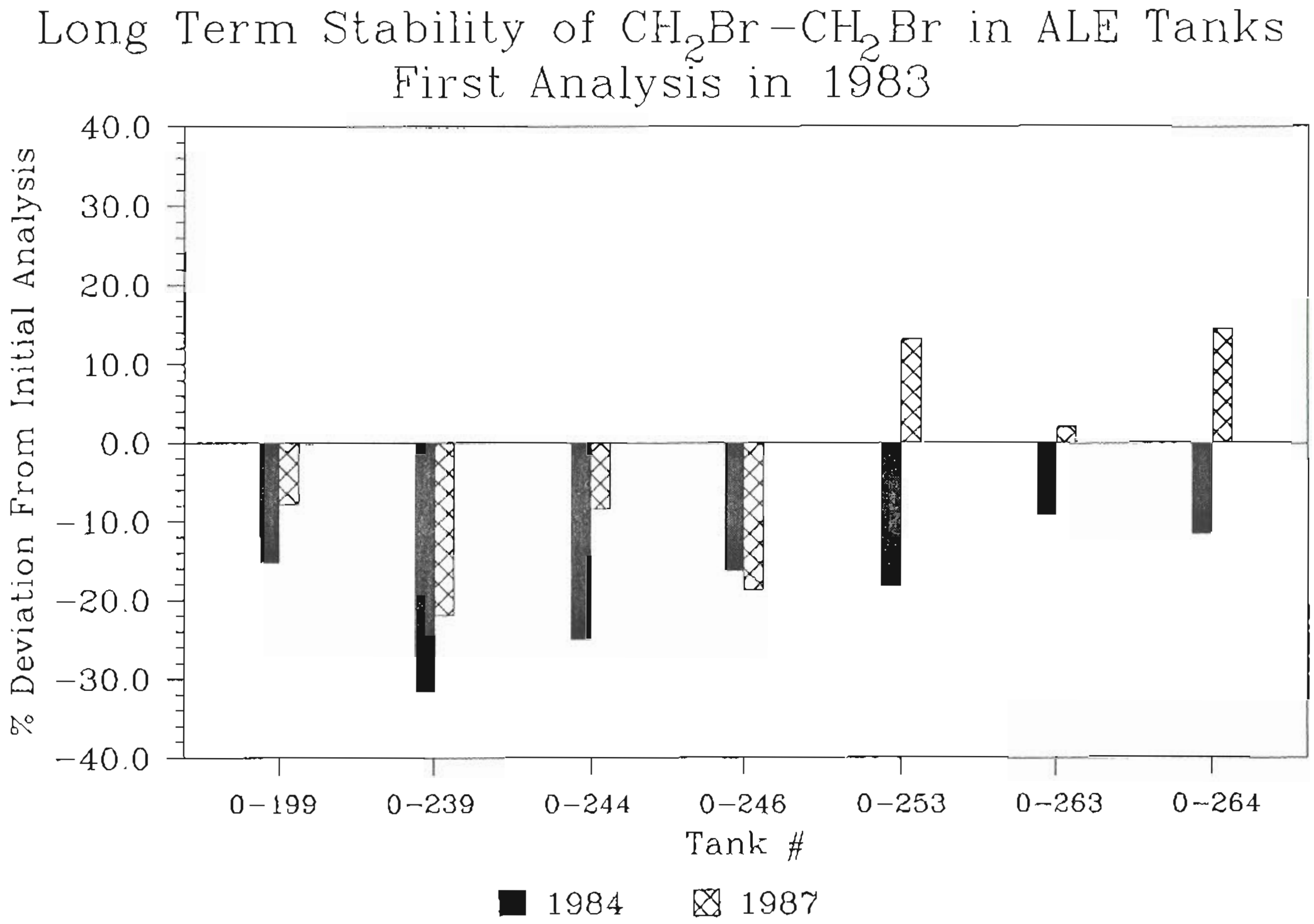

Figure 2.7.7 : Long term stability of CH_2Br-CH_2Br in ALE tanks

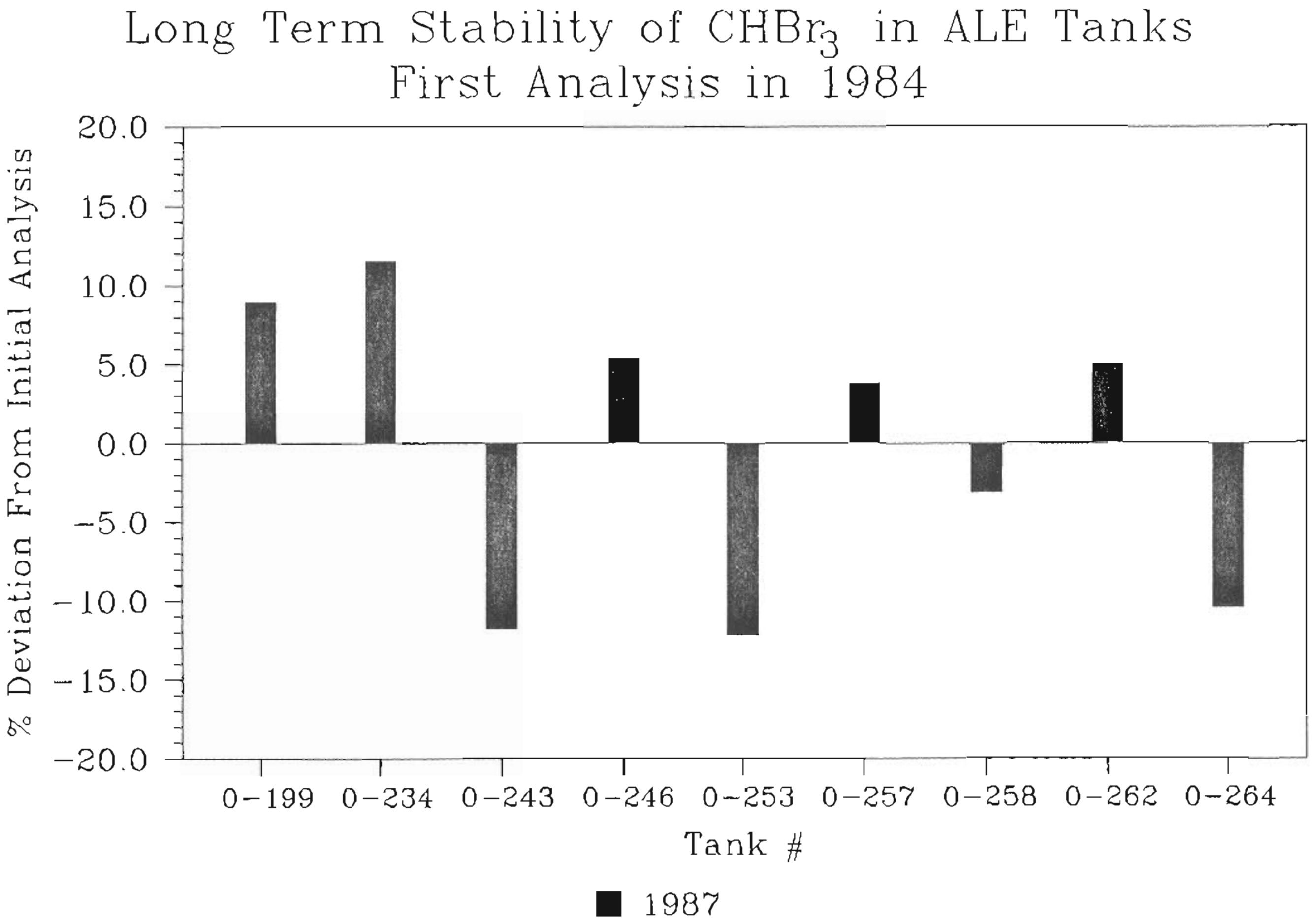

Figure 2.7.8 : Long term stability of $CHBr_3$ in ALE tanks

Stability in Low Pressure Containers

The majority of the atmospheric data gathered in this study were obtained from weekly samples collected in 0.85-liter cans. Therefore, the short-term (few weeks) stability of organo-bromine gases in these sample containers was studied. Five sample containers were filled to 30 psig with air at Cape Meares, Oregon. Air samples collected and held at pressures of 0 to 30 psig are designated to be low pressure samples. As such they are not expected to be as stable as high pressure 100 to 400 psig samples in the ALE tanks. These cans were first analyzed within one day after collection. They were analyzed again after a period of five weeks. The results (Table 2.7.2) showed that after five weeks, the concentration of each organo-bromine compound was within ±5% of the original value. This showed that the organo-bromine gases studied were stable in low pressure containers over a period of five weeks. Typically, samples are analyzed within four weeks of collection.

TABLE 2.7.2

Short term stability of organo-bromine gases in low pressure 0.85-liter sample containers (n=5)

Compound	Concentration range (pptv)	Variability from first analysis
1. $CBrF_3$	2.5 - 2.6	± 5%
2. $CBrClF_2$	1.9 - 2.0	± 1%
3. CH_3Br	10.5 - 11.1	± 1%
4. CH_3-CH_2Br	1.3 - 1.6	± 4%
5. CH_2BrCl	2.0 - 2.3	± 4%
6. CH_2Br_2	5.1 - 5.4	± 2%
7. $CHBr_2Cl$	0.9 - 1.2	± 4%
8. CH_2Br-CH_2Br	2.1 - 2.7	± 3%
9. $CHBr_3$	11.0 - 11.8	± 2%

3 OBSERVATIONS

The global distribution of nine organo-bromine gases was determined by analyzing samples collected at 12 stations from the Arctic Circle to the South Pole. The latitudes of these sampling stations are listed in Table 3.1 and their locations shown in Figure 3.1. Some of data obtained from these samples go back to 1977. The results from these analyses have been used to determine the latitudinal distribution, the altitudinal profile, seasonal cycles and long-term trends of these organo-bromine gases. Samples collected during two oceanic cruises were also used to establish in greater detail the latitudinal distribution of these gases. The first cruise on the U.S.S.R. research ship Academic Korolev (Cruise I) was on the Pacific Ocean in October and November of 1983. The second cruise on the Academic Korolev (Cruise II) was across the Pacific and Indian Oceans during May through July of 1987. The routes taken by these two cruises are shown in Figures 3.2 and 3.3.

TABLE 3.1

Sampling stations

Station	Latitude
1. Alert, NW Territories, Canada	82°N
2. Point Barrow, Alaska	72°N
3. Poker Flat, Alaska	66°N
4. Mace Head, Ireland	53°N
5. Cape Meares, Oregon	45°N
6. Sable Island, Canada	44°N
7. Cape Kumukahi, Hawaii	20°N
8. Mauna Loa, Hawaii (11,000 ft.)	20°N
9. St. Croix, U.S. Virgin Islands	12°N
10. Cape Matatula, American Samoa	15°S
11. Cape Grim, Tasmania	42°S
12. South Pole (9,000 ft.)	90°S

All stations are at sea level unless noted otherwise.

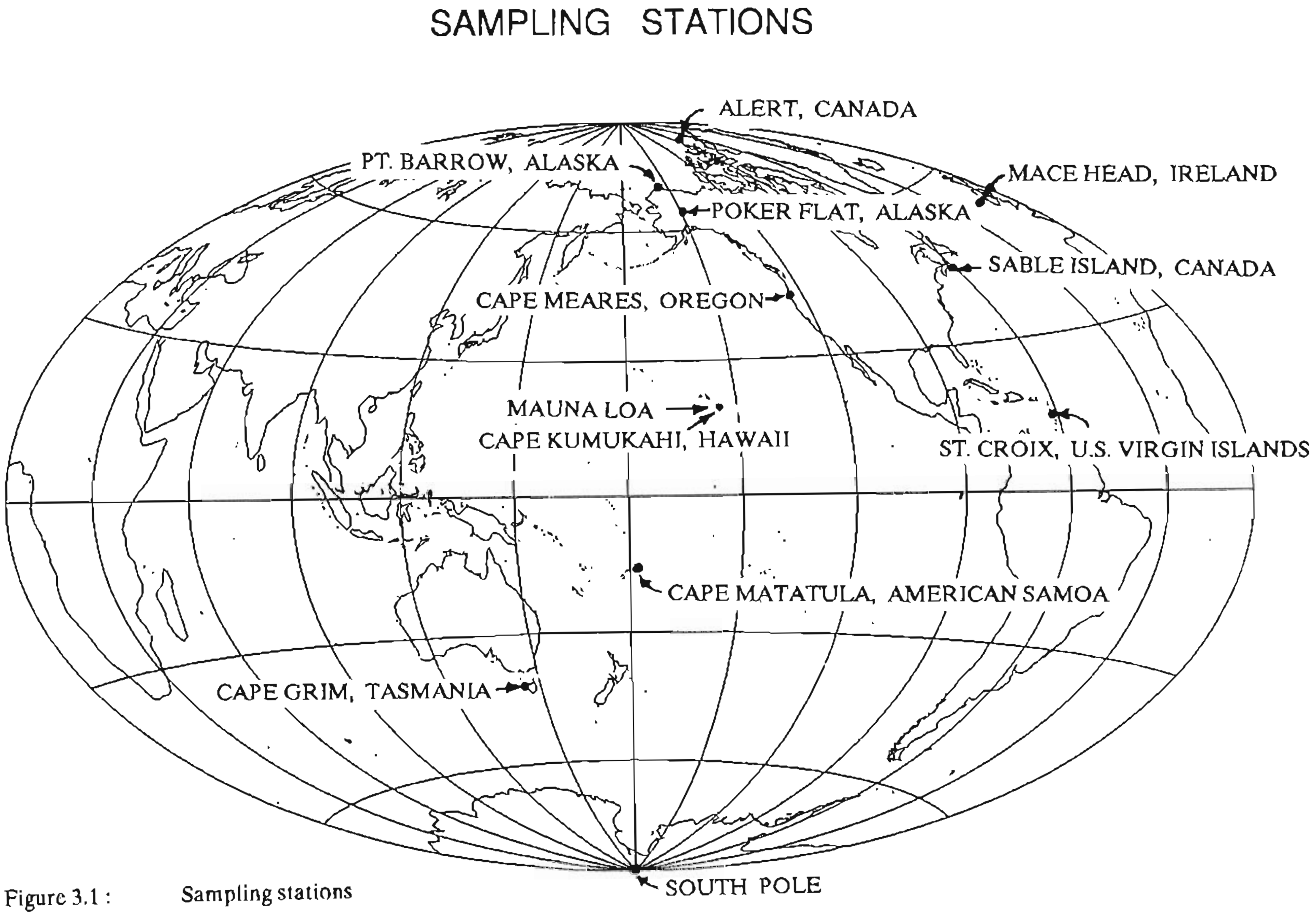

Figure 3.1 : Sampling stations

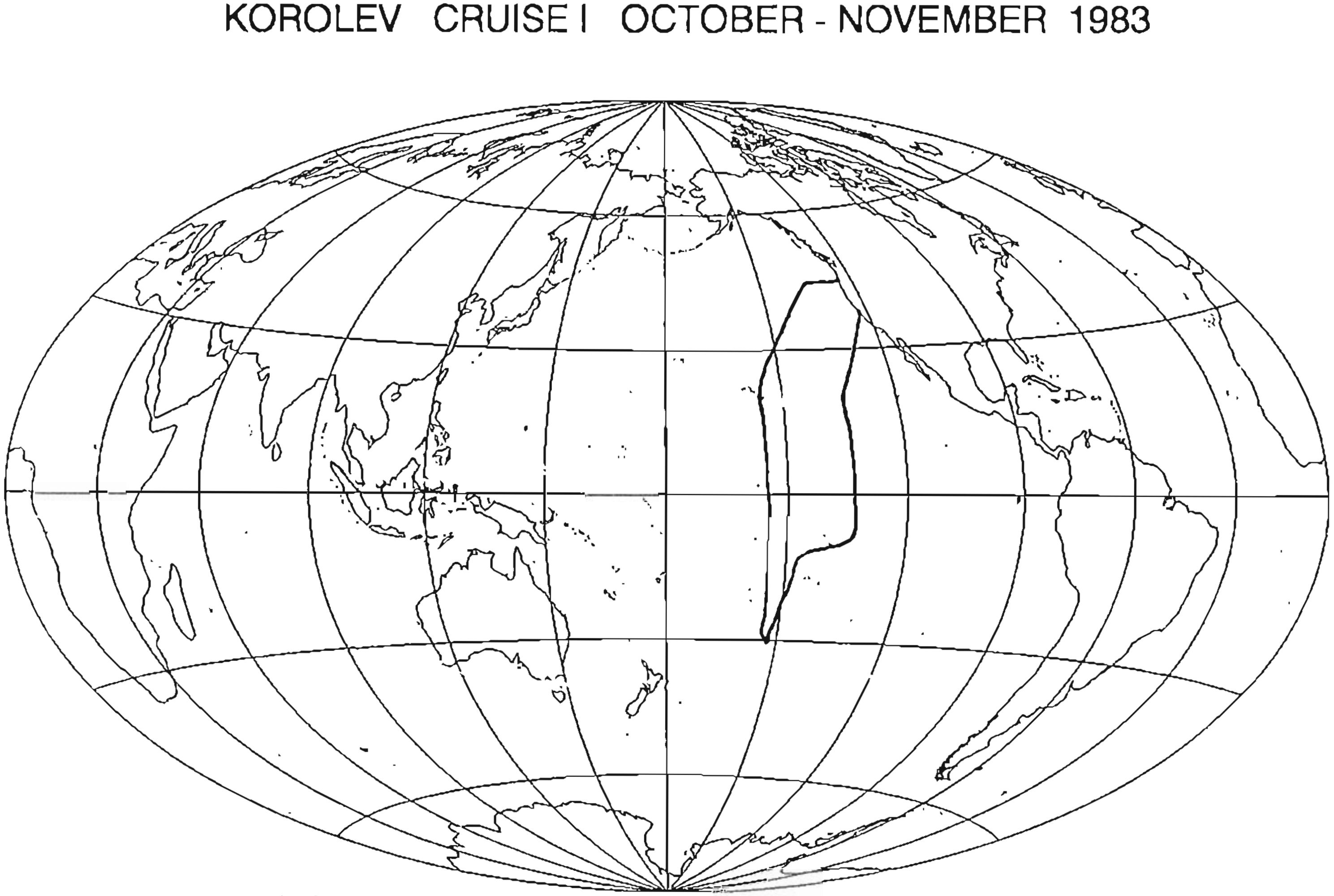

Figure 3.2 : Korolev Cruise I (1983)

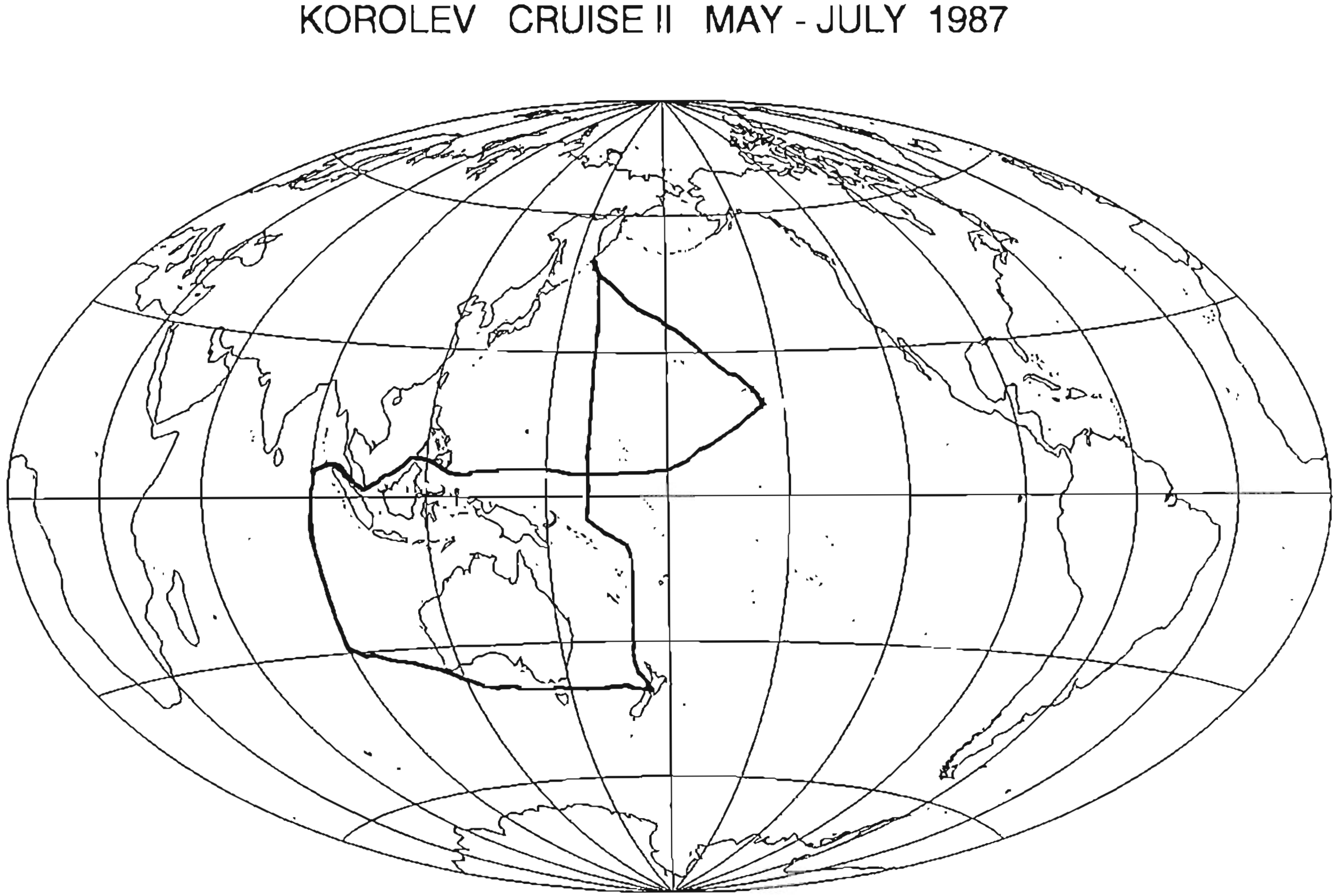

Figure 3.3 : Korolev Cruise II (1987)

3.1 Statistical Analysis of Observed Results

Large amounts of data on the atmospheric organo-bromine gases were collected during the course of this study. To determine how these gases are globally distributed in space and time, the data were examined for

(i) **Latitudinal variation** (mean concentration at each station vs. latitude).

(ii) **Altitudinal variation** (monthly or annual mean concentrations at Mauna Loa and Cape Kumukahi vs. time).

(iii) **Seasonal variations** (monthly mean concentration vs. months of the year).

(iv) **Long term trends** (annual mean concentration vs. year).

The apparent seasonal, monthly, latitudinal and altitudinal differences were further analyzed to determine if they were statistically significant. These differences were analyzed using the Student's t-test with modified t values [Snedecor and Cochran (1967)]. The modified t values were used because unequal variances and unequal number of samples were involved in the comparisons.

When the number of samples in two groups (1 and 2) compared are n_1 and n_2 and the respective standard deviations are s_1 and s_2, the t in the t-test was replaced by t', which was defined as:

$$t' = \frac{\overline{X}_1 - \overline{X}_2}{\sqrt{w_1 + w_2}}$$

where $\overline{X}_1$ and $\overline{X}_2$ are the sample means and

$$w_1 = \frac{s_1^2}{n_1} \text{ and } w_2 = \frac{s_2^2}{n_2}$$

In these comparisons, "single tailed t-tests" were used.

The significance levels of t in a standard t-table were looked up for $n_1 - 1$ and $n_2 - 1$ degrees of freedom (t_1 and t_2 respectively). The approximate significance level t' (at 95% level) is given by

$$t'_{95\%} = \frac{w_1 t_1 + w_2 t_2}{w_1 + w_2}$$

The level of significance considered was 95%. When the calculated t' value was not significant but close to the value $t'_{95\%}$, $t'_{90\%}$ was calculated at the 90% level.

3.2 Latitudinal Distribution - Interhemispheric Gradients

The majority of the sources of the two man-made gases $CBrF_3$ and $CBrClF_2$ are believed to be in the northern hemisphere. In this section, the interhemispheric gradients observed with these two man-made gases are discussed in detail.

Summary observations for the other species are:

Significant interhemispheric gradients (t-test, 95% level) were observed in the CH_3Br, CH_3-CH_2Br and CH_2BrCl data. The northern hemispheric concentration of CH_3Br was 38% higher than the southern hemispheric concentration. For CH_2BrCl the difference between the northern and southern hemispheres was 57%. From February through September, the mean CH_3-CH_2Br concentration in the northern hemisphere was 40% higher than in the southern hemisphere. During the months October through January the southern hemispheric concentration was 50% higher than the northern hemispheric value. The interhemispheric gradients observed for CH_3Br, CH_3-CH_2Br and CH_2BrCl are further discussed in Appendix B.

3.2.1 Latitudinal Distribution of $CBrF_3$ Bromotrifluoromethane (F-13B1)

$CBrF_3$ data from 1979 through 1987 were used to determine its latitudinal distribution. These represent 956 measurements. The northern hemispheric data were from samples collected at Cape Meares. The southern hemispheric data were obtained at Samoa, Cape Grim and South Pole. These four stations were selected because long term $CBrF_3$ data were available only for them. The mean $CBrF_3$ concentration in the northern hemisphere was $25 \pm 10\%$ higher than in the southern hemisphere. The differences in the $CBrF_3$ concentration between the northern and southern hemispheres from 1979 to 1987 are given Table 3.2.1.1. The trend of the $CBrF_3$ concentration in each hemisphere is plotted in Figure 3.2.1.1. This shows the long-term variation of the north-south gradient. The variation of the latitudinal distribution of $CBrF_3$ concentration from 1979 to 1987 is plotted in Figure 3.2.1.2. The significantly higher concentration of $CBrF_3$ in the northern hemisphere than in the southern hemisphere (t-test, 95% level) indicates that the majority of its sources are in the northern hemisphere.

TABLE 3.2.1.1

Interhemispheric gradient in $CBrF_3$ concentration

Year	Northern Hemisphere (pptv)	Southern Hemisphere (pptv)	North-South difference (pptv)	North-South difference (%)
1979	0.59	0.51	0.08	15
1980	0.72	0.58	0.14	25
1981	0.84	0.67	0.17	25
1982	1.00	0.82	0.18	22
1983	1.16	0.99	0.17	18
1984	1.44	1.23	0.21	16
1985	1.86	1.42	0.44	31
1986	2.06	1.61	0.45	28
1987	2.73	1.85	0.88	48
				Mean = 25

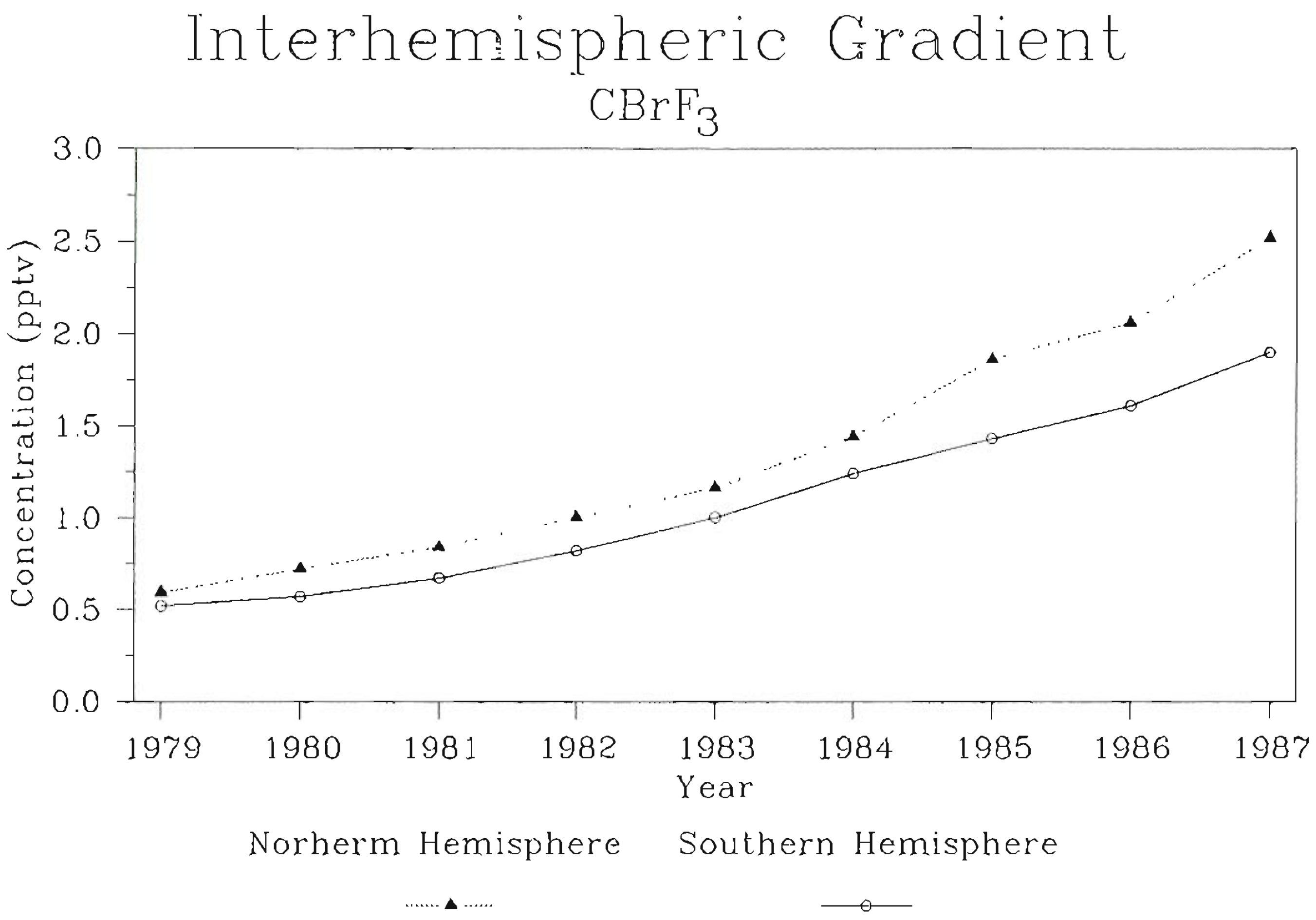

Figure 3.2.1.1 : Interhemispheric gradient of $CBrF_3$ concentration

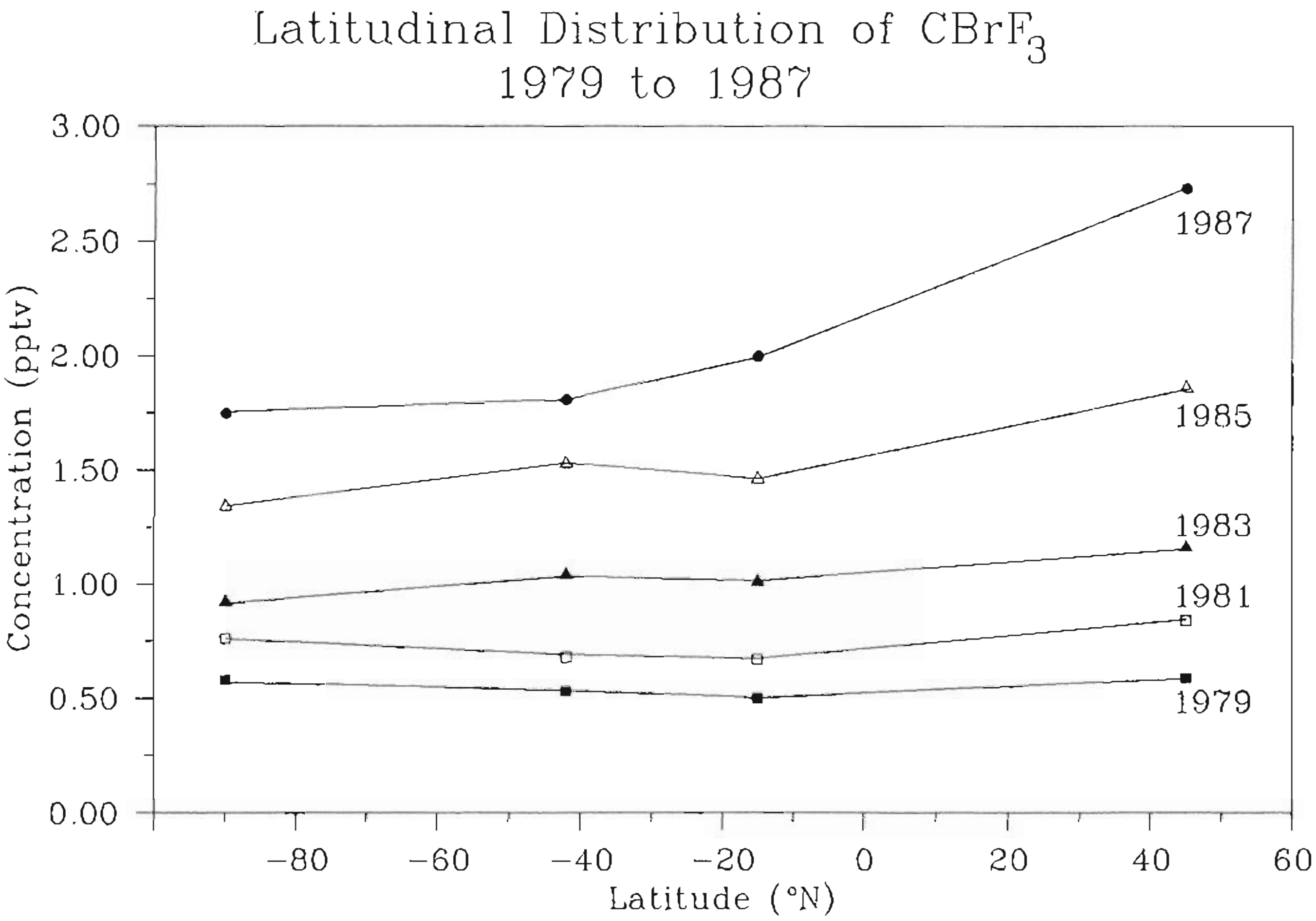

Figure 3.2.1.2 : Latitudinal distribution of $CBrF_3$ - 1979 to 1987

3.2.2 Latitudinal Distribution of $CBrClF_2$ Bromochlorodifluoromethane (BCF)

$CBrClF_2$ data from 1979 through 1987 were used to determine its latitudinal distribution. These represent 2109 measurements. Data from Point Barrow, Cape Meares and Cape Kumukahi were used to determine the mean northern hemispheric $CBrClF_2$ concentration. Data from Samoa, Cape Grim and South Pole were used to determine its mean southern hemispheric concentration. The results show significantly higher (t-test, 95% level) concentrations of $CBrClF_2$ in the northern hemisphere than in the southern hemisphere. The mean difference in the concentration between the two hemispheres from 1979 through 1987 was 0.24 pptv. The rates of increase in the $CBrClF_2$ concentration are identical and linear in both hemispheres. As a result, the difference between the two hemispheres remained close to 0.24 pptv during this period. Therefore, concentration units are used to show the difference instead of percentages. The concentrations of $CBrClF_2$ in each hemisphere from 1979 through 1987 and their differences are given in Table 3.2.2.1. The trend of $CBrClF_2$ in each hemisphere is plotted in Figure 3.2.2.1. This shows the constant difference in the $CBrClF_2$ concentration between the two hemispheres. The variation of the latitudinal distribution of the $CBrClF_2$ concentration from 1979 to 1987 is plotted in Figure 3.4.2.2. These observations indicate the presence of the majority of the sources of $CBrClF_2$ in the northern hemisphere.

TABLE 3.2.2.1

Interhemispheric gradient of $CBrClF_2$

Year	Northern Hemisphere (pptv)	Southern Hemisphere (pptv)	North-South difference (pptv)	North-South difference (%)
1979	0.72	0.45	0.27	60
1980	0.87	0.57	0.30	53
1981	1.03	0.81	0.21	27
1982	1.10	0.90	0.20	22
1983	1.23	1.00	0.23	23
1984	1.41	1.13	0.28	25
1985	1.57	1.29	0.28	22
1986	1.66	1.49	0.17	11
1987	1.83	1.59	0.24	15
			Mean = 0.24	

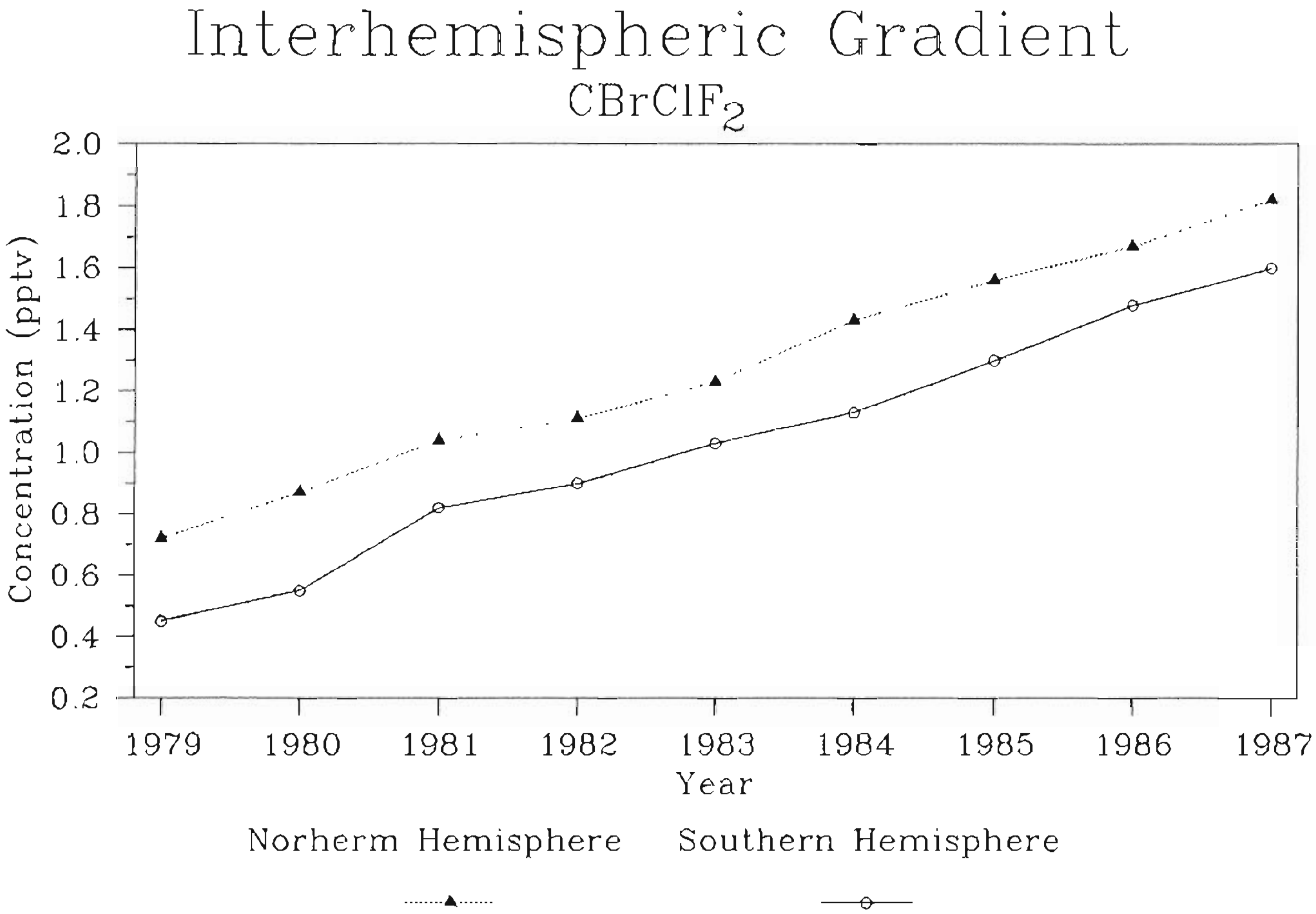

Figure 3.2.2.1 : Interhemispheric gradient of $CBrClF_2$ concentration

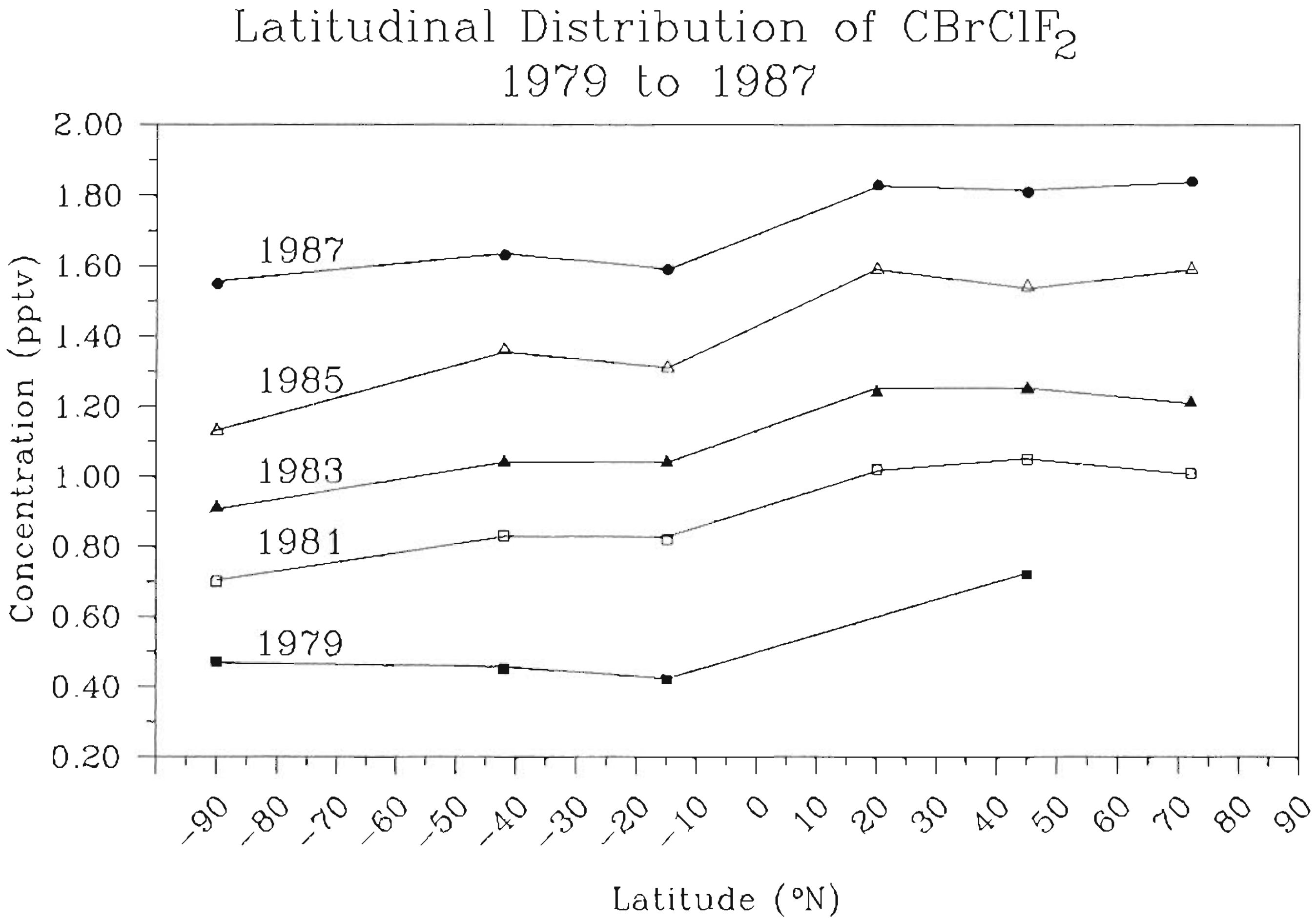

Figure 3.2.2.2 : Latitudinal distribution of $CBrClF_2$ - 1979 to 1987

3.3 Latitudinal Distribution - Korolev Cruises I (1983) and II (1987)

Air samples were collected during two oceanic cruises aboard the Soviet research ship "Academic Korolev". The first cruise, Korolev Cruise I, was in October and November of 1983 on the Pacific Ocean. The forty four samples collected during the first cruise were analyzed using System III. The second cruise, Korolev Cruise II, was in May, June and July of 1987 across the Pacific and Indian Oceans. The one hundred and ninesamples collected during the second cruise were analyzed using System V. These two cruises provided additional data to determine the latitudinal distribution of organo-bromine gases in greater detail than with the data from the ground-based stations. In this section, the $CBrClF_2$ data from these two cruises are discussed in detail. The $CBrClF_2$ data from the two cruises are given in Table 3.3.1 and they show the higher values in the northern hemisphere than in the southern hemisphere.

Significantly different concentrations of CH_3Br and CH_2BrCl (t-test, 95% level) were observed between the northern and southern hemisphere during the second Korolev cruise. The CH_3Br concentration in the northern hemisphere was 53% than in the southern hemisphere. This difference was larger than that observed in the data from the ground-based stations (38%). The difference in the CH_2BrCl concentration between the two hemispheres was 69% during the second Korolev cruise. This difference was also larger than that observed in the data from the ground based stations (57%). The CH_2Br_2 values were significantly lower (t-test, 95% level) in the equatorial region than in the higher latitudes in each hemisphere. The latitudinal distribution of CH_3Br, CH_2BrCl and CH_2Br_2 observed during Korolev Cruise II are further discussed in Appendix B.

TABLE 3.3.1

$CBrClF_2$ concentrations observed during Korolev Cruises I and II

Latitude (° N)	Korolev Cruise I			Korolev Cruise II		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
45	1.2	0.1	3	1.9	0.4	31
35	1.2	0.1	4	1.7	0.1	8
25	1.2	0.1	5	1.7	0.1	3
15	1.2	0.0	5	1.7	0.0	2
5	1.1	0.1	5	1.7	0.1	16
-5	1.0	0.0	5	1.6	0.1	10
-15	1.1	0.1	9	1.6	0.1	8
-25	1.0	0.0	8	1.6	0.1	8
-35	-	-	-	1.7	0.1	20
-45	-	-	-	1.6	0.1	3

3.3.1 $CBrClF_2$ - IN KOROLEV CRUISE I SAMPLES

The $CBrClF_2$ data from Korolev Cruise I showed significantly higher $CBrClF_2$ concentration in the northern hemisphere than in the southern hemisphere (t-test, 95% level). The mean concentrations in the northern and southern hemispheres were 1.19 and 1.05 pptv respectively. These values were comparable to the observations made at ground-based sampling stations in 1983 which had respective values of 1.23 and 1.03 pptv. A comparison of the weekly $CBrClF_2$ data from 1983 and the Korolev Cruise I $CBrClF_2$ data are plotted against latitude in Figure 3.3.1.1. The observed concentration gradient indicates that the majority of the sources are in the northern hemisphere.

3.3.2 $CBrClF_2$ - IN KOROLEV CRUISE II SAMPLES

The $CBrClF_2$ data from Korolev Cruise II also showed significantly higher concentration in the northern hemisphere than in the southern hemisphere (t-test, 95% level). The respective concentrations were 1.80 and 1.58 pptv. This distribution was comparable to the $CBrClF_2$ concentrations observed in the northern and southern hemispheres in 1987 from the ground-based observations, which had 1.82 and 1.60 pptv respectively. The weekly $CBrClF_2$ data from 1987 and the Korolev Cruise II $CBrClF_2$ data plotted against the latitude in Figure 3.3.2.1 show its interhemispheric gradient. A further comparison of the weekly ground based $CBrClF_2$ data (1983 and 1987) with the data from Korolev Cruises I and II are plotted in Figure 3.3.2.2. This shows the increase in the $CBrClF_2$ concentration over the four-year period. The data from the two cruises show that the $CBrClF_2$ concentration in the northern and southern hemispheres grew at rates of 0.15 and 0.13 pptv per year respectively. These values are comparable to the growth rates observed from the weekly data, which was 0.14 pptv in each hemisphere.

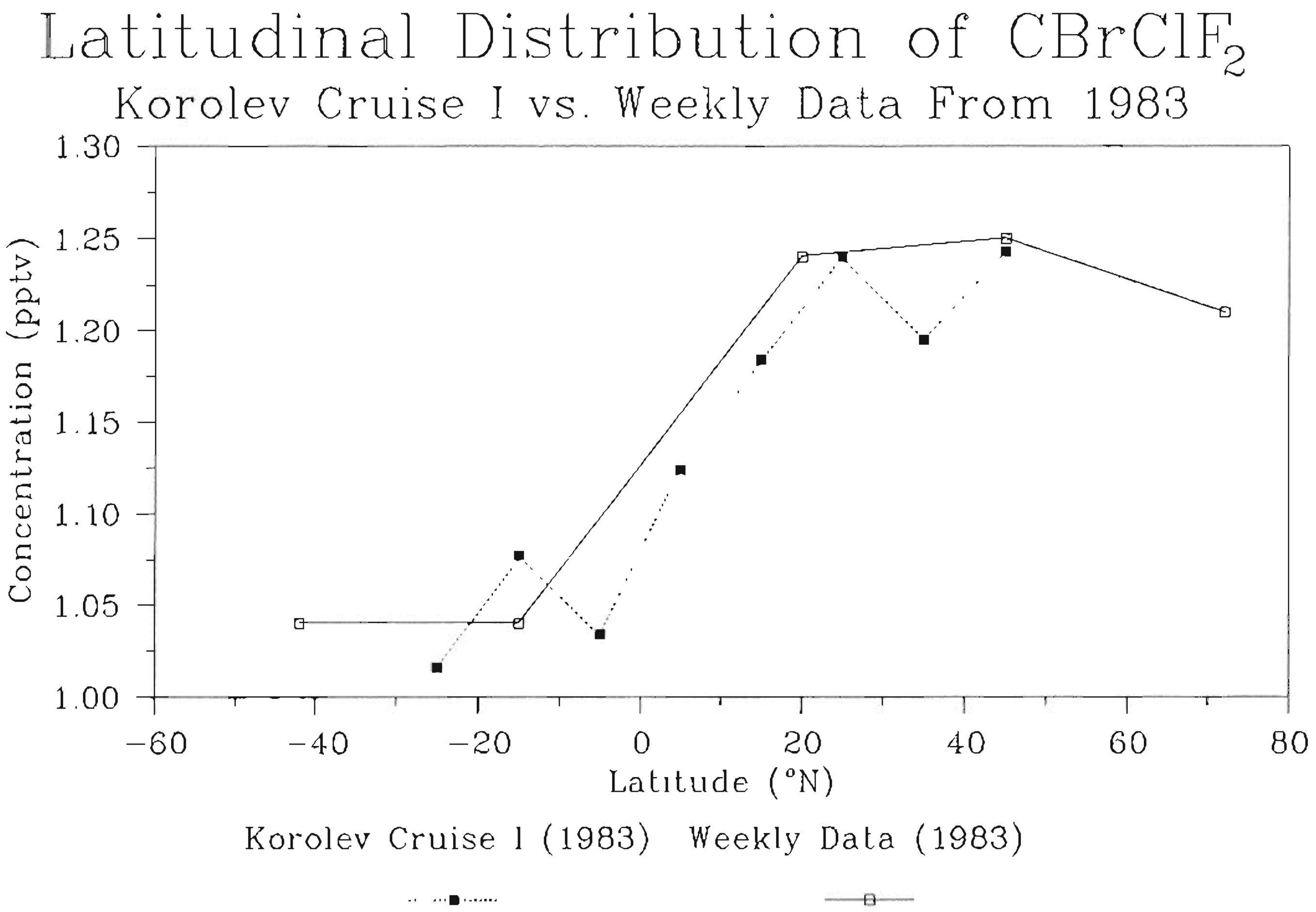

Figure 3.3.1.1 : CBrClF$_2$ concentrations observed during Korolev Cruise I (1983) and weekly data from 1983

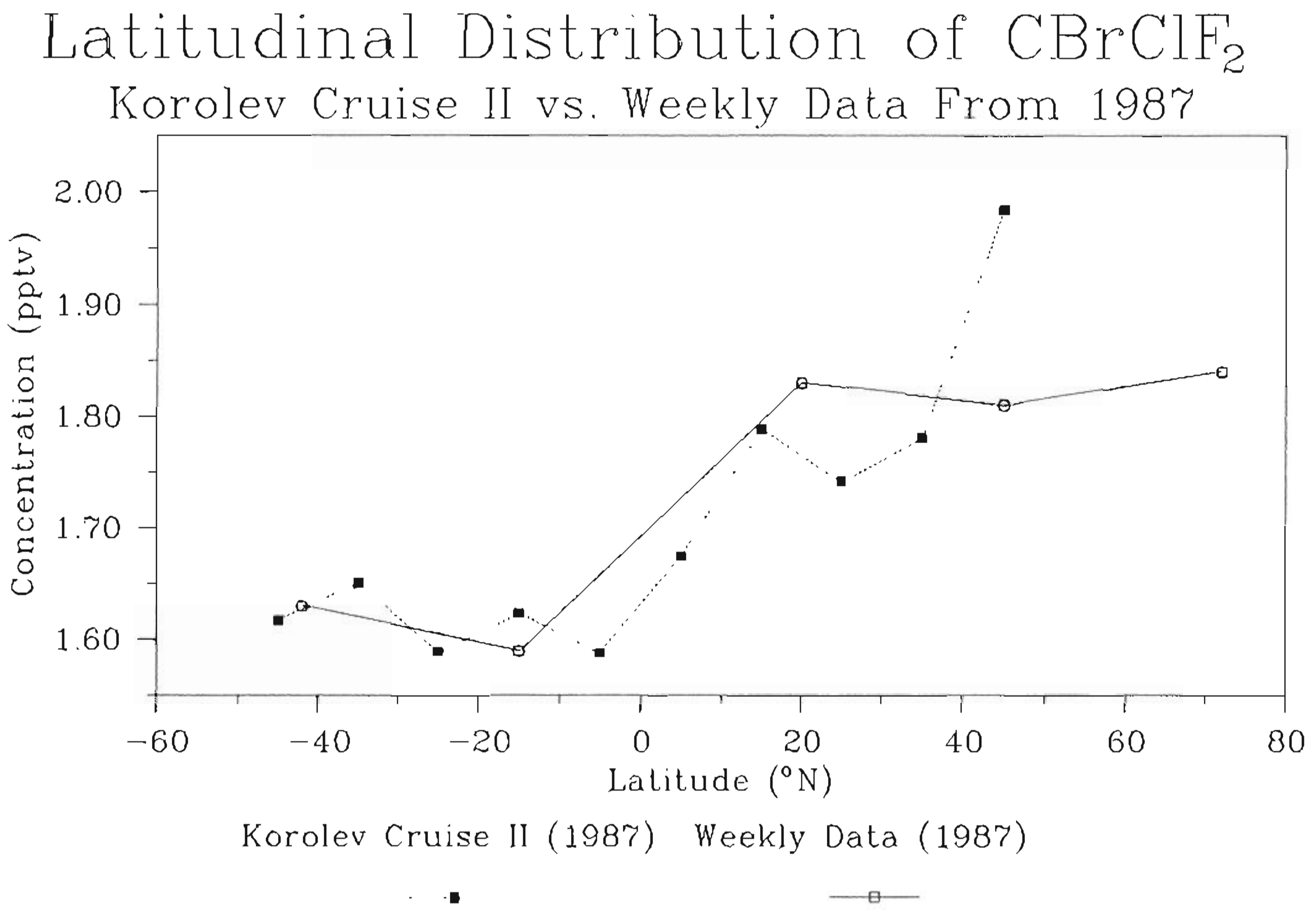

Figure 3.3.2.1 : $CBrClF_2$ concentrations observed during Korolev Cruise II (1987) and weekly data from 1987

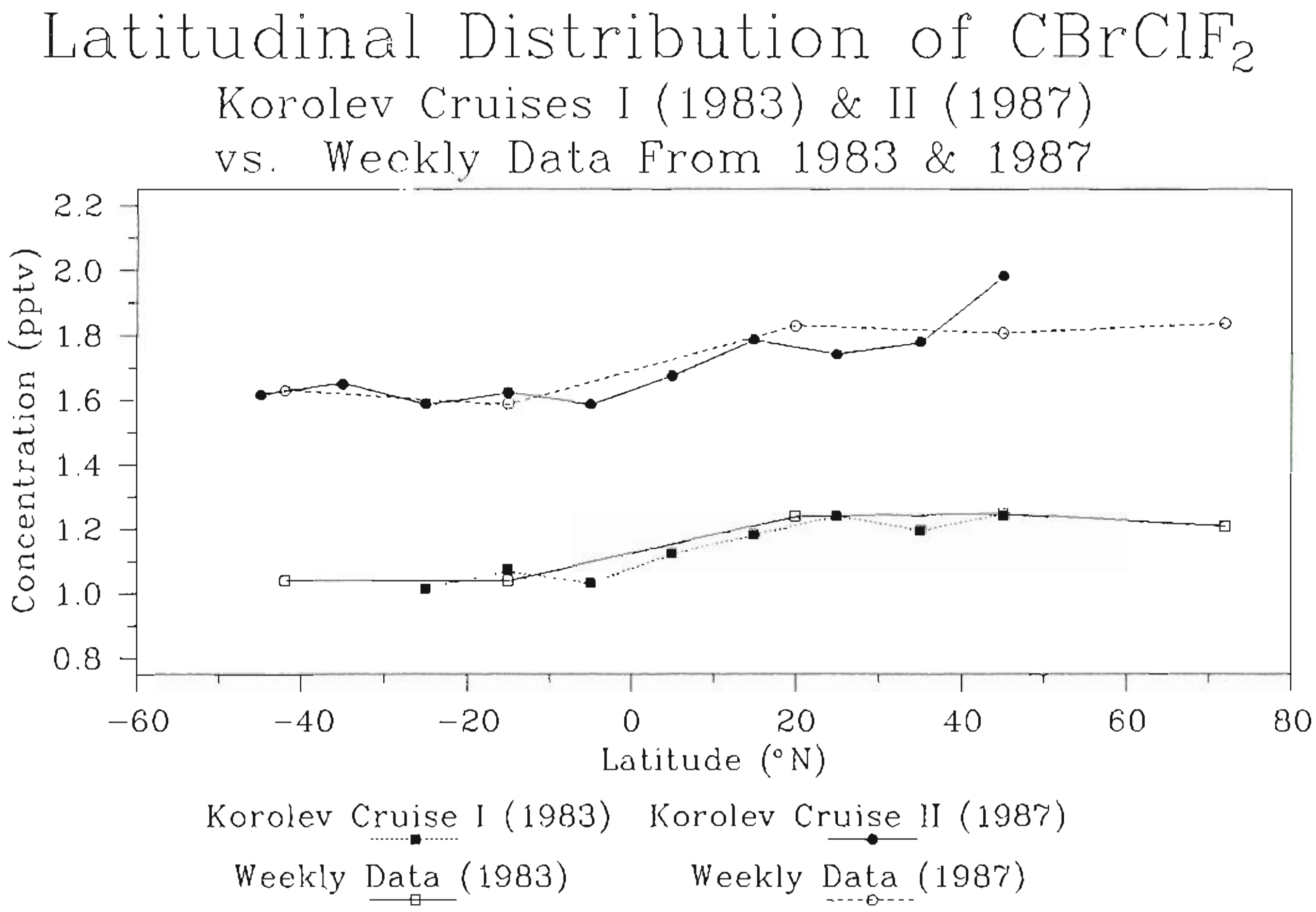

Figure 3.3.2.2 : Comparison of 1983 and 1987 $CBrClF_2$ data - weekly data vs. Korolev Cruise I and II data

3.4 Altitudinal Profile - Cape Kumukahi vs. Mauna Loa in Hawaii

Weekly samples collected at Cape Kumukahi (sea level) and Mauna Loa (11,000 feet) in Hawaii were analyzed to determine the altitudinal profile in the concentrations of the organo-bromine gases. The differences in the $CBrF_3$ concentration between Cape Kumukahi and Mauna Loa appear to be random (Table 3.4.1). This is believed to be due to the long-term stability of $CBrF_3$ in the atmosphere. In this section, the altitudinal profile of $CBrClF_2$ concentration is discussed.

The summary observations for the other species measured were:
The concentrations of CH_2Br_2, CH_2Br-CH_2Br and $CHBr_3$ were significantly higher (t-test, 95% level) at Cape Kumukahi than at Mauna Loa. The CH_3Br concentration at Mauna Loa was significantly higher (t-test, 95% level) than at Cape Kumukahi. These differences are further discussed in Appendix C.

TABLE 3.4.1

$CBrF_3$ concentrations at Cape Kumukahi and Mauna Loa

Year	Cape Kumukahi		Mauna Loa	
	Mean (pptv)	std.dev. (pptv)	Mean (pptv)	std.dev. (pptv)
1985	1.66	0.26	1.71	0.26
1986	1.90	0.25	1.79	0.27
1987	2.32	0.31	2.14	0.26

3.4.1 $CBrClF_2$ - Bromochlorodifluoromethane (BCF)

Air samples collected at Mauna Loa and Cape Kumukahi from 1981 through 1987 were analyzed for $CBrClF_2$ (BCF), except in 1983 when no samples were available from Cape Kumukahi. Over this time span the analyses were done using all five systems. The results showed that for each year from 1981 through 1987, the mean $CBrClF_2$ concentration at Cape Kumukahi was 0.08 pptv higher than at Mauna Loa, which was statistically significant. This difference may be due to photo-dissociation of the $CBrClF_2$ molecules at an altitude of 11,000 feet. The results are shown in Table 3.4.1.1. The trend in the $CBrClF_2$ concentration at Cape Kumukahi and Mauna Loa are plotted in Figure 3.4.1.1.

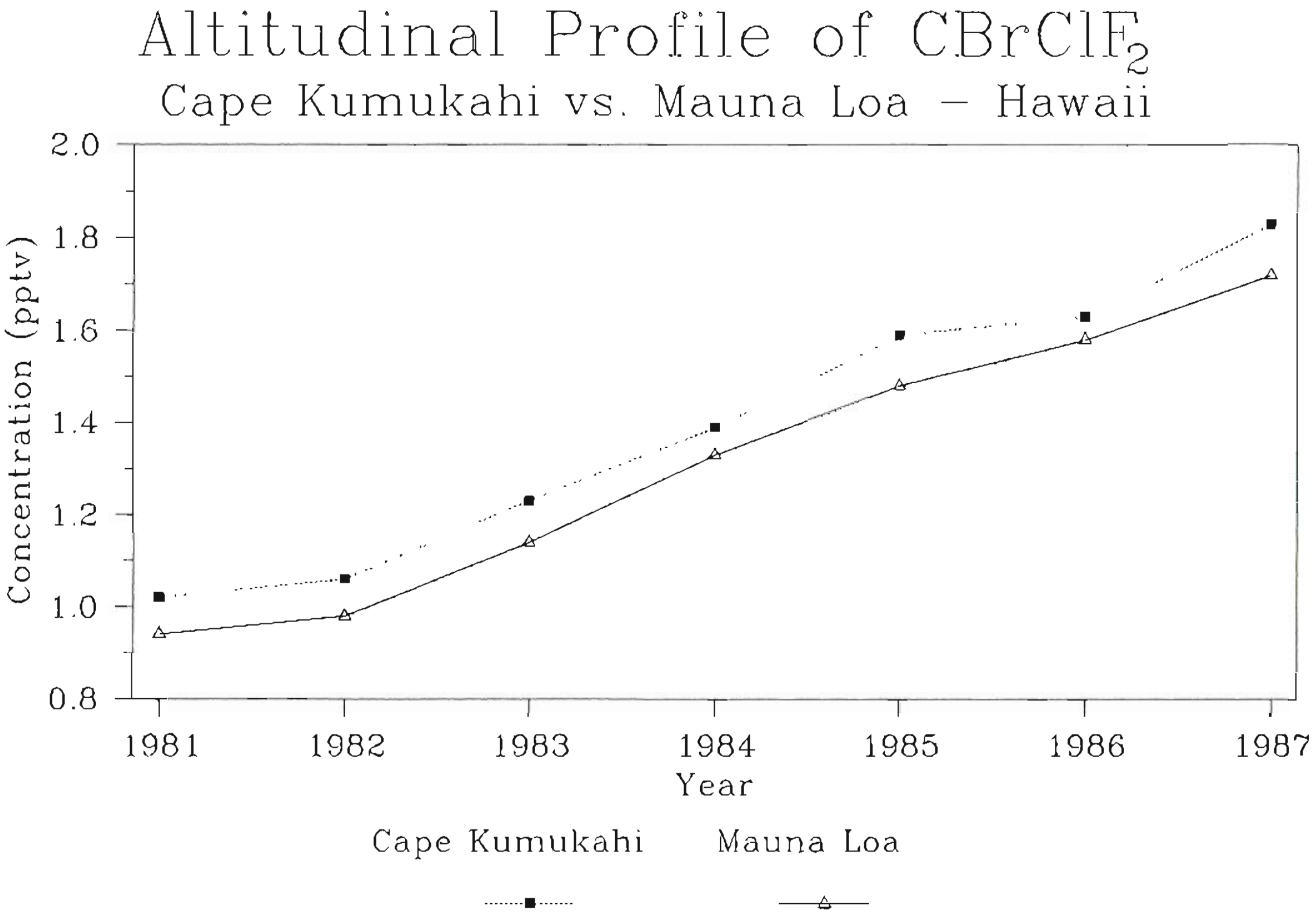

Figure 3.4.1.1 : Altitudinal Profile of $CBrClF_2$ concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

TABLE 3.4.1.1

Altitudinal difference in $CBrClF_2$ (BCF) concentration

Year	Cape Kumukahi			Mauna Loa		
	Mean (pptv)	Std.dev. (pptv)	Number of samples	Mean (pptv)	Std.dev. (pptv)	Number of samples
1981	1.02	0.05	11	0.94	0.03	10
1982	1.06	0.17	24	0.98	0.06	115
1983	--	--	--	1.10	0.18	47
1984	1.39	0.26	5	1.33	0.22	20
1985	1.59	0.24	37	1.48	0.18	27
1986	1.63	0.07	34	1.58	0.15	34
1987	1.83	0.25	40	1.72	0.16	37

No data were available for Cape Kumukahi in 1983.

3.5 Seasonal Variations

The weekly samples analyzed with all five systems were used to determine the seasonal variation of the organo-bromine gases in the atmosphere. These data did not show any seasonal variations for the two man-made gases $CBrF_3$ and $CBrClF_2$. The absence of seasonal cycles for these two gases may indicate their stability in the atmosphere. The other seven organo-bromine gases, CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, CH_2Br-CH_2Br and $CHBr_3$, showed significant seasonal cycles. These are discussed in detail in Appendix D.

3.6 LONG-TERM TRENDS

The two man-made gases $CBrF_3$ and $CBrClF_2$ are believed to have long life times in the atmosphere - 62 to 112 years for $CBrF_3$ and about 25 years for $CBrClF_2$ [Prather et al. (1984), Gammon et al. (1985) and Fabian et al. (1986)]. With the long lifetimes, these gases are expected to accumulate in the atmosphere. The data collected during this study were used to determine the long-term trends in the atmospheric concentration of these gases. Increasing trends in the $CBrF_3$ and $CBrClF_2$ concentrations were observed at each station. No long-term trends were observed for the other organo-bromine gases.

3.6.1 Long-Term Trend of $CBrF_3$ (F-13B1)

The analytical capability to measure $CBrF_3$ has been available since April of 1985 (with System V). Therefore, $CBrF_3$ data from the analysis of weekly samples are available only since 1985. These data were not sufficient to determine long-term trend in the atmospheric concentration of $CBrF_3$. Air samples from Cape Meares, Samoa, Cape Grim and the South Pole that form the "Air Bank" at OGC were analyzed to determine the $CBrF_3$ concentration prior to

April 1985. The samples from Cape Meares dated back to 1977 and the samples from Samoa, Cape Grim and the South Pole dated back to 1979. These data were used to determine the long-term trend of the atmospheric $CBrF_3$ concentration.

The data showed that $CBrF_3$ has been increasing 20% per year from 1977 to 1987 at Cape Meares. At Samoa the rate of increase since 1979 has been 19% per year. At Cape Grim and South Pole $CBrF_3$ concentration has increased at a rate of 17% per year. The $CBrF_3$ concentration data for these four stations are given in Table 3.6.1.1. The long-term trend of the $CBrF_3$ concentration at Cape Meares, Cape Matatula, Cape Grim and South Pole are plotted in Figures 3.6.1.1, 3.6.1.2, 3.6.1.3 and 3.6.1.4 respectively. If the increase of $CBrF_3$ continue at these rates, in twenty years its global burden will increase by a factor of 36, to about 100 pptv in the northern hemisphere, and by a factor of 27, to about 50 pptv in the southern hemisphere. Such an increase can decrease the column density of O_3 by 4% [Prather et al. (1984), McElroy et al. (1986)].

TABLE 3.6.1.1

Long term trend of $CBrF_3$

Year	Annual mean $CBrF_3$ concentration (pptv)			
	Cape Meares	Samoa	Cape Grim	South Pole
1977	0.3	*	*	*
1978	0.5	*	*	*
1979	0.6	0.5	0.5	0.5
1980	0.7	0.6	0.6	0.6
1981	0.8	0.7	0.7	0.7
1982	1.0	0.9	0.8	0.8
1983	1.2	1.0	1.0	0.9
1984	1.4	*	1.2	1.2
1985	1.9	1.5	1.5	1.3
1986	2.1	1.6	1.6	1.6
1987	2.7	2.0	1.8	1.7

* No data available

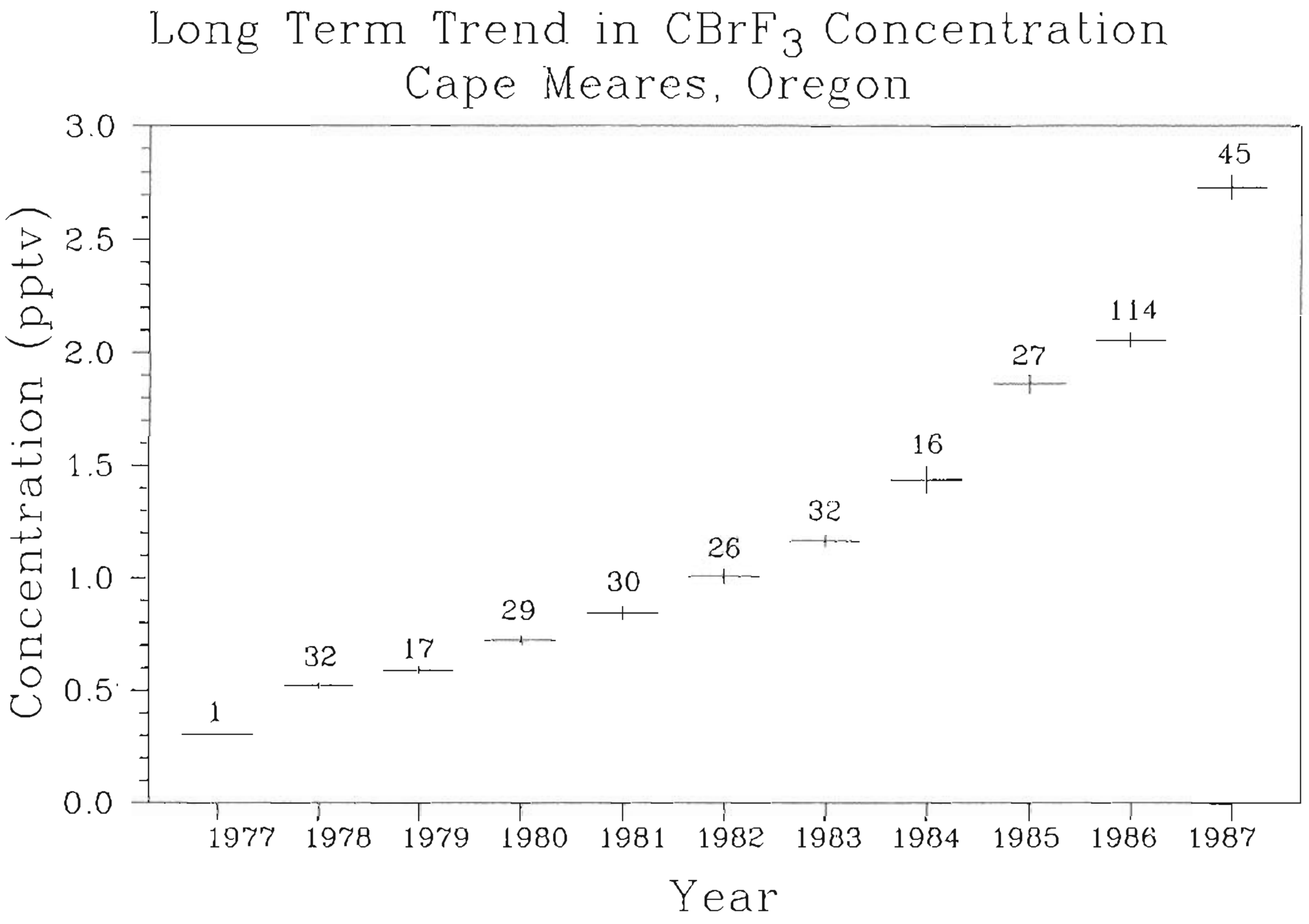

Figure 3.6.1.1 : Long term trend in $CBrF_3$ concentration at Cape Meares, Oregon (Error bars are ±1 Standard error)

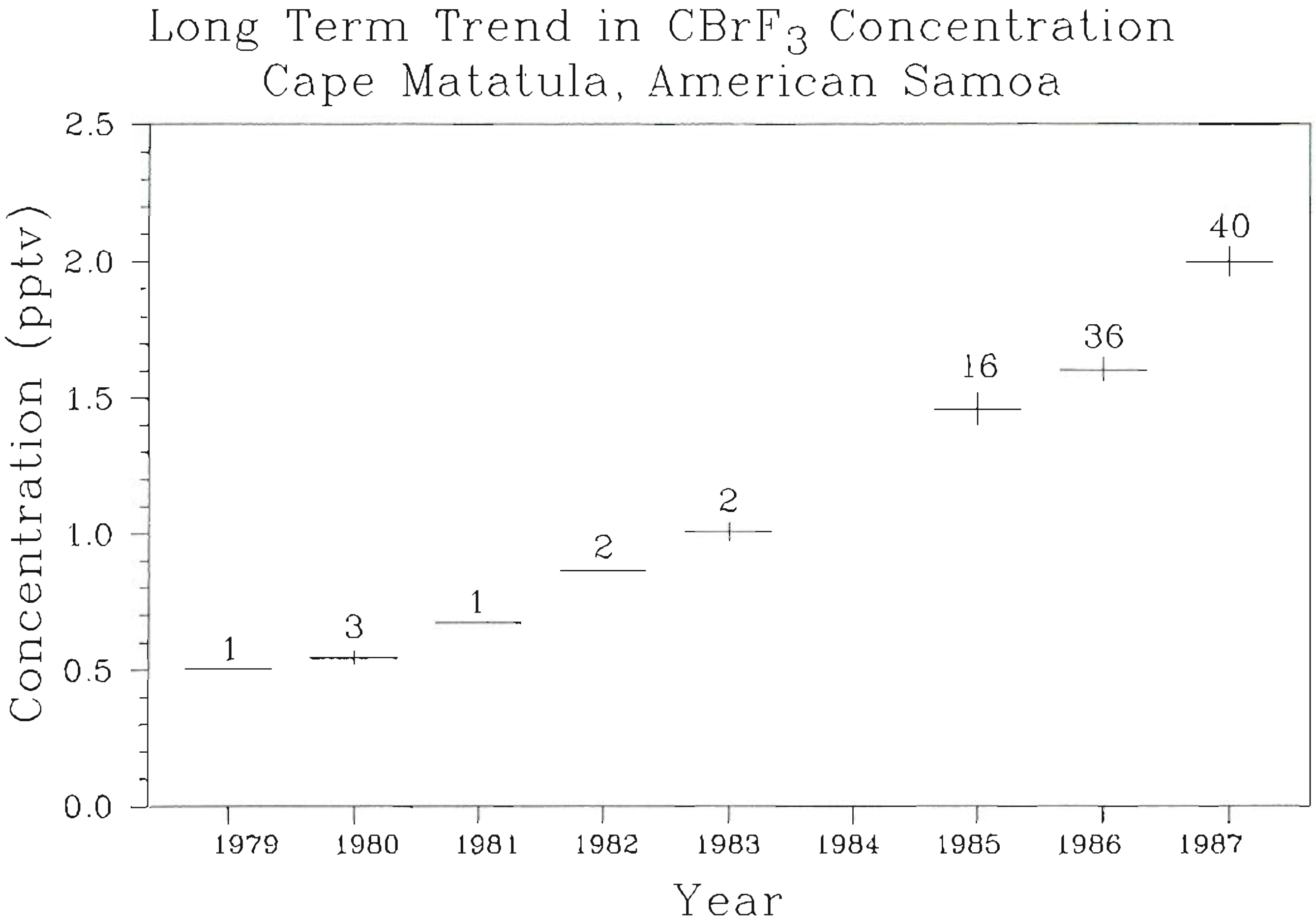

Figure 3.6.1.2 : Long term trend in $CBrF_3$ concentration at Cape Matatula, Samoa (Error bars are ±1 Standard error)

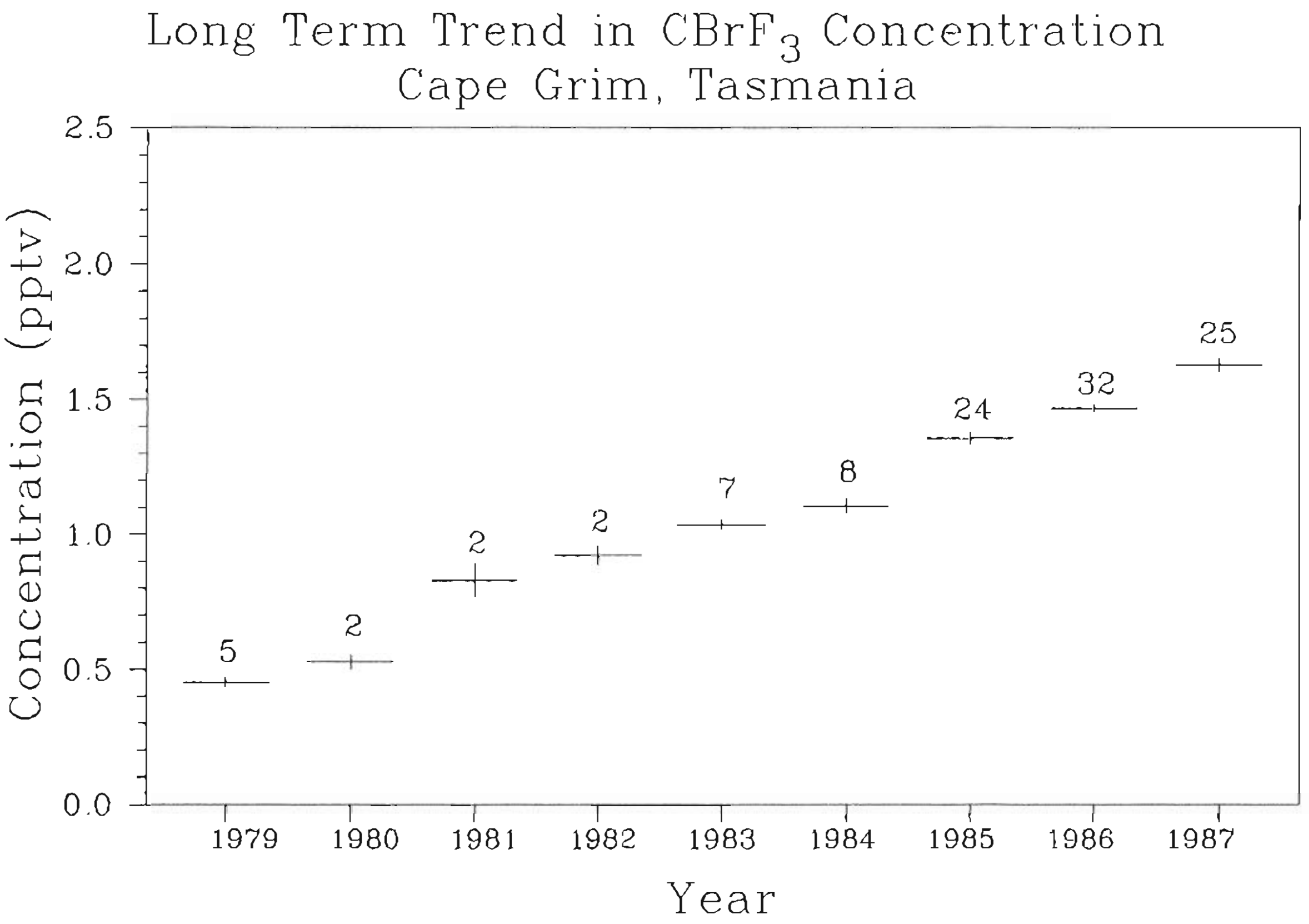

Figure 3.6.1.3 : Long term trend in $CBrF_3$ concentration at Cape Grim, Tasmania (Error bars are ±1 Standard error)

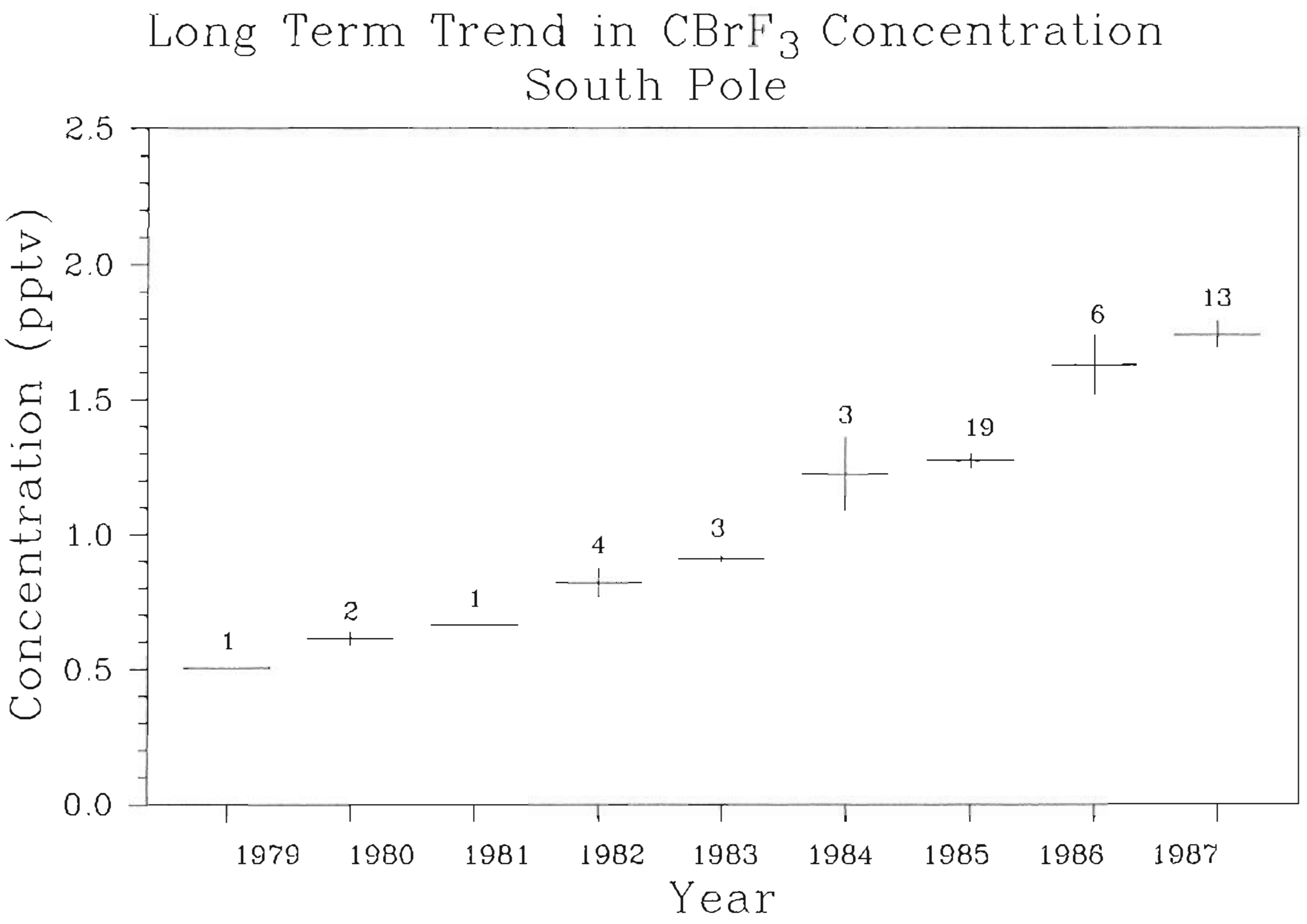

Figure 3.6.1.4 : Long term trend in $CBrF_3$ concentration at the South Pole
(Error bars are ±1 Standard error)

3.6.2 Long-Term Trend of $CBrClF_2$ (BCF)

$CBrClF_2$ was measured with all five systems. Weekly samples collected at Point Barrow, Cape Meares, Cape Kumukahi, Mauna Loa, Samoa, Cape Grim and the South Pole were analyzed from 1981 through 1987. The "Air Bank" at OGC provided samples from Cape Meares for the time period 1977 to 1981 and samples from Samoa, Cape Grim and South Pole for the time period 1979 to 1981. These "Air Bank" samples were analyzed on System V. These data were used to determine the long-term trend of the $CBrClF_2$ concentration in the atmosphere.

The data showed that the global $CBrClF_2$ concentration has increased linearly at a rate of 0.14 pptv per year since 1977. This rate of increase is comparable to the observations made during the two Korolev cruises, when the rate of increase in the northern and southern hemispheres were 0.15 and 0.13 pptv per year respectively. The $CBrClF_2$ concentration data for these seven stations are listed in Table 3.6.2.1. The long-term trend of the $CBrClF_2$ concentration at Point Barrow, Cape Meares, Cape Kumukahi, Mauna Loa, Samoa, Cape Grim and South Pole are plotted in Figures 3.6.2.1, 3.6.2.2, 3.6.2.3, 3.6.2.4, 3.6.2.5, 3.6.2.6 and 3.6.2.7 respectively. If the increase of $CBrClF_2$ concentration continues at this rate (0.14 pptv per year), in twenty years its atmospheric burden will increase by a factor of about 2.5, to 4.5 pptv. This increase is not as significant to the Chlorofluorocarbon-Ozone depletion scheme of reactions as the increase expected for $CBrF_3$.

TABLE 3.6.2.1

Long term trend of $CBrClF_2$

Year	Annual mean $CBrClF_2$ concentration (pptv)						
	Point Barrow	Cape Meares	Cape Kumukahi	Mauna Loa	Samoa	Cape Grim	South Pole
1977	*	0.4	*	*	*	*	*
1978	*	0.6	*	*	*	*	*
1979	*	0.7	*	*	0.4	0.5	0.5
1980	*	0.9	*	*	0.5	0.5	0.6
1981	1.0	1.1	1.0	0.9	0.8	0.8	0.8
1982	1.1	1.2	1.1	1.0	0.9	0.9	0.9
1983	1.2	1.2	*	1.1	1.0	1.0	0.9
1984	1.4	1.4	1.4	1.3	1.2	1.1	1.1
1985	1.6	1.5	1.6	1.5	1.3	1.4	1.2
1986	1.7	1.7	1.6	1.6	1.5	1.5	1.5
1987	1.8	1.8	1.8	1.7	1.6	1.6	1.6

* No data available

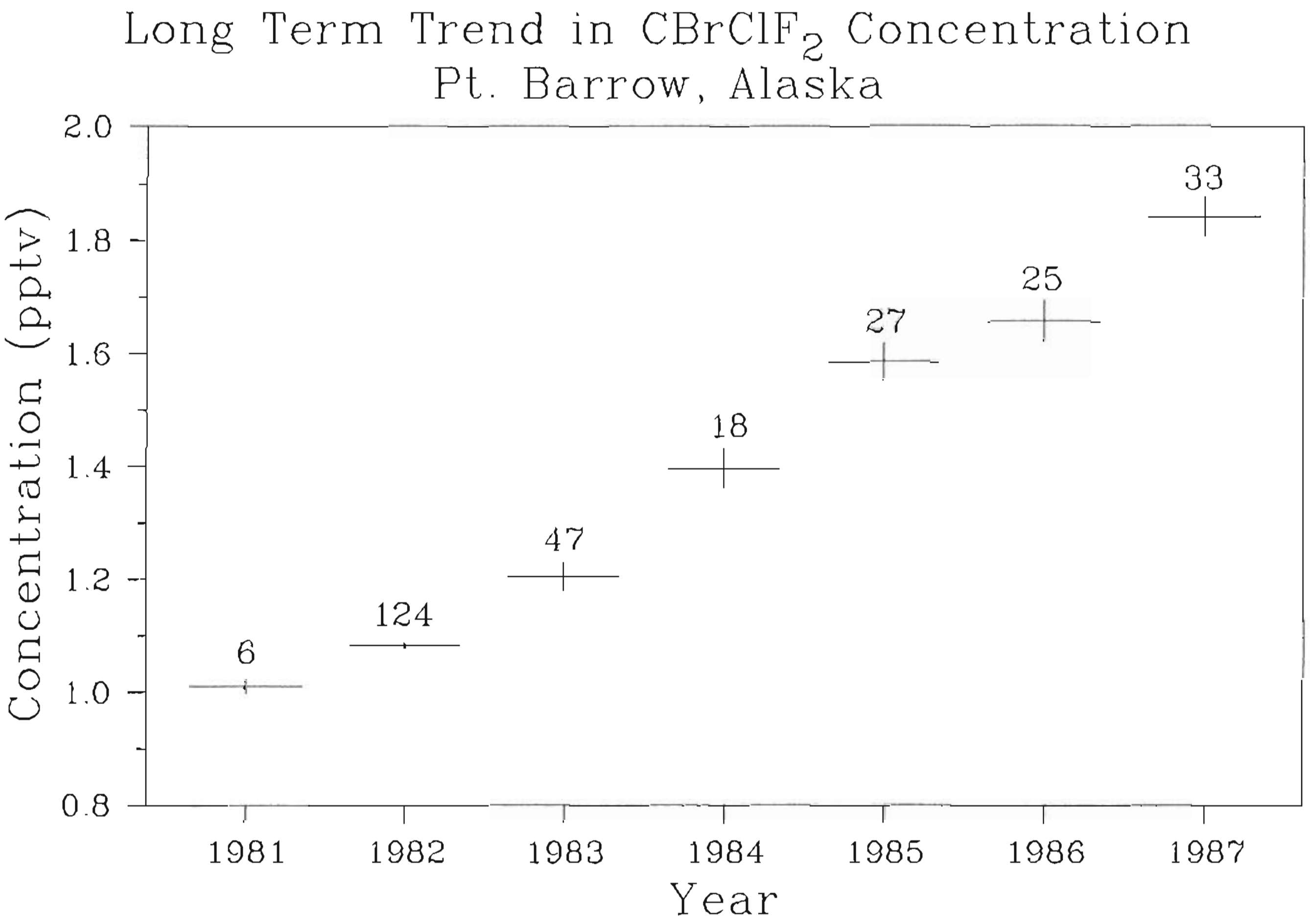

Figure 3.6.2.1 : Long term trend in $CBrClF_2$ concentration at Pt. Barrow, Alaska (Error bars are ±1 Standard error)

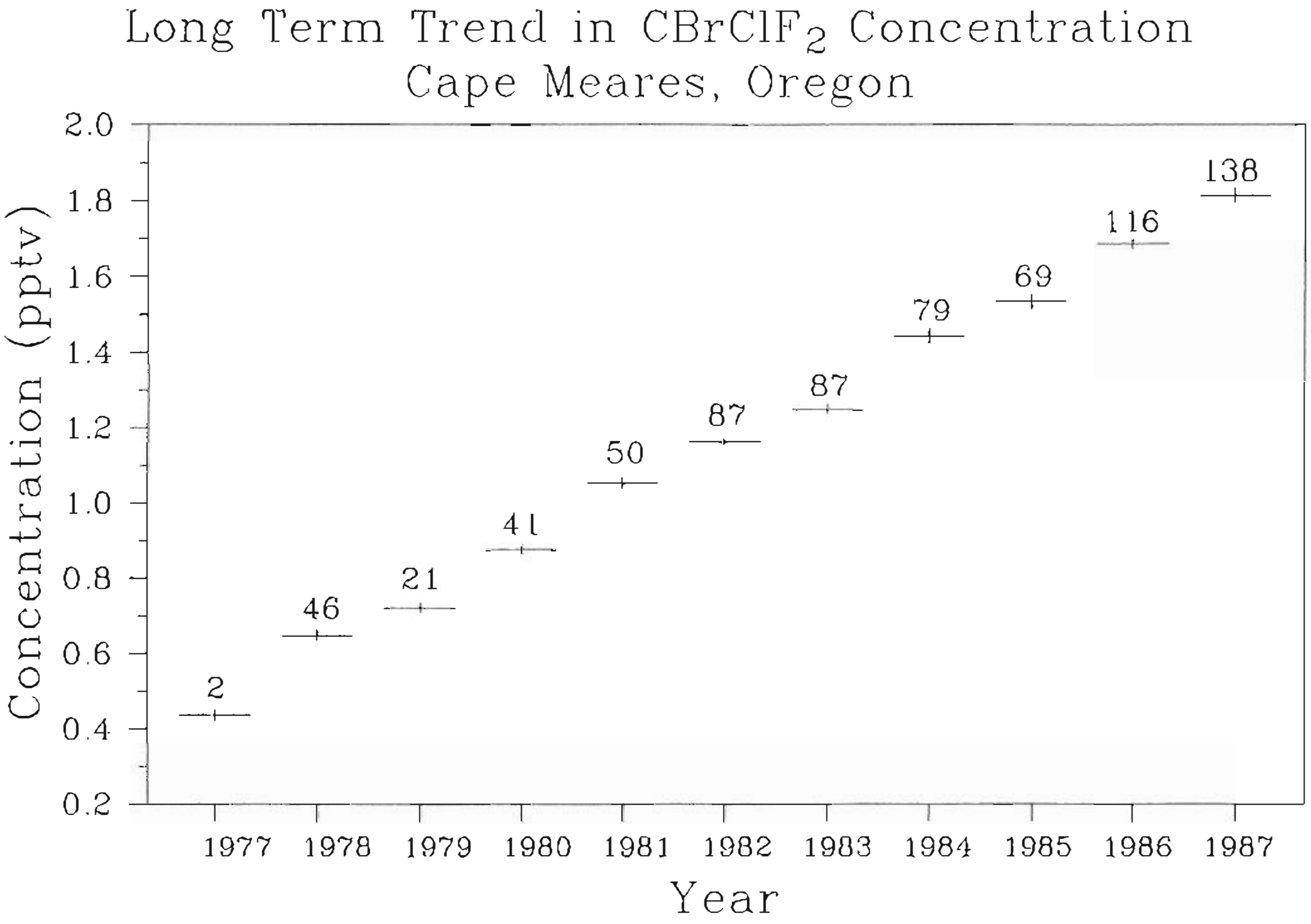

Figure 3.6.2.2 : Long term trend in $CBrClF_2$ concentration at Cape Meares, Oregon (Error bars are ±1 Standard error)

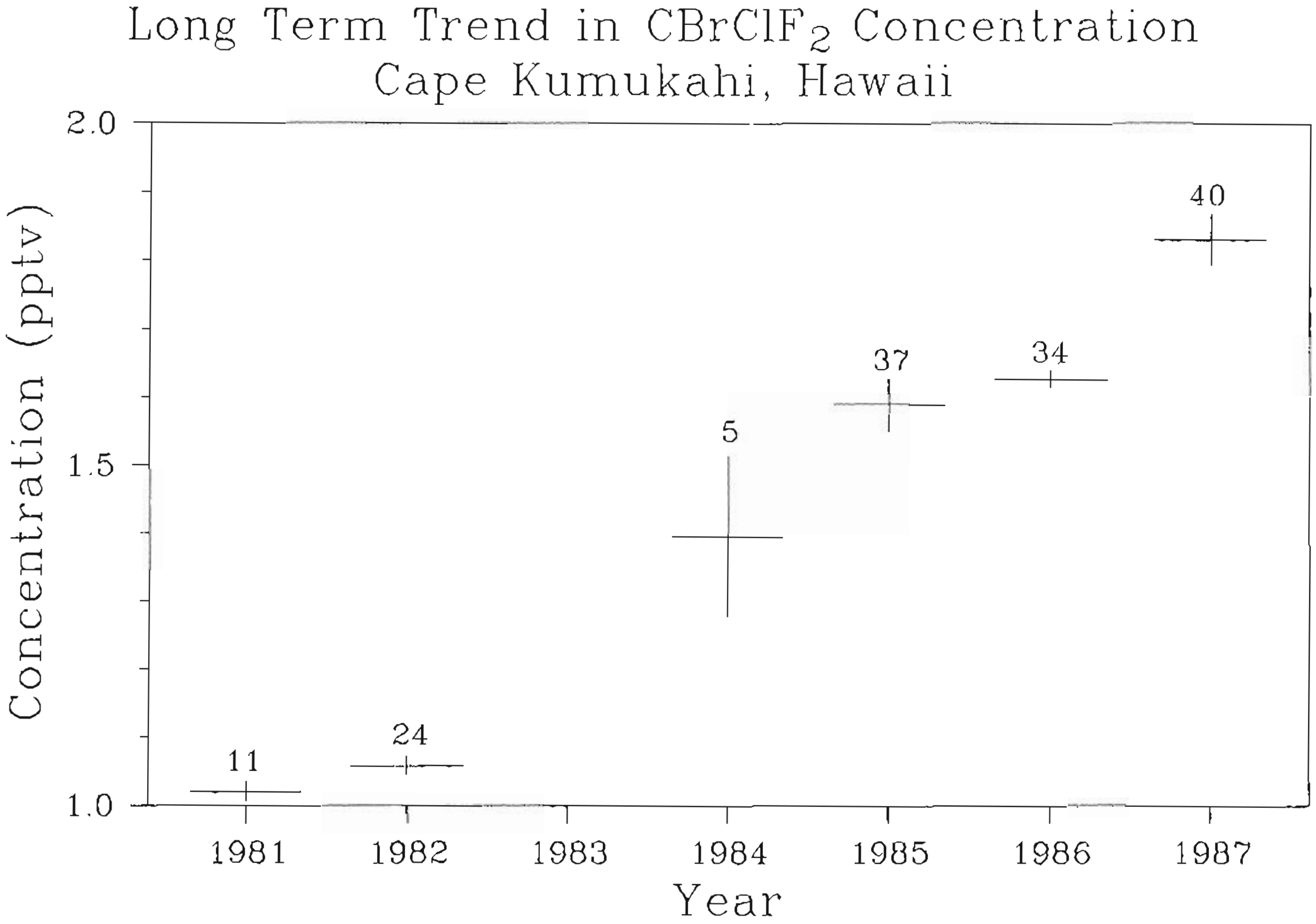

Figure 3.6.2.3 : Long term trend in $CBrClF_2$ concentration at Cape Kumukahi, Hawaii (Error bars are ±1 Standard error)

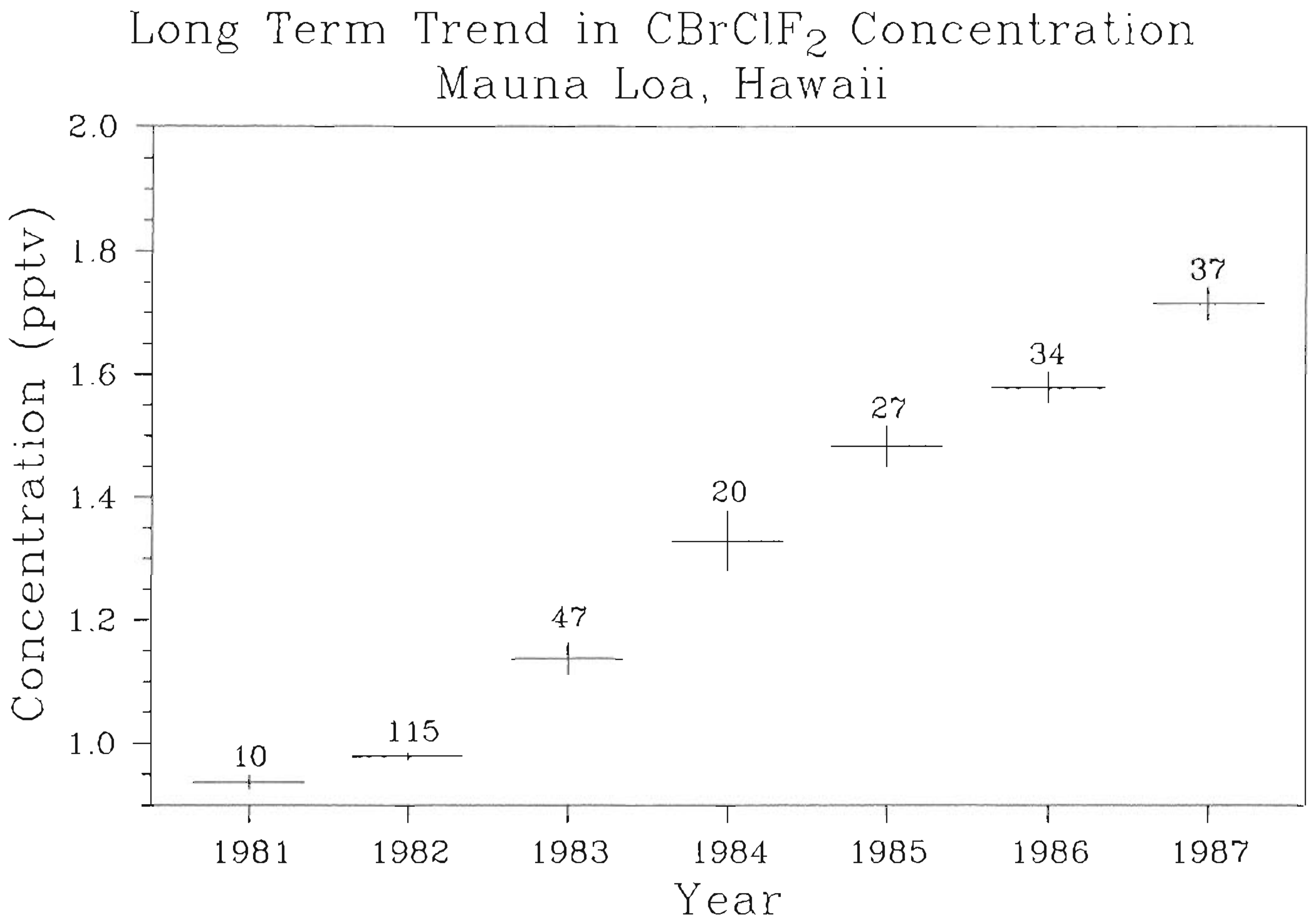

Figure 3.6.2.4 : Long term trend in $CBrClF_2$ concentration at Mauna Loa, Hawaii (Error bars are ±1 Standard error)

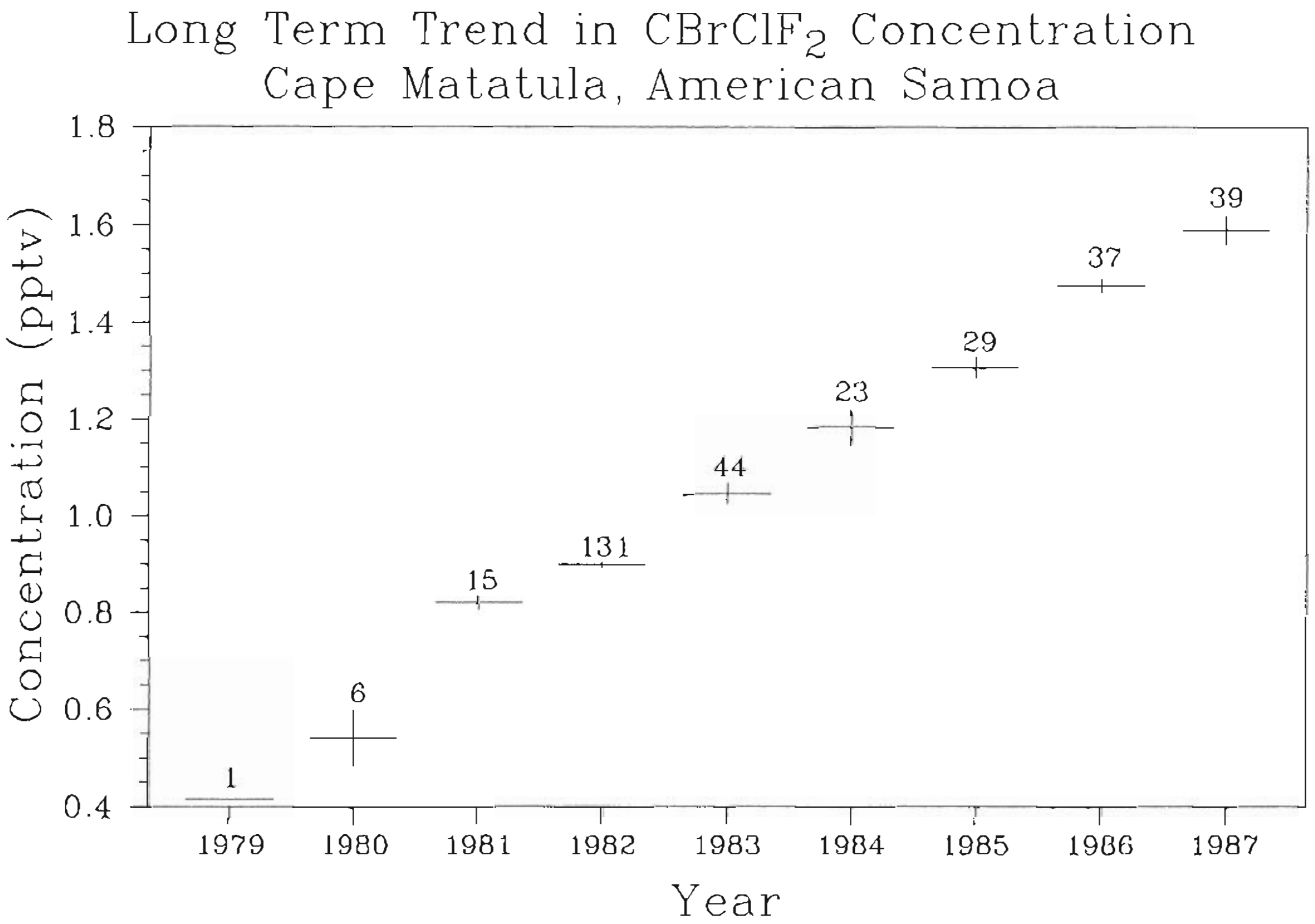

Figure 3.6.2.5 : Long term trend in $CBrClF_2$ concentration at Cape Matatula, Samoa
(Error bars are ±1 Standard error)

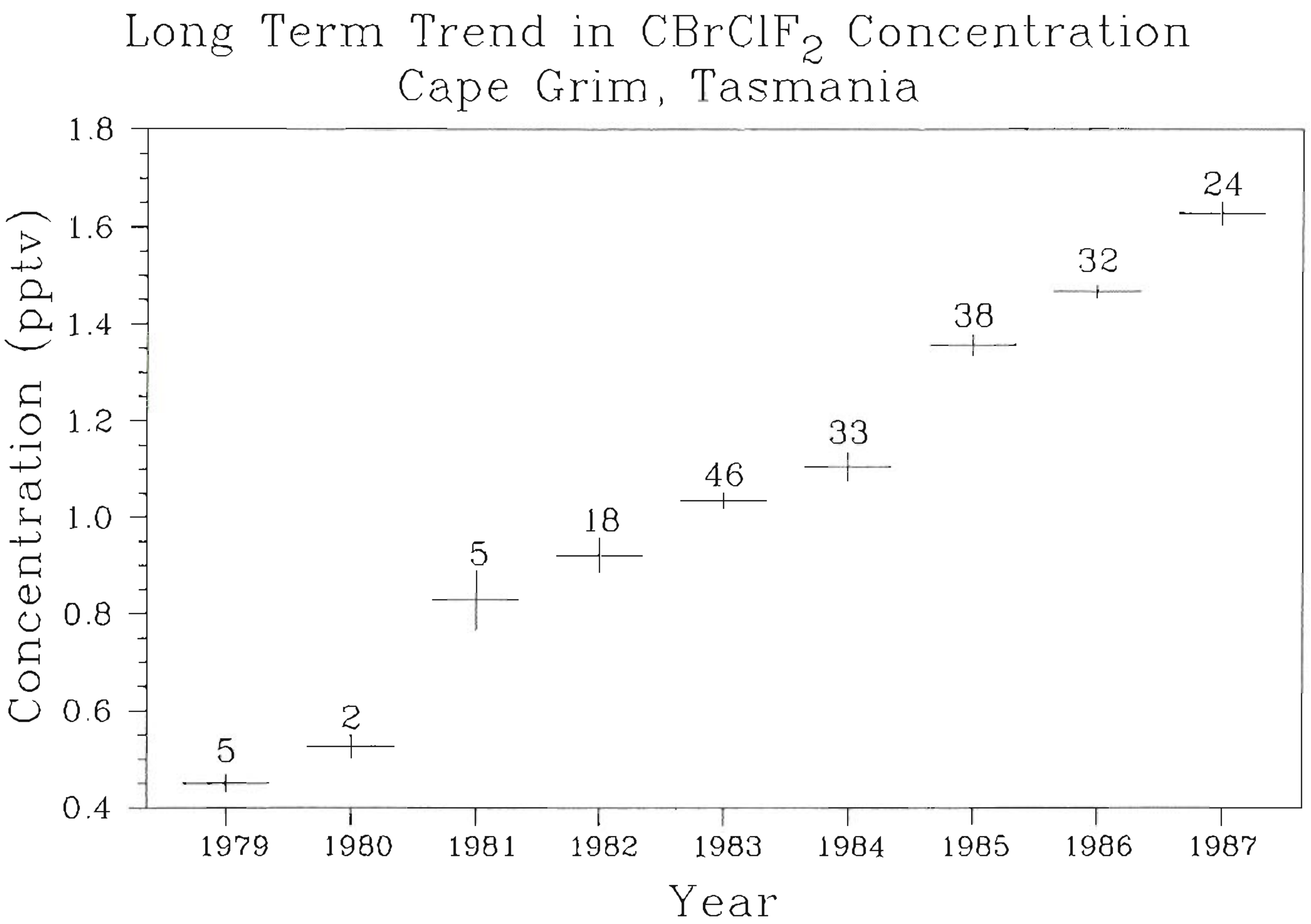

Figure 3.6.2.6 : Long term trend in $CBrClF_2$ concentration at Cape Grim, Tasmania (Error bars are ±1 Standard error)

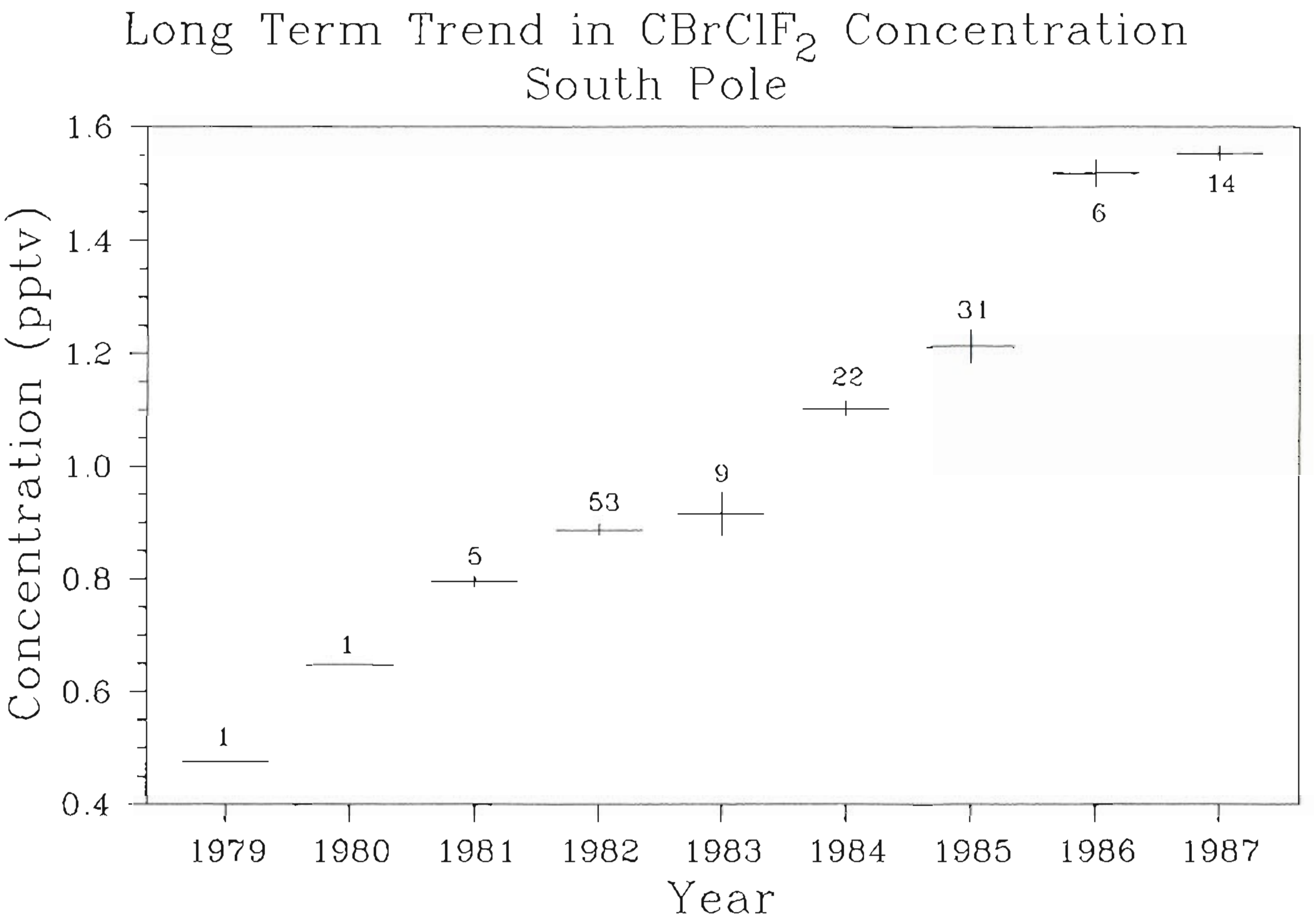

Figure 3.6.2.7 : Long term trend in $CBrClF_2$ concentration at the South Pole
(Error bars are ±1 Standard error)

4 MODELING

A 2-BOX model of the atmosphere was used to determine the atmospheric lifetimes of $CBrF_3$ and $CBrClF_2$ and annual emission rates. This model is applicable to long-lived trace gases. $CBrF_3$ and $CBrClF_2$ are believed to have long atmospheric lifetimes (>10 years) [Prather et al. 1984, Gammon et al. (1985) and Fabian et al. (1986)]. In this model, the relationships among concentrations, sources and the lifetime of a trace gas in the northern and southern hemispheres (NH and SH) are described by equations (1) and (2):

$$\frac{dC_N}{dt} = S_N - \frac{1}{\tau}C_N - \frac{1}{\tau_T}(C_N - C_S) \tag{1}$$

$$\frac{dC_S}{dt} = S_S - \frac{1}{\tau}C_S + \frac{1}{\tau_T}(C_N - C_S) \tag{2}$$

where C_N = concentration in the NH

C_S = concentration in the SH

S_N = source in the NH = $(1-\epsilon)S$

S_S = source in the SH = ϵS

$S = ae^{bt}$ = global source

ϵ = fraction of sources in the SH

τ = atmospheric life time of the trace gas (same in NH and SH)

τ_T = mean interhemispheric transport time

Equations (1) and (2) can be used to show that the interhemispheric gradient G is given by:

$$G = \frac{C_N - C_S}{C_S} = \left(b + \frac{1}{\tau}\right)\tau_T \tag{3}$$

The concentrations of $CBrF_3$ and $CBrClF_2$ at Cape Meares, Oregon (45°N), and Cape Grim, Tasmania (42°S) were taken as the representative values in the northern hemisphere and southern hemisphere, respectively.

A computer program of this atmospheric model developed by M.A.K. Khalil (personal communication) was used to calculate the lifetimes, interhemispheric gradients and sources of these two gases. The unique feature of this model is that one can calculate both the global emissions and the lifetime, given a time series of measured atmospheric concentrations. The best estimates for τ, G, a, b and ϵ for $CBrF_3$ and $CBrClF_2$ are given in Table 4.1. The $CBrClF_2$ data do not have sufficient information, just a linear increase. This limits the number of independent parameters available to estimate the sources and sinks by using M.A.K. Khalil's computer model. Therefore, the results given are preliminary. Other information, such as emission estimates, may be needed before the $CBrClF_2$ budget can be solidified. The interhemispheric transport time, τ_T, used was 1.2 years (M.A.K. Khalil - personal communication). The calculated lifetime of $CBrF_3$ is about 80 years and the lifetime of $CBrClF_2$ is between 16 and 20 years. The source parameters, a and b, were used to estimate the annual global emission rates of these two gases. In 1987, $CBrF_3$ emission rate was 1.8×10^{10} grams per year and for $CBrClF_2$ it was 1.3×10^{10} grams per year. The computer model also calculated the best fit $CBrF_3$ and $CBrClF_2$ concentrations for the northern and the southern hemispheres for each year from 1979 to 1987. The measured and modeled values for $CBrF_3$ and $CBrClF_2$ are given in Tables 4.2 and 4.3 respectively. Figures 4.1 and 4.2 show the close agreement between the measured and the modeled values for $CBrF_3$ and $CBrClF_2$, respectively.

TABLE 4.1

Parameters calculated with the 2 BOX model

	$CBrF_3$	$CBrClF_2$
Lifetime τ (years)	80	16 - 20
Gradient G	0.21	0.28
a (pptv)	0.17	0.30
b (per year)	0.20	0.06 - 0.07
Fraction of sources in SH, ϵ	0	0

TABLE 4.2

Measured and Modeled $CBrF_3$ concentrations in northern hemisphere (NH) and southern hemisphere (SH)

Year	NH Measured (pptv)	SH Measured (pptv)	NH Modeled (pptv)	SH Modeled (pptv)
1979	0.54	0.45	0.54	0.45
1980	0.63	0.51	0.64	0.53
1981	0.72	0.60	0.76	0.62
1982	0.90	0.72	0.90	0.74
1983	1.08	0.90	1.08	0.88
1984	1.26	1.08	1.30	1.05
1985	1.71	1.35	1.56	1.26
1986	1.89	1.44	1.89	1.52
1987	2.43	1.62	2.29	1.84

TABLE 4.3

Measured and Modeled $CBrClF_2$ concentrations in northern hemisphere (NH) and southern hemisphere (SH)

Year	NH Measured (pptv)	SH Measured (pptv)	NH Modelled (pptv)	SH Modelled (pptv)
1979	0.65	0.41	0.65	0.38
1980	0.78	0.48	0.74	0.55
1981	0.95	0.75	0.86	0.67
1982	1.04	0.83	0.99	0.79
1983	1.13	0.94	1.12	0.91
1984	1.30	1.00	1.26	1.03
1985	1.39	1.22	1.40	1.16
1986	1.51	1.32	1.54	1.29
1987	1.63	1.47	1.69	1.42

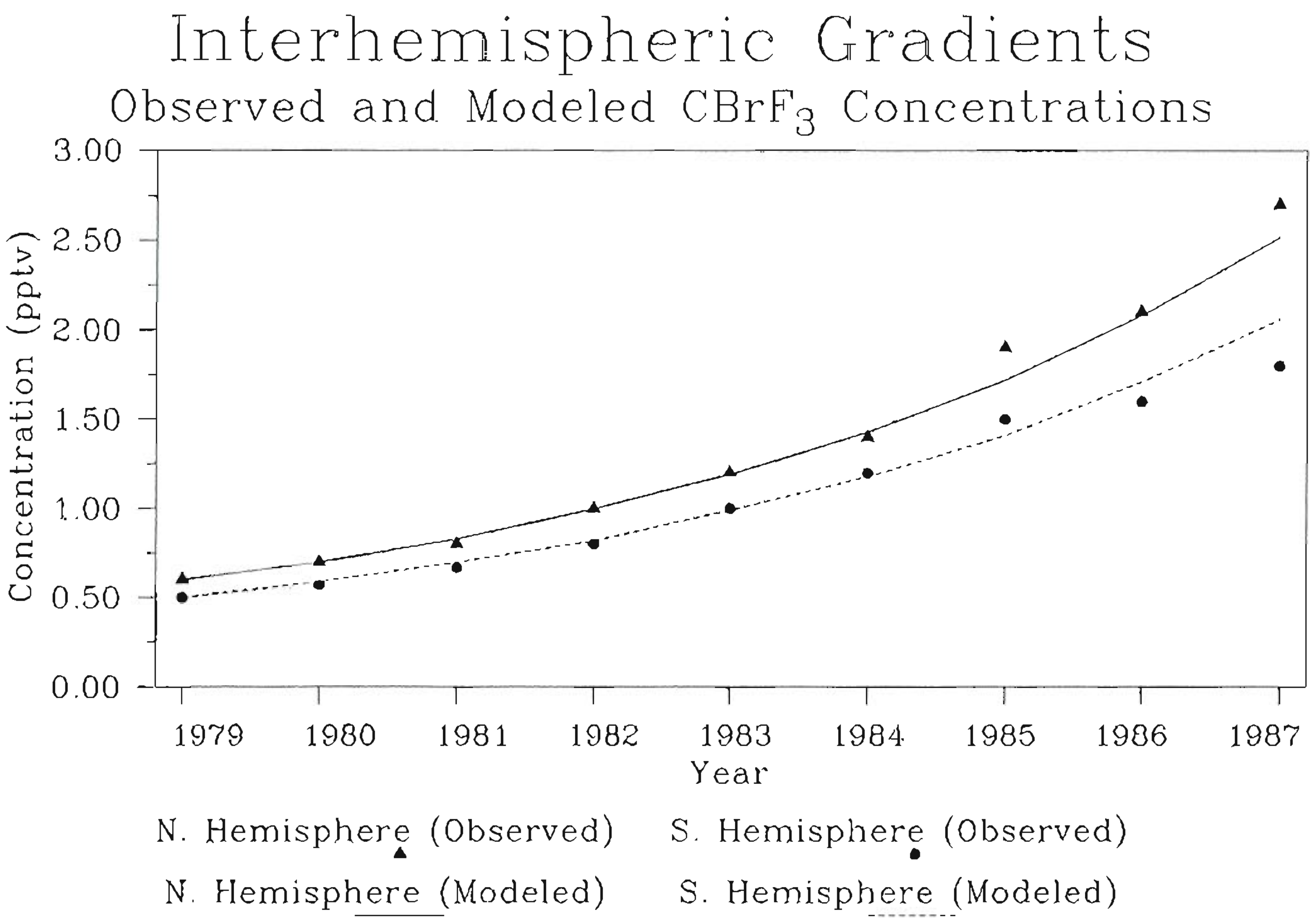

Figure 4.1 : Observed and modeled $CBrF_3$ concentrations in the northern and southern hemispheres

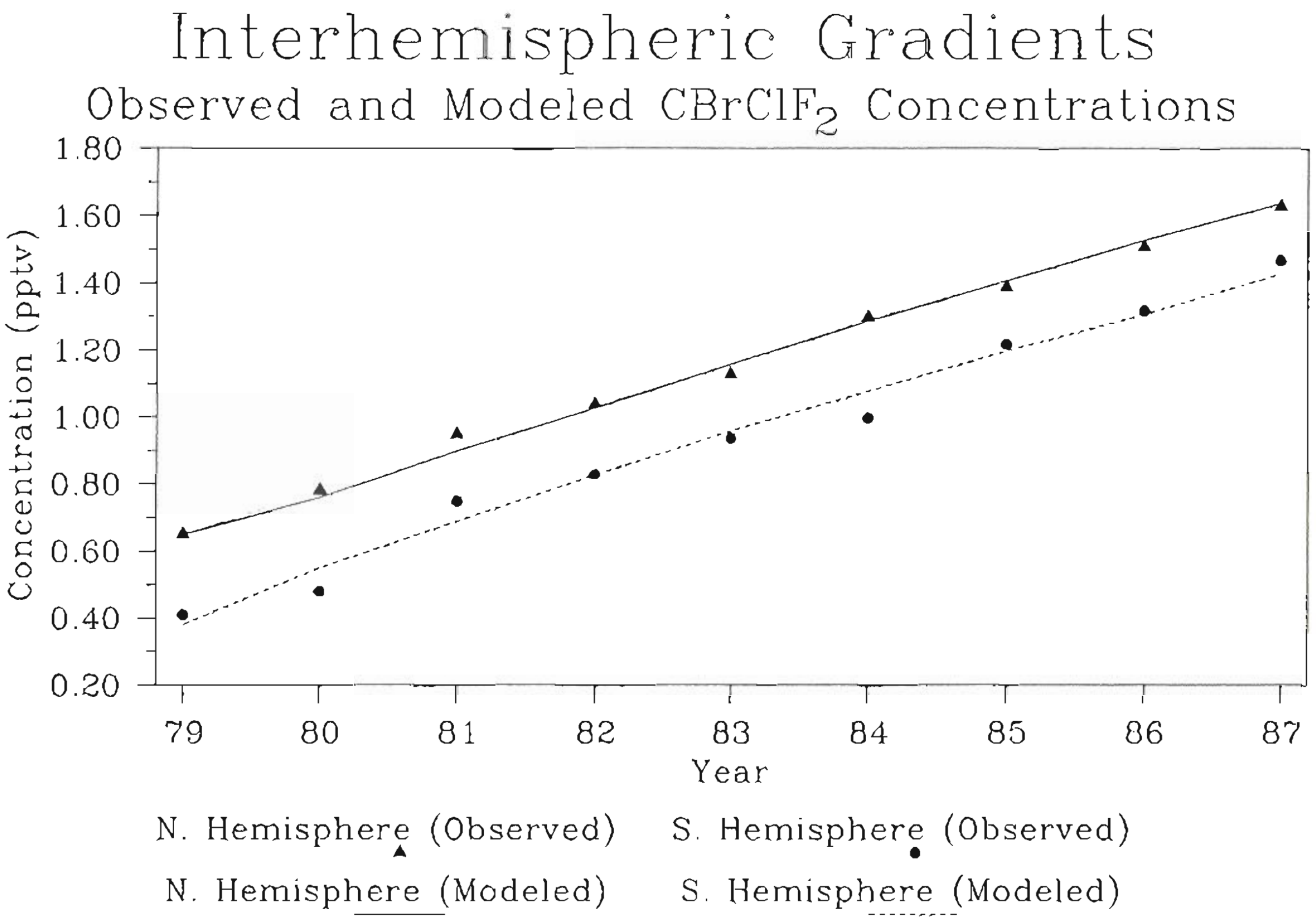

Figure 4.2 : Observed and modeled $CBrClF_2$ concentrations in the northern and southern hemispheres

5 CONCLUSIONS

Conclusion 1 : Developed a Method to Measure Atmospheric Organo-Bromine Compounds at the sub-pptv Level

The most important result of this study is that an EC-GC analytical system has been developed and proven that can precisely measure $CBrF_3$, $CBrClF_2$, CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$ in clean background air at the sub-pptv level.

A high resolution capillary column GC system with an O_2 doped electron capture detector was developed. This configuration is the fifth system developed for these atmospheric trace gas measurements. It is designated as EC-GC System V. It was developed from a packed column EC-GC method that had limited resolution of the peaks and lower sensitivity (System I). The development work involved testing and matching different types of columns, carrier gases, make-up gases to the detector and detector temperatures to obtain operating conditions with optimum resolution, very high sensitivity and sufficiently stable baselines to measure organo-bromine compounds at the trace pptv levels. All of the development work used the same Perkin-Elmer 3920 B instrument. In the process of developing EC-GC system V, nine organo-bromine compounds were identified in clean background air.

Linearity of Response and Minimum Detection Limit

The response of the EC-GC System V to the organo-bromine compounds in air was linear in the concentration ranges used in this study. The concentrations studied ranged from 0.3 to

3.0 pptv for $CBrClF_2$ and 1.0 to 50.0 pptv for $CHBr_3$. The minimum detection limit of each organo-bromine compound was lower by at least a factor of 2 than the observed atmospheric concentration.

Precision of Analysis and Reproducibility

The precision of analysis for all compounds with System V were within ±10%. The day-to-day reproducibility of these measurements were within ±10% for each organo-bromine compound. This precision was sufficient to determine the distribution and time course behavior of the species studied.

Organo-Bromine Compounds Were Stable in Sample Containers

The organo-bromine compounds at ambient concentrations were determined to be stable in 0.85 liter stainless steel low pressure (~30 psig) sample containers over a period of five weeks. The concentrations did not vary by more than ±5% in 5 weeks. These compounds were also stable in 34-liter stainless steel tanks at high pressures (100 to 400 psig) over periods of two to five years. All of the containers were internally electropolished and passivated. $CBrF_3$, $CBrClF_2$ and CH_2Br_2 were the most stable and the deviations from the initial analysis were within ±8%. CH_3Br, CH_2BrCl and $CHBr_3$ showed deviations that were within ±14% from the initial analysis. CH_3-CH_2Br and CH_2Br-CH_2Br showed deviations as high as ±28% from the initial analysis.

This Study Provides an Internally Consistent Data Set

All of the calibration tanks used in this study were cross calibrated against each other. The close agreement in repetitive analyses over two to five years (depending on organo-bromine gas) provided an internally consistent data set.

Conclusion 2 : Interhemispheric Gradients for Five Organo-Bromine Gases

The data from twelve stations, from 82°N to 90°S, were used to determine interhemispheric gradients of five organo-bromine compounds. From 1979 to 1987, the mean annual $CBrF_3$ concentration in the northern hemisphere was about 25% higher than in the southern hemisphere. During this time period, the mean annual $CBrClF_2$ concentration in the northern hemisphere was 0.14 pptv higher than in the southern hemisphere. The differences in the CH_3Br and CH_2BrCl concentrations between the northern and southern hemispheres were 3.1 pptv (38%), 0.60 pptv (57%) respectively. The CH_3-CH_2Br concentration in the northern hemisphere was 0.44 pptv (40%) higher than in the southern hemisphere from February through September. The CH_3-CH_2Br concentration in the northern hemisphere was 0.50 pptv (50%) lower than in the southern hemisphere from October through January. These differences were statistically significant (t-test, 95% level).

Conclusion 3 : Altitudinal Profile for Five Organo-Bromine Gases

The concentrations of $CBrClF_2$, CH_2Br_2, CH_2Br-CH_2Br and $CHBr_3$ were significantly higher (t-test, 95% level) at Cape Kumukahi (sea level) than at Mauna Loa (11,000 feet). For example, the mean $CHBr_3$ at Cape Kumukahi and Mauna Loa were 6.6 and 2.2 pptv respectively The CH_3Br concentration at Mauna Loa (10.7 pptv) was significantly higher (t-test, 95% level) than at Cape Kumukahi (9.7 pptv). This altitudinal profile for CH_3Br was unexpected and I have no explanation for it. Between these two stations, no significant difference was observed in the $CBrF_3$ concentration (t-test, 95% level).

Conclusion 4 : Some Organo-Bromine Gases Follow Seasonal Cycles

Seasonal cycles were observed for CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$ at several sampling stations. These results are based on five years of data. The differences between the maxima and minima in these seasonal cycles were statistically significant (t-test, 95% level). The amplitude of these seasonal cycles and the time of year they occurred varied from station to station and from species to species.

Conclusion 5 : Increasing Trends for Some Organo-Bromine Gases

Increasing trends in the atmospheric concentration were observed for two anthropogenic organo-bromine compounds, $CBrF_3$ and $CBrClF_2$. Model calculations indicated that their sources are increasing exponentially.

Nine years of data, a total of 956 measurements, indicated that the northern hemispheric concentration of $CBrF_3$ is increasing at 21% per year and in the southern hemisphere its concentration is increasing at 18% per year.

From nine years of data, a total of 2109 measurements, the atmospheric concentration of $CBrClF_2$ is observed to be increasing linearly at a rate of 0.14 pptv per year.

Conclusion 6 : Atmospheric Lifetimes of Two Organo-Bromine Gases Determined

The atmospheric life times of $CBrF_3$ and $CBrClF_2$ were determined using model calculations. They are about 80 and 20 years respectively.

6 DISCUSSION

Analytical Method

A variety of analytical methods have been used by different investigators to measure atmospheric bromine. With one of these methods, total bromine (particulate, gaseous inorganic and gaseous organic) was measured. With other methods, particulate, gaseous inorganic and gaseous organic bromine were measured separately. These methods used different types of filters to trap the bromine, followed by neutron activation analysis (NAA). It was not possible to determine the concentrations of the different bromine species with these filter-NAA methods. A discrete organo-bromine species was first measured using an electron capture gas chromatographic (EC-GC) method [Lovelock (1975)]. Since then several investigators have measured different organo-bromine gases in the atmosphere using EC-GC and gas chromatographic mass spectrometric (GC-MS) techniques. These methods had limited sensitivities and could measure only a few organo-bromine gases. Some investigators used large sample volumes (up to 20 liters) to improve on the sensitivity and had to compromise on the precision. A routine analytical method to measure these organo-bromine gases was not available.

In this work five EC-GC systems were developed and improved upon. The final method, System V, had sufficient sensitivity and precision to measure $CBrF_3$, $CBrClF_2$ (the Halons) and seven other organo-bromine gases, CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$, in clean background air samples at the low pptv (parts per trillion by volume) level. This EC-GC method used a bonded capillary column for improved resolution of the chromatographic peaks and an O_2 doped detector for increased sensitivity.

Internal consistency in the cross-calibration method made it possible to use the data from each of the systems to determine the latitudinal distribution, altitudinal profile, seasonal variations and long term trends of these organo-bromine gases.

Comparison of observations: Organo-bromine gases vs. other organo-halogen gases

Interhemispheric gradients

Concentrations of the two Halons, $CBrF_3$ and $CBrClF_2$, were 21% and 20% higher (t-test, 95% level) in the northern hemisphere than in the southern hemisphere in 1985. The respective northern hemispheric concentrations were 1.9 and 1.6 pptv. For CCl_3F (F-11) and CCl_2F_2 (F-12), the northern hemispheric concentrations in 1985 were 9% and 8% higher than in the southern hemisphere. The concentrations of F-11 and F-12 were about two orders of magnitude higher than for the Halons (the respective northern hemispheric concentrations were 223 and 384 pptv), [Rasmussen and Khalil (1986)]. The sources for these gases are believed to be in the northern hemisphere. The larger interhemispheric gradients observed for the Halons (as compared to F-11 and F-12) may indicate higher release rates in the northern hemisphere, short lifetimes for the Halons or both. The CH_3Br concentration in the northern hemisphere was 38% higher (t-test, 95% level) than in the southern hemisphere with a mean northern hemispheric concentration of 11.0 pptv. This observed gradient and a lifetime of only 1.4 years [Khalil and Rasmussen (1984)] may indicate natural as well as anthropogenic sources for CH_3Br.

Altitudinal profiles

$CBrF_3$ concentrations at Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.) did not show any significant differences. The 1987 concentration at these two locations was 2.5 pptv. This may be due to the stability of $CBrF_3$ in the atmosphere. During this study, the lifetime of $CBrF_3$ was determined to be 76 years. F-11 and F-12 concentrations at Cape Kumukahi were significantly higher (t-test, 95% level) than at Mauna Loa [Rasmussen and Khalil (1981)]. The differences in concentration were 2% and 1% respectively with the mean concentrations at Cape Kumukahi being 193 and 326 pptv. In 1987 the $CBrClF_2$ concentration at Cape Kumukahi was 6% higher (t-test, 95% level) than at Mauna Loa. The $CBrClF_2$ concentration at Cape Kumukahi was 1.8 pptv. The $CHClF_2$ (F-22) concentration in 1981 at Cape Kumukahi (64 pptv) was 5% higher (t-test, 95% level) than at Mauna Loa [Rasmussen and Khalil (1981)]. During this study, the lifetime of $CBrClF_2$ was determined to be about 20 years. F-22, with a lifetime of about 20 years (M.A.K. Khalil, personal communication), has a altitudinal profile similar to that of $CBrClF_2$.

The CH_2Br_2 concentration was a factor of 2.5 higher and $CHBr_3$ concentration was a factor of 3 higher at Cape Kumukahi than at Mauna Loa (t-test, 95% level). The respective concentrations at Cape Kumukahi were 7.4 and 6.6 pptv. The decrease in the concentrations of CH_2Br_2 and $CHBr_3$ were lower than for CH_3I, which was a factor of 3.7 higher at Cape Kumukahi than at Mauna Loa (t-test, 95% level) [Gunawardena (1985)]. The atmospheric lifetime of CH_3I is about 5 days. Therefore, the CH_2Br_2 and $CHBr_3$ should have longer atmospheric lifetimes.

The CH_3Br concentrations at Mauna Loa (10.7 pptv) was significantly higher (t-test, 95% level) than at Cape Kumukahi (9.7 pptv). This was an unexpected result. A possible explanation is a local source of volcanic origin. A similar observation has been made for CH_3Cl (R.A. Rasmussen, personal communication).

Seasonal Cycles

Seasonal cycles were not observed for $CBrF_3$ and $CBrClF_2$. The other seven organo-bromine gases measured with System V showed seasonal variations. The seasonal variations were unique for each species at each station. The seasonal variations of the sources and sinks for these organo-bromine gases need to be studied in great detail to understand the observed seasonal variations in the concentrations.

Long-term trends

An exponential increase in the concentration was observed for $CBrF_3$. In 1987, its concentration was increasing at a rate of 22% per in the northern hemisphere and 18% per year in the southern hemisphere. The northern and southern hemispheric concentrations of $CBrF_3$ in 1987 were 2.5 and 1.9 pptv respectively. $CBrClF_2$ was increasing in the atmosphere linearly. In 1987, the rate of increase in the northern hemisphere was 9% and in the southern hemisphere it was 8%. The northern and southern hemispheric concentrations of $CBrClF_2$ in 1987 were 1.8 and 1.6 pptv respectively. In 1985 the northern and southern hemispheric concentrations of F-11 and F-12 were increasing at about 5% per year in each hemisphere but their concentrations were about two orders of magnitude higher than for the Halons. The northern hemispheric concentrations for F-11 and F-12 were 223 and 384 pptv in 1985 and for the southern hemisphere the values were 205 and 354 pptv respectively [Rasmussen and Khalil (1986)]. It is apparent that the concentrations of Halons are increasing in the atmosphere at a faster rate than the other chlorofluorocarbons.

Significance of observed concentrations of organo-bromine gases

At current levels, the seven non-Halon organo-bromine gases appear to have no significant impact on the stratospheric ozone depletion. As no long-term trends were observed for these seven gases, the long-term impact also seem to be not significant. As far as the Halons are concerned, at 1987 concentrations, stratospheric ozone could be depressed by less than 0.3% [Prather (1984)]. If current rate of increase continues for $CBrF_3$ (about 21% per year), the northern hemispheric concentration could increase to about 100 pptv in 20 years. This may lead to a 4% loss in the column density of ozone. $CBrClF_2$ increasing at 0.14 pptv per year may not have such an impact on the stratospheric burden of bromine.

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APPENDIX A

Measurements of Atmospheric Bromine Using Filters and Neutron Activation Analysis

Bromine in the gaseous form has been observed in the marine atmosphere before the first measurements of organo-bromine gases in the atmosphere were made [Moyers and Duce (1972)]. Their measurements were made in the Hawaiian marine atmosphere and did not indicate what specific bromine species were measured.

Several other observers have measured atmospheric bromine as total bromine, particulate bromine, total gaseous bromine, total gaseous inorganic bromine or total gaseous organic bromine [Duce et al. (1973), Rahn et al. (1976), Berg et al. (1980), Rancher and Kritz (1980) and Berg et al. (1983)]. These observers used filters followed by neutron activation analysis (NAA) to estimate the bromine concentrations. The particulate matter was trapped on Nuclepore ^{R} membrane filters. The total inorganic gaseous bromine gases were trapped on cellulose filters that had been impregnated with a LiOH solution after particulate matter had been removed. The total organic gaseous bromine was trapped on activated charcoal after particulate matter and inorganic bromine had been removed. The collected bromine gases were then subjected to NAA to estimate the total bromine concentration in each category (particulate, gaseous inorganic and gaseous organic). But it was not possible to measure the concentration of individual bromine gases (organically bound or inorganic) using filters and NAA.

APPENDIX B

Latitudinal Distribution of Organo-Bromine Gases

Air samples collected weekly between 1983 and 1987 were analyzed for CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$. The data from Point Barrow, Cape Meares and Cape Kumukahi were used to determine the northern hemispheric concentrations of these organo-bromine gases, and data from Samoa and Cape Grim were used to estimate the southern hemispheric values. Organo-bromine data from Korolev Cruise II (1987) were used to support the results observed from weekly samples. Statistically significant differences in the concentrations of CH_3Br, CH_3-CH_2Br and CH_2BrCl were observed between the northern and southern hemispheres (t-test, 95% level). But no such differences were observed for CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$.

CH_3Br Bromomethane (Methyl Bromide)

Samples collected at Point Barrow, Cape Meares, Cape Kumukahi, Samoa and Cape Grim were analyzed for CH_3Br using Systems II - V. The results, summarized in table B.1, indicated significantly higher CH_3Br concentration each month in the northern hemisphere than in the southern hemisphere (t-test, 95% level). In figure B.1, the data were plotted as the mean monthly CH_3Br concentration in each hemisphere over twelve months. The mean northern hemispheric CH_3Br concentration (11.0 pptv) was 38% higher than in the southern hemisphere (8.0 pptv).

CH_3-CH_2Br Bromoethane (Ethyl Bromide)

Samples collected at Point Barrow, Cape Meares, Cape Kumukahi, Samoa and Cape Grim were analyzed for CH_3-CH_2Br using System V. The results are summarized in table B.2. From February through September, the monthly CH_3-CH_2Br concentrations were significantly higher in the northern hemisphere than in the southern hemisphere (t-test, 95% level). The mean northern hemispheric concentration (1.6 pptv) was 40% higher than the southern hemispheric value (1.1 pptv) during these months. From October through January, the monthly mean southern hemispheric concentrations were significantly higher than the northern hemispheric values. The mean northern hemispheric concentration (1.5 pptv) was 50% higher than the southern hemispheric value (1.0 pptv) during these months. In figure B.2, the data were plotted as the mean monthly CH_3-CH_2Br concentration in each hemisphere over twelve months.

CH_2BrCl Bromochloromethane

Samples collected at Point Barrow, Cape Meares, Cape Kumukahi, Samoa and Cape Grim were analyzed for CH_2BrCl using Systems III - V. The results, summarized in table B.3 indicated significantly higher CH_2BrCl concentration each month in the northern hemisphere than in the southern hemisphere (t-test, 95% level). In figure B.3, the data were plotted as the mean monthly CH_2BrCl concentration in each hemisphere over twelve months. The mean northern hemispheric CH_2BrCl concentration (1.57 pptv) was 57% higher than in the southern hemisphere (1.00 pptv).

TABLE B.1

Monthly average CH_3Br concentration in the Northern Hemisphere and Southern Hemisphere

Month	Northern Hemisphere			Southern Hemisphere		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	10.4	2.0	106	7.9	1.2	25
2	10.4	1.6	100	7.8	1.2	34
3	10.5	1.9	105	8.4	1.3	20
4	11.0	2.4	135	8.0	1.4	26
5	11.7	2.5	116	8.1	0.8	24
6	11.3	2.7	100	8.2	1.2	27
7	10.6	2.8	109	7.9	1.1	26
8	11.3	2.8	103	7.8	1.5	30
9	11.2	3.0	105	8.2	1.8	31
10	11.4	3.1	114	7.2	1.3	23
11	10.2	2.0	113	7.8	1.4	29
12	10.9	2.0	116	8.0	1.5	31

TABLE B.2

Monthly average CH_3-CH_2Br concentration in the Northern Hemisphere and Southern Hemisphere

Month	Northern Hemisphere			Southern Hemisphere		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	0.9	0.6	87	1.9	0.8	16
2	1.0	0.5	73	0.9	0.7	14
3	1.3	0.8	83	1.2	0.9	9
4	1.5	0.9	104	1.3	0.6	15
5	1.9	1.0	97	1.3	0.8	10
6	1.7	1.0	81	1.4	0.4	8
7	1.8	1.1	86	0.9	0.5	13
8	1.6	1.0	83	0.8	0.7	8
9	1.5	1.0	88	1.3	0.6	15
10	1.2	0.6	96	1.3	0.6	12
11	1.0	0.4	87	1.2	0.6	15
12	0.8	0.5	94	1.6	0.8	12

TABLE B.3

Monthly average CH_2BrCl concentration in the Northern Hemisphere and Southern Hemisphere

Month	Northern Hemisphere			Southern Hemisphere		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	1.8	1.0	66	0.9	0.2	14
2	1.7	0.6	64	0.9	0.2	21
3	1.8	0.6	75	1.1	0.6	15
4	1.8	0.9	97	1.0	0.3	19
5	1.5	0.6	73	1.1	0.3	13
6	1.6	0.6	48	1.2	0.3	19
7	1.5	0.6	80	1.0	0.4	16
8	1.4	0.6	78	1.0	0.3	14
9	1.5	0.6	71	0.9	0.5	17
10	1.4	0.6	76	1.1	0.7	16
11	1.7	1.0	81	1.2	0.7	21
12	1.9	0.8	84	0.9	0.4	20

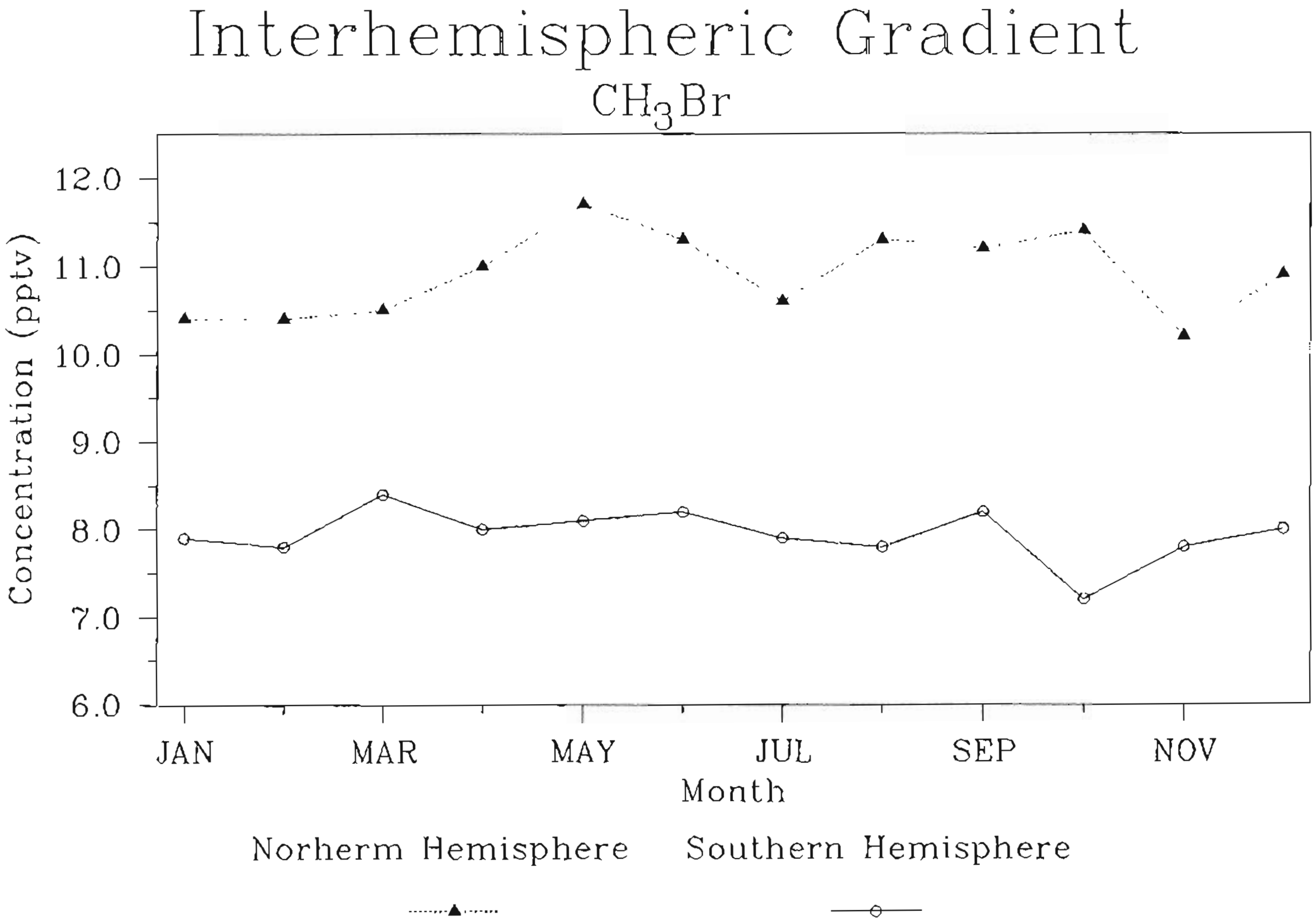


Figure B.1 : Monthly mean CH_3Br concentrations in the northern and southern hemispheres

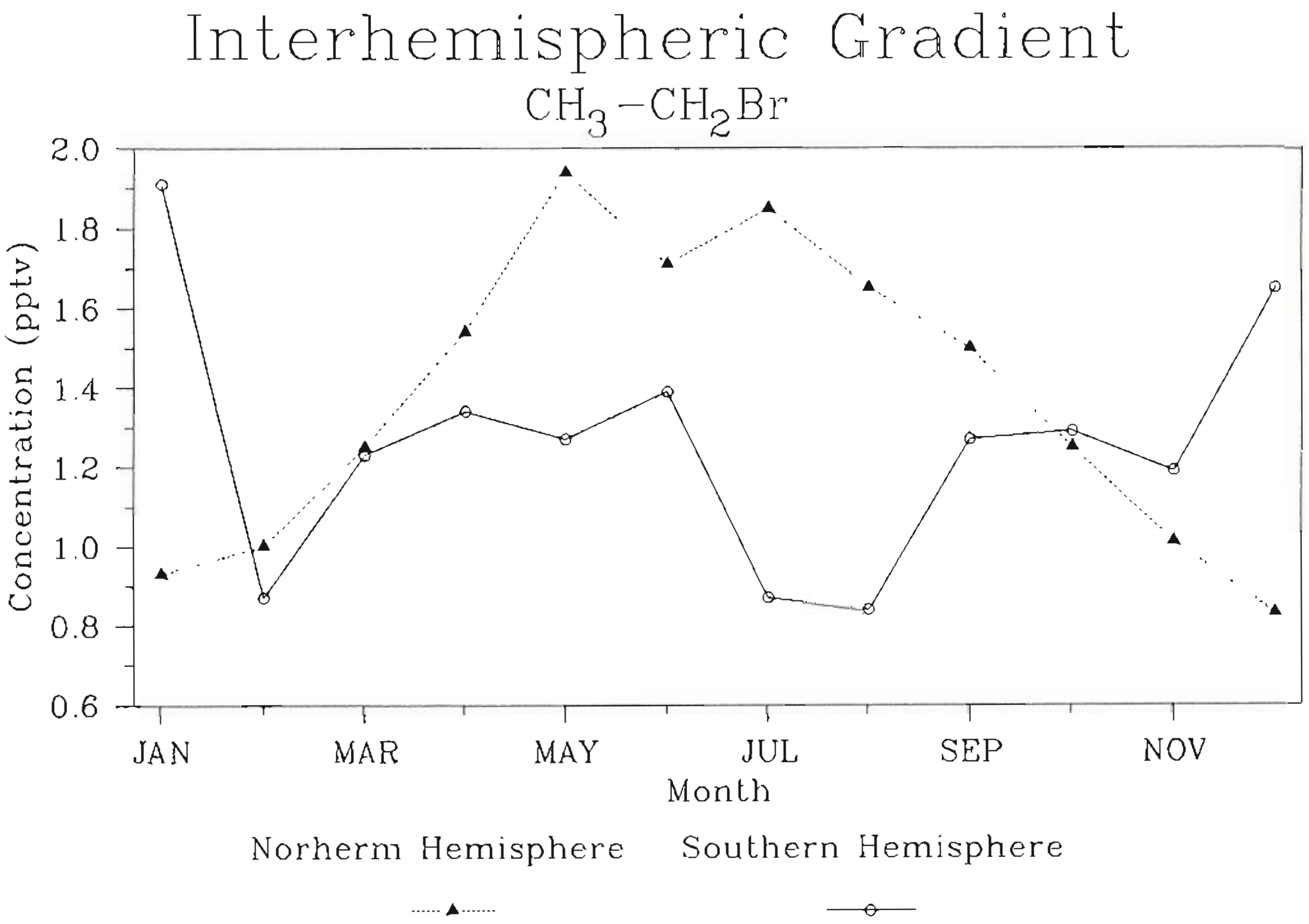


Figure B.2 : Monthly mean CH_3-CH_2Br concentrations in the northern and southern hemispheres

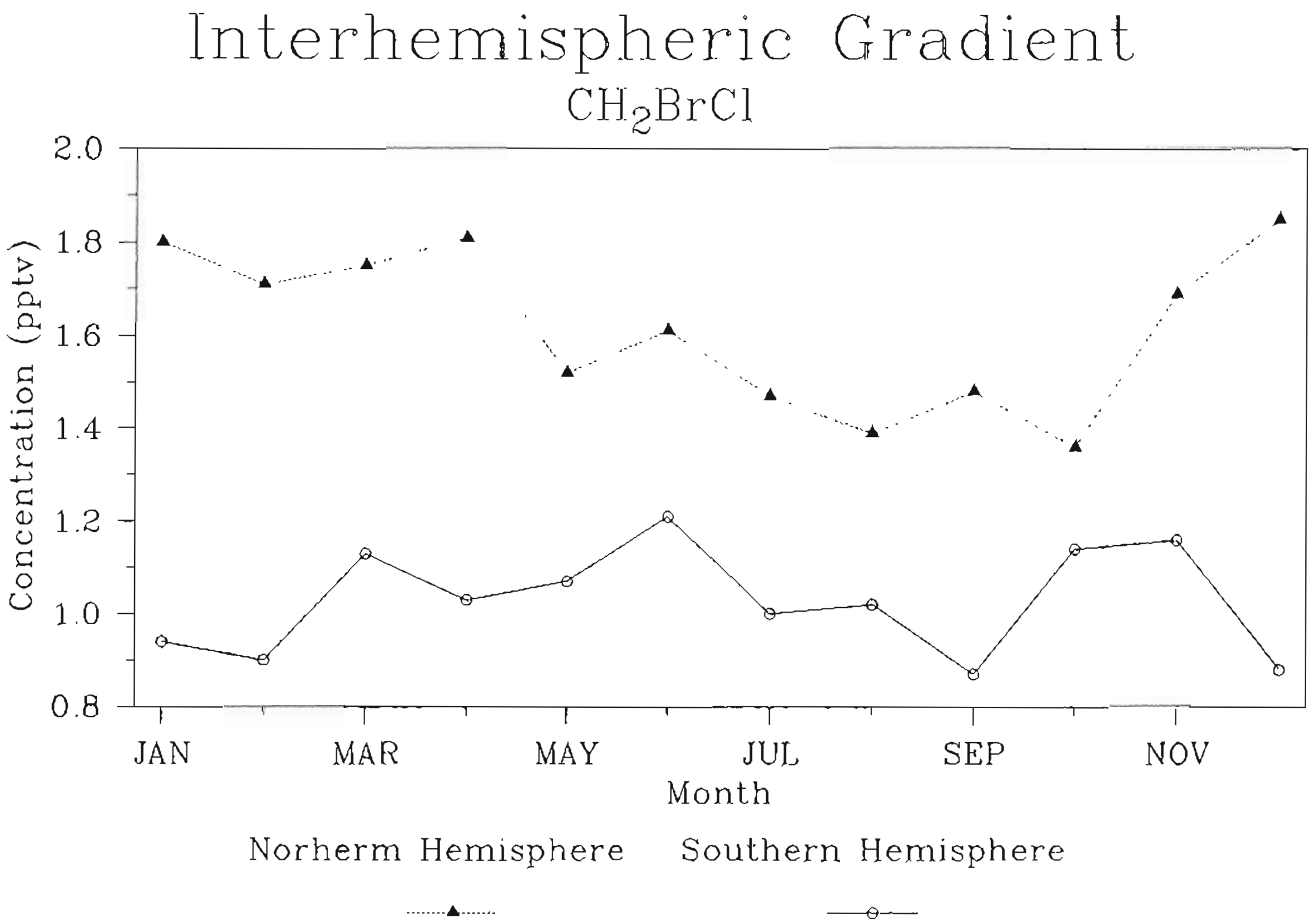


Figure B.3 : Monthly mean CH_2BrCl concentrations in the northern and southern hemispheres

CH_3Br - in Korolev Cruise II Samples

Samples collected during Korolev Cruise II (1987) were analyzed using System V. These data indicated significantly higher mean CH_3Br concentration (t-test, 95% level) in the northern hemisphere (13.3±3.3 pptv) than in the southern hemisphere (8.7±1.5 pptv). These results were comparable to the values from the ground-based weekly data for the northern hemisphere (11.0±3.0 pptv) and the southern hemisphere (8.0±1.5 pptv). See table B.4 for a comparison of CH_3Br concentrations between the northern and southern hemispheres from Korolev Cruise II samples. Figure B.4 shows that the CH_3Br concentrations observed during Korolev Cruise II. The CH_3Br concentration at 5°N was comparable to the southern hemispheric concentrations.

CH_2BrCl - in Korolev Cruise II Samples

The CH_2BrCl data from Korolev Cruise II (1987) showed significantly higher (t-test, 95% level) mean concentrations in the northern hemisphere (2.2±1.4 pptv) than in the southern hemisphere (1.3±0.7 ptv). The northern hemispheric CH_2BrCl concentration was 69% higher than in the southern hemisphere. The weekly data showed a difference of 57%. The CH_2BrCl data from Korolev Cruise II are plotted in figure B.5. This figure and Table B.5 show the latitudinal distribution of the CH_2BrCl. As in the case of CH_3Br, the CH_2BrCl concentration at 5°N was comparable to the southern hemispheric values.

TABLE B.4

CH_3Br concentrations observed during Korolev Cruise II

Latitude (°N)	Mean (pptv)	std.dev. (pptv)	N
45	14.7	2.4	23
35	15.3	2.6	7
25	14.9	2.5	2
15	14.2	0.7	2
5	8.9	0.8	12
-5	10.5	1.7	9
-15	8.4	0.9	7
-25	9.2	1.1	6
-35	7.8	0.7	18

TABLE B.5

CH_2BrCl concentrations observed during Korolev Cruise II

Latitude (°N)	Mean (pptv)	std.dev. (pptv)	N
45	2.7	1.4	24
35	2.1	1.7	8
25	2.0	0.9	3
15	3.3	0.6	2
5	1.0	0.5	12
-5	1.3	0.5	8
-15	1.5	0.8	8
-25	1.2	0.3	4
-35	1.1	0.7	18
-45	1.7	0.5	3

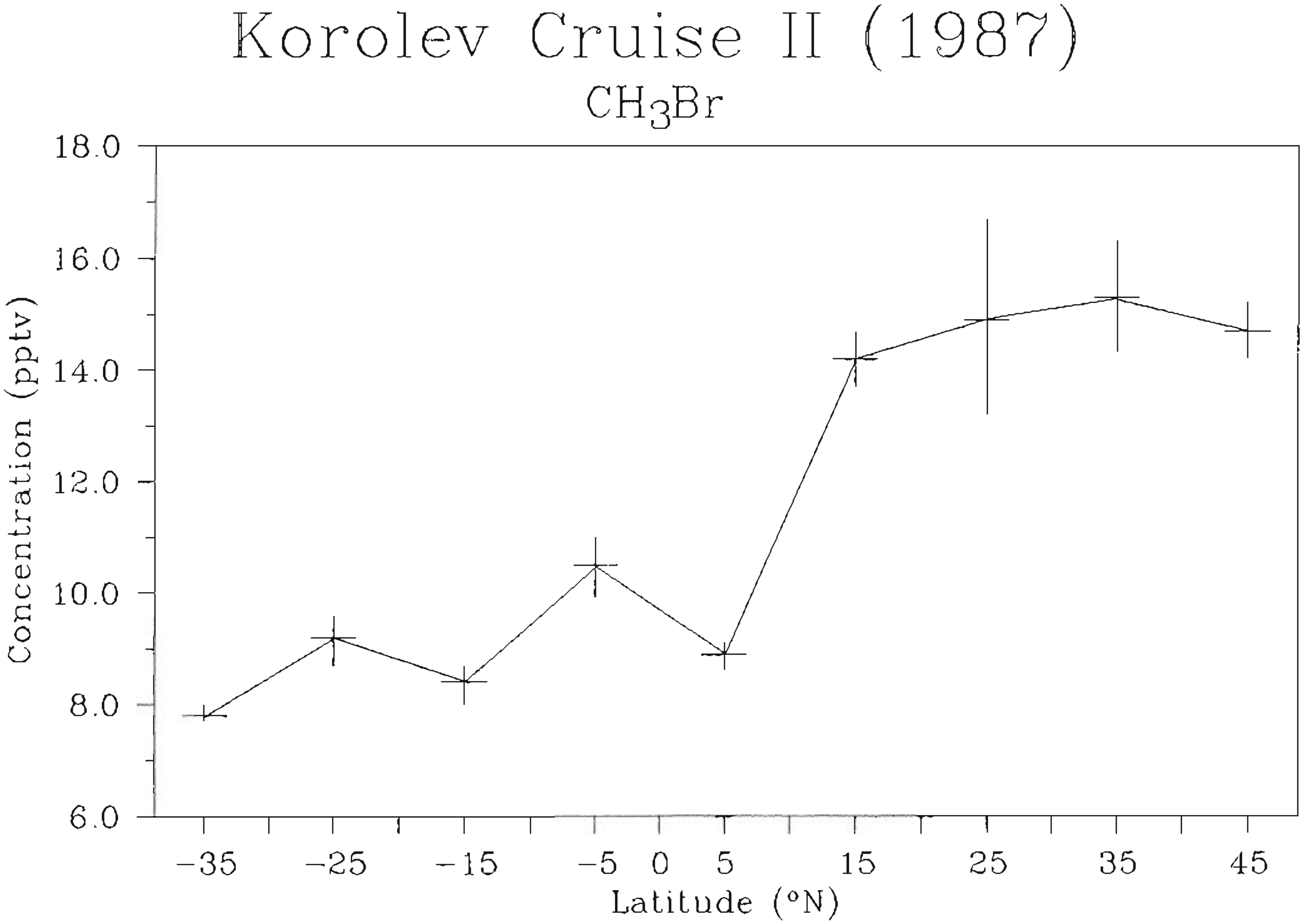


Figure B.4 : CH_3Br concentrations observed during Korolev Cruise II (1987)

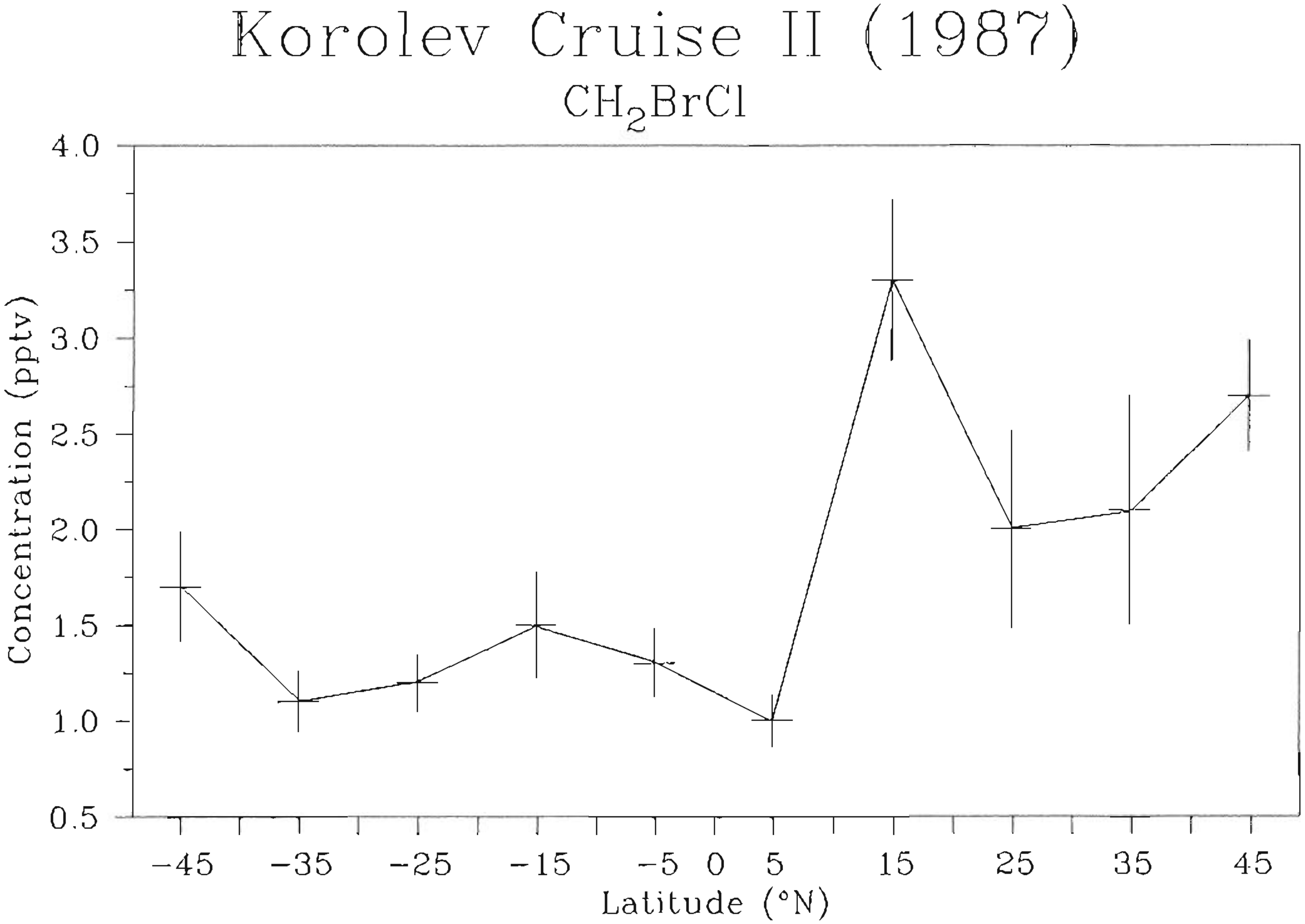


Figure B.5 : CH_2BrCl concentrations observed during Korolev Cruise II (1987)

APPENDIX C

Altitudinal Profile - Cape Kumukahi vs. Mauna Loa in Hawaii

Weekly samples collected at Cape Kumukahi (sea level) and Mauna Loa (11,000 feet) in Hawaii from 1984 to 1987 were analyzed to determine the altitudinal profile in the concentrations of the organo-bromine gases. Significant differences in the monthly mean concentrations were observed for these gases between these two stations.

Altitudinal Profile of CH_3Br Bromomethane

Air samples collected at Mauna Loa and Cape Kumukahi 1984 through 1987 were analyzed using Systems III - V. The results showed significantly higher monthly mean CH_3Br concentrations at Mauna Loa than at Cape Kumukahi during the months February through August, November and December (t-test, 95% level). In February and September the Mauna Loa value was higher than at Cape Kumukahi at a 90% level of significance. There was no significant difference in the mean CH_3Br concentration between these two stations during October. The monthly mean CH_3Br values for these two stations are given in Table C.1. These concentrations are plotted in Figure C.1. This was an unexpected result. The only explanation is a local volcanic source of CH_3Br at Mauna Loa. A similar result has been observed for CH_3Cl between these two station by Rasmussen (private communication). The elevated levels of CH_3Cl at Mauna Loa was contrary to their observations over the Pacific Ocean [Rasmussen et al (1980)] where the boundary layer CH_3Cl concentrations were higher than the above boundary layer values. Stratospheric measurements done by Fabian et al. (1981) showed decreasing CH_3Br concentrations with increasing altitude.

Altitudinal Profile of CH_3-CH_2Br Bromoethane

Samples collected at Mauna Loa and Cape Kumukahi from 1984 through 1987 were analyzed using Systems IV and V. The results, in Table C.2, were plotted in Figure C.2 as the monthly mean CH_3-CH_2Br concentrations over twelve months. These show significantly higher monthly mean CH_3-CH_2Br concentrations at Cape Kumukahi than at Mauna Loa during the months of May, October and November (t-test, 95% level). The opposite was observed during the other nine months, with monthly mean CH_3-CH_2Br values at Mauna Loa significantly higher (t-test, 95% level) than at Cape Kumukahi.

Altitudinal Profile of CH_2BrCl Bromochloromethane

Samples collected at Mauna Loa and Cape Kumukahi from 1984 through 1987 were analyzed using Systems III - V. The results indicated significantly higher monthly mean CH_2BrCl concentrations at Cape Kumukahi than at Mauna Loa in January (t-test, 95% level). In May the difference was not significant. During the other ten months the mean monthly CH_2BrCl at Mauna Loa was significantly higher than at Cape Kumukahi. The results are given in Table C.3 and plotted in Figure C.3

Altitudinal Profile of CH_2Br_2 Dibromomethane

Samples collected at Mauna Loa and Cape Kumukahi 1984 through 1987 were analyzed using Systems III - V. The results are given in Table C.4 as monthly mean CH_2Br_2 concentration over twelve months at each station. The results are also plotted in Figure C.4. This figure shows the higher CH_2Br_2 concentration at Cape Kumukahi than at Mauna Loa. This difference was statistically significant for all year round except during April (t-test, 95% level).

Altitudinal Profile of CH_2Br-CH_2Br 1,2-Dibromoethane (EDB)

Samples collected at Mauna Loa and Cape Kumukahi 1984 through 1987 were analyzed using Systems III - V. The results are given in Table C.5 as monthly mean CH_2Br-CH_2Br concentration over twelve months at each station. The results are also plotted in Figure C.5. This figure shows the higher CH_2Br-CH_2Br concentration at Cape Kumukahi than at Mauna Loa. This difference was statistically significant (t-test, 95% level) for all year round except during April and May when there large variabilities in the CH_2Br-CH_2Br concentrations at Cape Kumukahi.

Altitudinal Profile of $CHBr_3$ Tribromomethane (Bromoform)

Samples collected at Mauna Loa and Cape Kumukahi 1984 through 1987 were analyzed using Systems III - V. The results, in Table C.6, showed significantly higher monthly mean $CHBr_3$ concentrations at Cape Kumukahi than the monthly average $CHBr_3$ concentrations at Mauna Loa during the months January, March through September and December (t-test, 95%

level). The monthly mean $CHBr_3$ values during October and November at Cape Kumukahi were higher than at Mauna Loa, but this difference was significant only at a 90% level. The difference in the monthly average $CHBr_3$ concentrations at these two stations was not significant in February. These results are plotted in Figure C.6.

TABLE C.1

Monthly average CH_3Br concentration at Cape Kumukahi and Mauna Loa in Hawaii

MONTH	Mauna Loa (sea level)			Cape Kumukahi (11,000 ft.)		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	11.3	2.7	10	9.6	0.6	10
2	10.5	1.9	13	10.1	0.8	8
3	10.2	1.1	11	9.9	0.9	11
4	11.0	1.5	13	10.0	0.7	10
5	11.0	2.0	16	9.9	0.8	6
6	10.8	1.9	19	9.9	0.3	11
7	11.1	2.3	15	9.0	0.6	8
8	10.8	2.3	12	9.6	0.9	10
9	10.6	1.3	12	10.4	1.0	13
10	10.9	0.9	8	10.9	1.2	8
11	10.5	2.0	13	9.2	0.7	8
12	10.4	1.0	11	9.4	0.6	9

TABLE C.2

Monthly average CH_3-CH_2Br concentration at Cape Kumukahi and Mauna Loa in Hawaii

Month	Mauna Loa (11,000 ft.)			Cape Kumukahi (sea level)		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	0.83	0.60	6	0.61	0.32	9
2	0.94	0.72	7	0.57	0.19	5
3	0.75	0.47	7	0.65	0.29	9
4	1.18	0.41	8	0.91	0.24	8
5	1.02	0.61	10	1.06	0.28	7
6	0.89	0.20	4	0.84	0.27	11
7	1.16	0.45	7	0.96	0.24	7
8	0.76	0.15	4	0.73	0.41	10
9	1.48	0.63	7	0.87	0.32	12
10	0.75	0.34	5	1.07	0.47	9
11	0.53	0.14	3	0.89	0.34	8
12	0.94	0.57	11	0.63	0.18	10

TABLE C.3

Monthly average CH_2BrCl concentration at Cape Kumukahi and Mauna Loa in Hawaii

Month	Mauna Loa (11,000 ft.)			Cape Kumukahi (sea level)		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	1.28	0.70	6	1.66	0.28	5
2	1.80	1.20	10	1.43	0.33	6
3	1.90	1.17	7	1.66	0.29	6
4	2.19	1.38	8	1.38	0.49	8
5	1.66	0.81	4	1.75	0.30	6
6	2.04	0.66	3	1.36	0.47	10
7	1.67	1.04	6	1.02	0.39	9
8	2.10	0.76	4	1.34	0.20	7
9	1.74	0.91	6	1.20	0.31	9
10	1.87	0.61	2	0.90	0.27	8
11	2.59	1.05	5	1.70	0.70	7
12	1.48	0.22	4	1.42	0.38	9

TABLE C.4

Monthly average CH_2Br_2 concentration at Cape Kumukahi and Mauna Loa in Hawaii

Month	Mauna Loa (11,000 ft.)			Cape Kumukahi (sea level)		
	Mean (pptv)	std.dev. (pptv)	N	Mean	std.dev. (pptv)	N
1	3.18	0.33	9	6.42	2.34	9
2	3.38	0.55	10	4.94	1.75	8
3	3.53	0.39	10	7.23	2.47	9
4	3.69	0.37	8	7.27	4.77	7
5	3.13	0.23	11	9.22	5.81	6
6	2.82	0.35	18	7.31	4.18	11
7	2.70	0.20	11	6.42	2.44	9
8	2.56	0.26	9	9.08	2.60	10
9	2.45	0.35	8	8.39	3.81	13
10	2.65	0.59	4	8.40	3.09	9
11	2.79	0.43	11	7.83	2.84	8
12	2.98	0.37	8	6.20	2.45	11

TABLE C.5

Monthly average CH_2Br-CH_2Br concentration at Cape Kumukahi and Mauna Loa in Hawaii

Month	Mauna Loa (11,000 ft.)			Cape Kumukahi (sea level)		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	0.79	0.51	9	4.25	3.00	9
2	0.26	0.14	7	3.19	2.80	8
3	1.30	0.82	11	3.99	3.11	11
4	1.85	0.84	12	9.39	8.59	10
5	1.67	1.33	15	7.66	6.81	7
6	1.60	0.82	17	3.49	2.38	11
7	1.42	0.95	12	2.66	1.42	9
8	0.99	0.65	9	3.81	1.79	8
9	1.41	1.05	10	4.42	2.50	13
10	1.27	0.97	6	5.18	2.22	9
11	1.07	0.60	9	3.66	1.09	7
12	0.47	0.32	8	4.84	1.93	10

TABLE C.6

Monthly average $CHBr_3$ concentration at Cape Kumukahi and Mauna Loa in Hawaii

Month	Mauna Loa (11,000 ft.)			Cape Kumukahi (sea level)		
	Mean (pptv)	std.dev. (pptv)	N	Mean (pptv)	std.dev. (pptv)	N
1	2.64	0.69	9	8.16	2.11	9
2	3.18	1.76	10	6.97	3.57	6
3	1.97	1.33	6	6.00	3.47	10
4	2.70	0.68	9	8.29	2.85	9
5	2.28	0.82	8	6.27	0.96	5
6	1.37	0.67	3	5.06	1.32	7
7	1.23	0.57	6	5.44	1.73	5
8	1.45	1.13	5	4.45	1.32	7
9	1.68	1.37	7	5.59	2.31	6
10	2.79	1.40	4	7.17	2.84	6
11	2.47	0.90	7	8.08	3.13	5
12	3.12	1.09	11	8.06	3.69	11

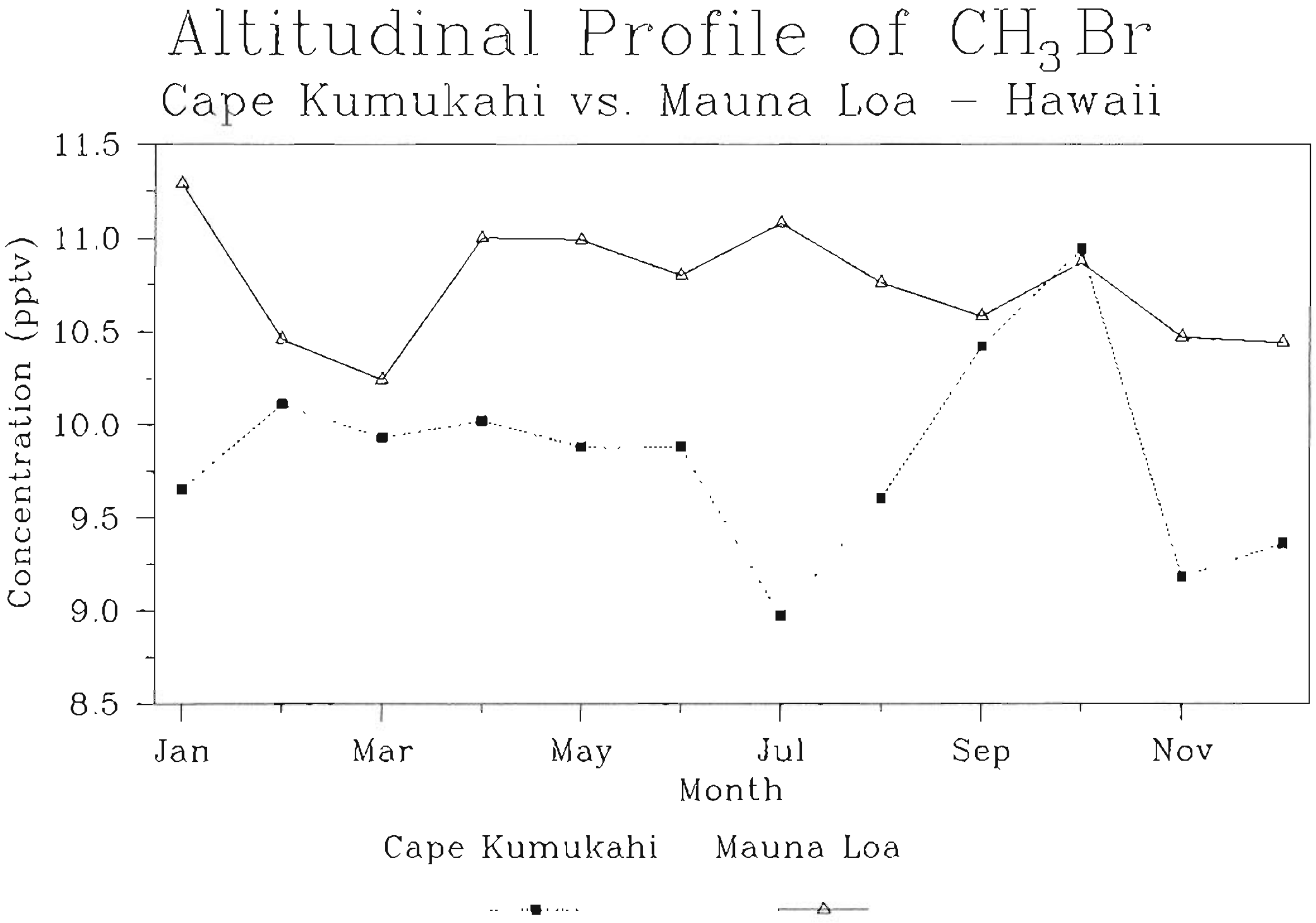


Figure C.1 : Altitudinal Profile of CH_3Br concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

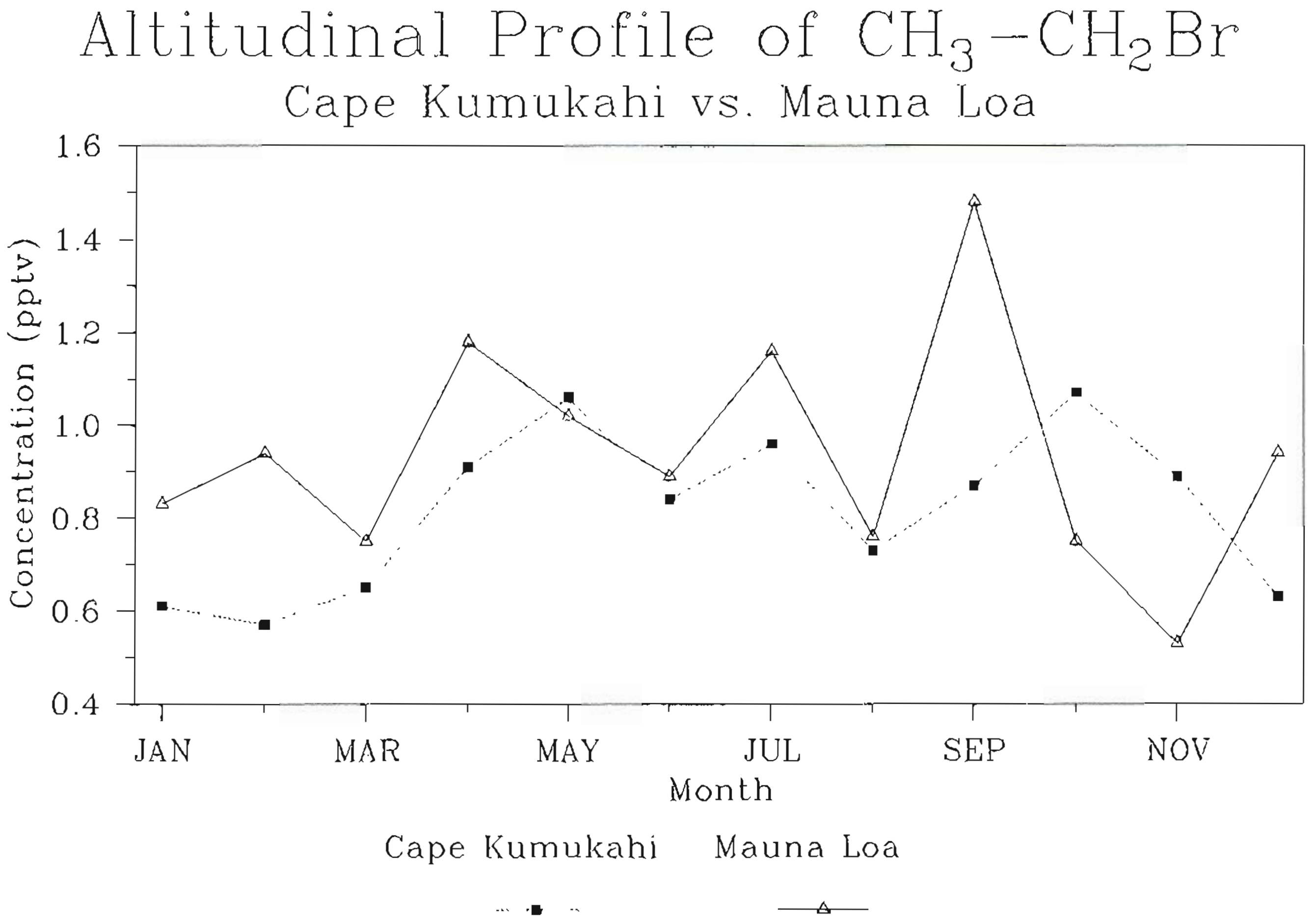


Figure C.2 : Altitudinal Profile of CH_3-CH_2Br concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

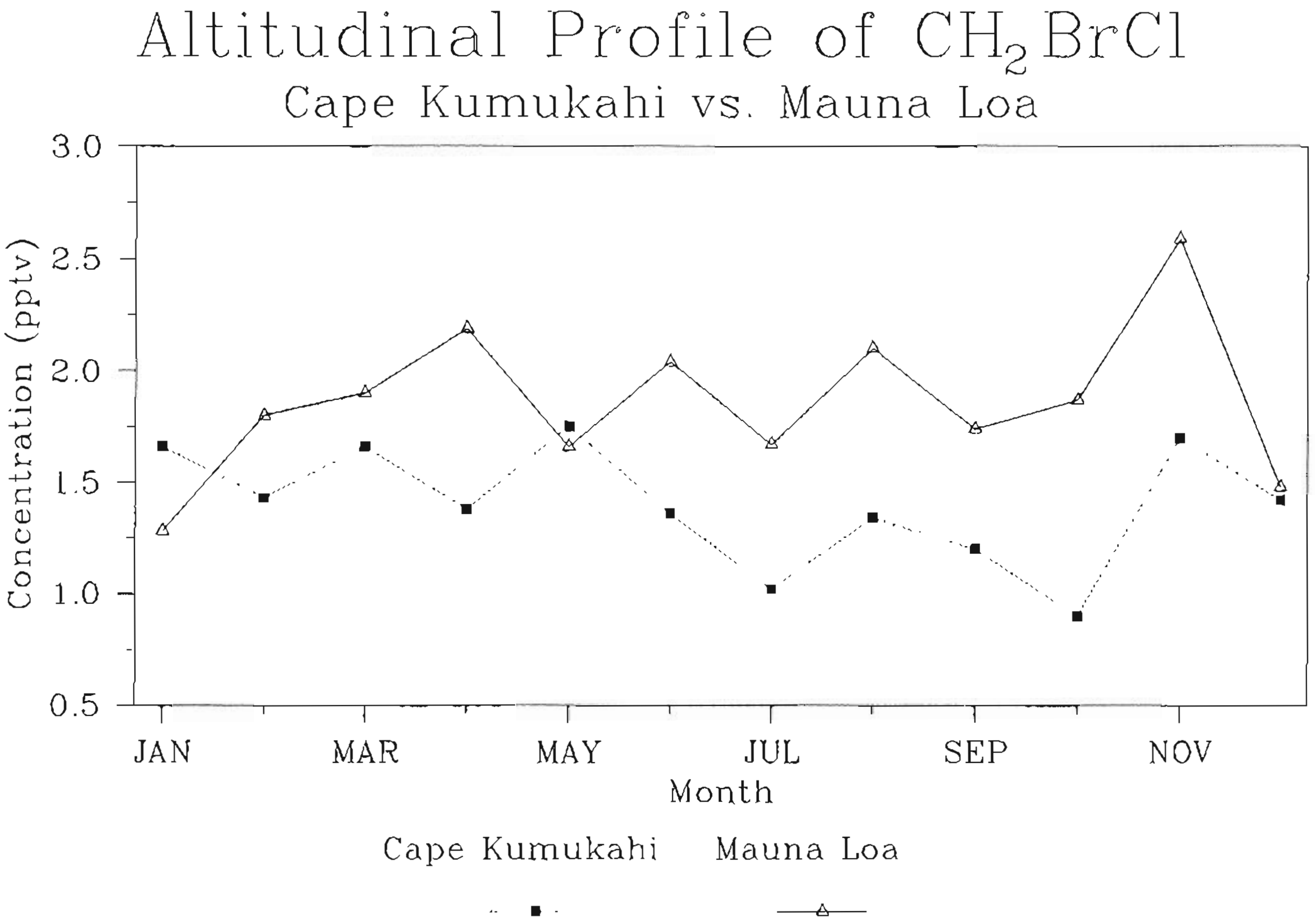


Figure C.3 : Altitudinal Profile of CH_2BrCl concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

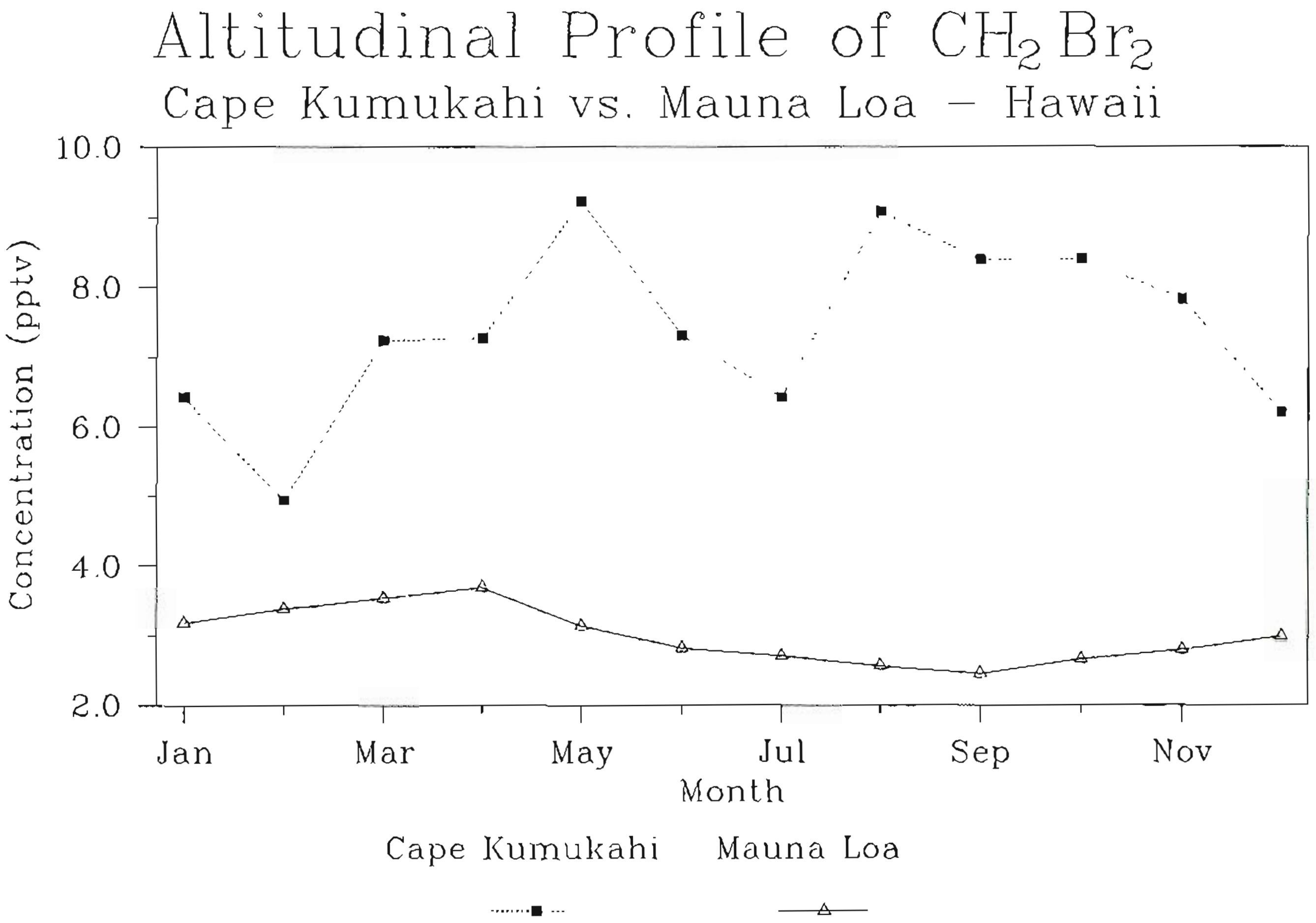


Figure C.4 : Altitudinal Profile of CH_2Br_2 concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

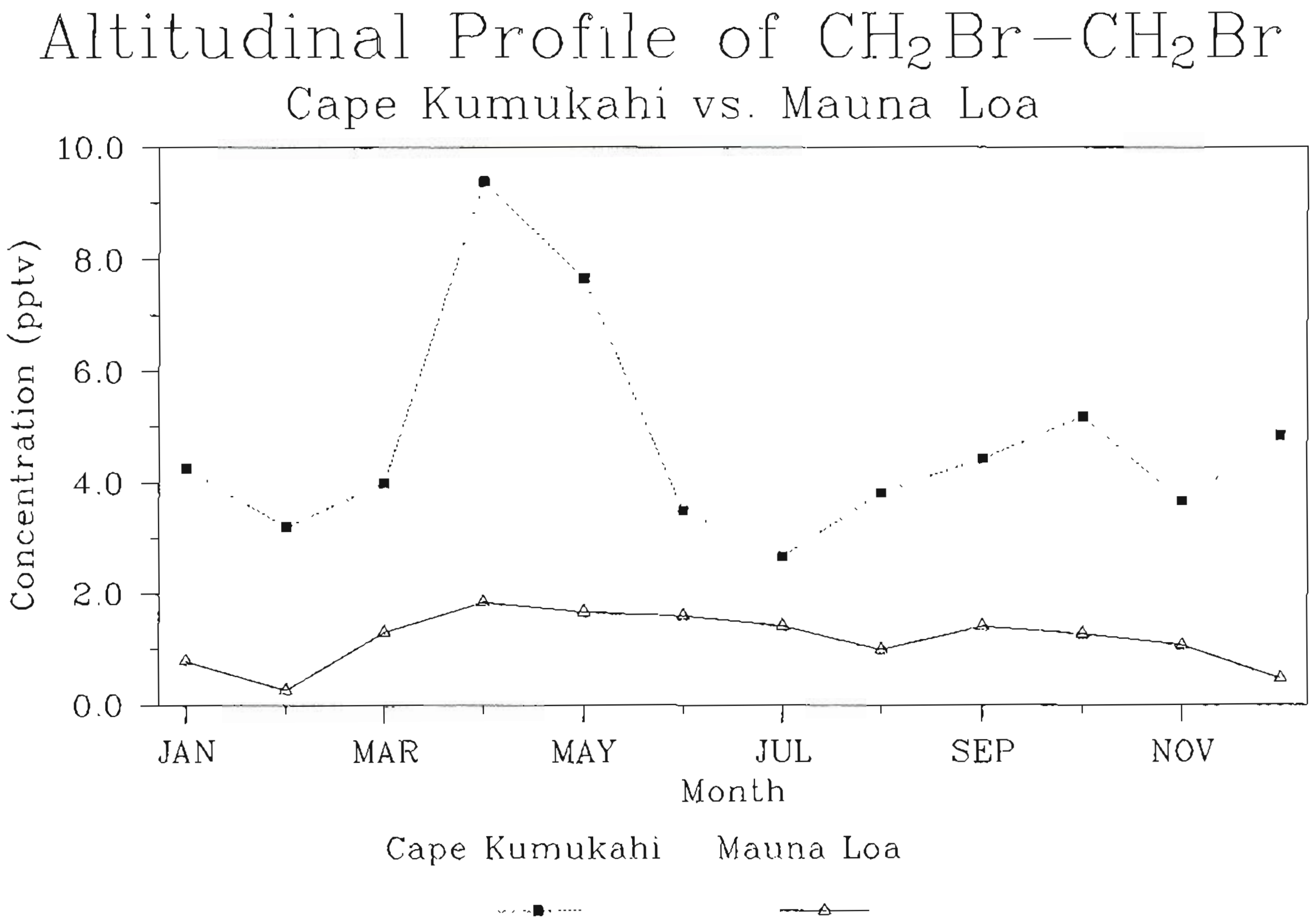


Figure C.5 : Altitudinal Profile of CH$_2$Br-CH$_2$Br concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

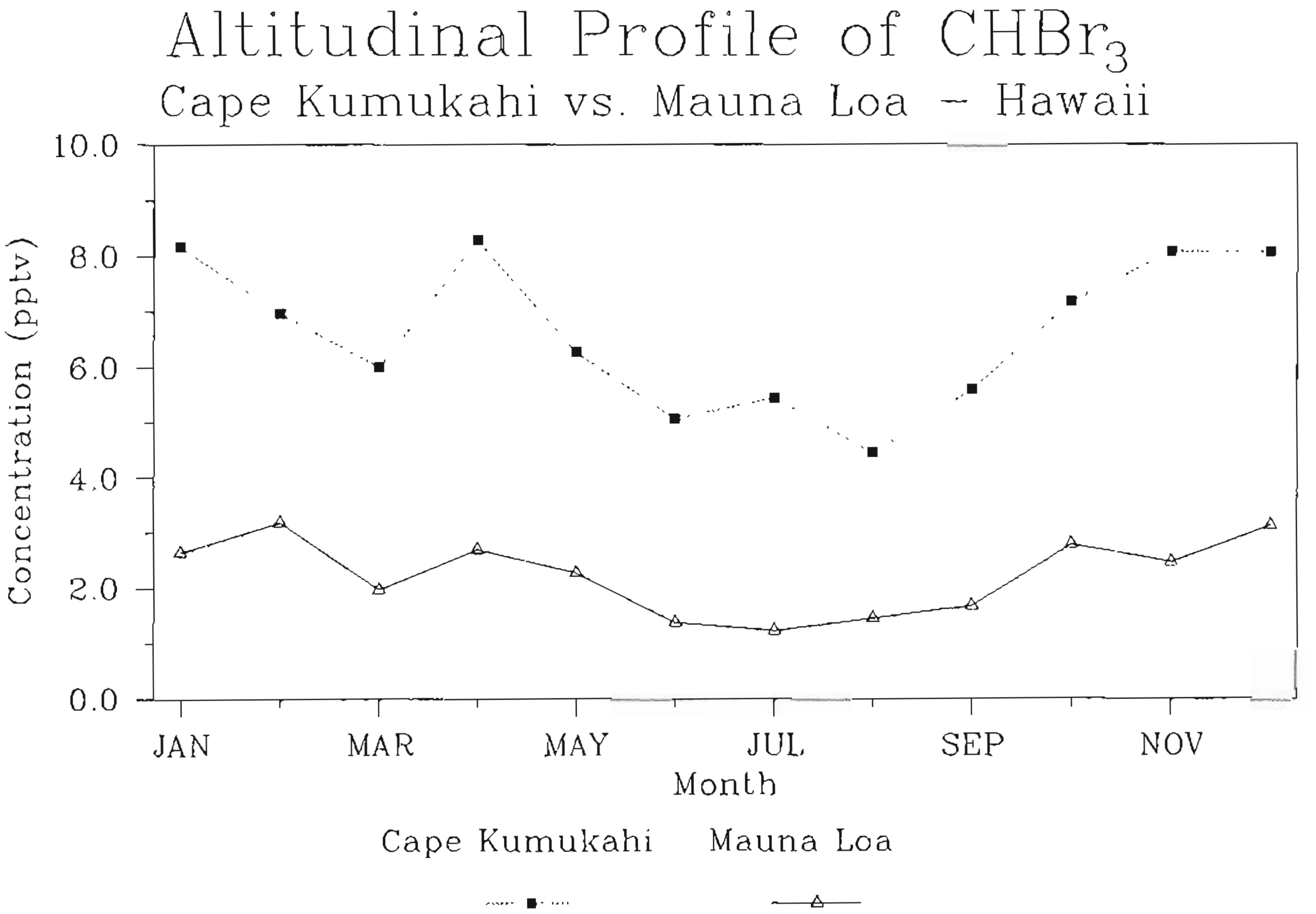


Figure C.6 : Altitudinal Profile of $CHBr_3$ concentration - Cape Kumukahi (sea level) and Mauna Loa (11,000 ft.), Hawaii

APPENDIX D

Seasonal Variations of Organo-Bromine Gases

Samples collected at Alert - Canada, Point Barrow and Poker Flat - Alaska, Mace Head - Ireland, Cape Meares - Oregon, Sable Island - Canada, Cape - Kumukahi and Mauna Loa - Hawaii, St. Croix - U.S. Virgin Islands, Cape Matatula - Samoa and Cape Grim - Tasmania were analyzed using Systems II - V. The data were used to determine the seasonal variation of the organo-bromine gases CH_3Br, CH_3-CH_2Br, CH_2BrCl, CH_2Br_2, $CHBr_2Cl$, CH_2Br-CH_2Br and $CHBr_3$ at these stations. Significant seasonal differences (t-test, 95% level) were observed for these gases at these stations. These seasonal variations are discussed in this section.

Seasonal Variations of CH_3Br at Alert, Canada

Air samples from Alert, Canada, collected November 1985 through October 1987 were analyzed using System V. Significantly higher mean CH_3Br concentrations, 11.5±0.7 pptv, were observed (t-test, 95% level) during the months of April and May as compared to the mean CH_3Br value during rest of the year, 9.5±0.8 pptv. Figure D.1 shows a seasonal cycle in the CH_3Br concentration with a maximum in spring and a minimum in late summer. The minimum in summer may be due to increased HO radicals during that period of the year.

Seasonal Variations of CH_3Br at Pt. Barrow, Alaska

Samples collected at Point Barrow, Alaska, from December of 1982 through November of 1987 were analyzed using Systems II through V. The results plotted in Figure D.2 indicated a seasonal cycle with significantly higher (t-test, 95% level) mean CH_3Br concentration from May through October, 14.6±3.8 pptv, than the mean value during rest of the year, 10.4±1.2 pptv.

Seasonal Variations of CH_3Br at Poker Flat, Alaska

Samples from Poker Flat, Alaska, collected from February of 1985 through October of 1987 were analyzed for CH_3Br using Systems IV and V. The results plotted in Figure D.3 indicate a seasonal cycle in the with significantly higher CH_3Br concentration, 10.3±0.3 pptv, during the months of April through June and significantly lower concentration, 8.0±0.8 pptv, during the months of September and October than the average CH_3Br concentration during rest of the year, 9.2±0.6 pptv (t-test, 95% level).

Seasonal Variations of CH_3Br at Cape Meares, Oregon

Weekly samples collected at Cape Meares, Oregon, from December 1982 through December of 1987 were analyzed for CH_3Br using Systems II through V. The monthly mean CH_3Br concentrations are plotted in Figure D.4. This figure shows seasonal cycles with significantly lower (t-test, 95% level) mean CH_3Br concentration during the months of January and July 10.2±1.4 pptv as compared to the average CH_3Br concentration during rest of the year 11.2±1.9 pptv.

Seasonal Variations of CH_3Br at Sable Island, Canada

Samples collected at Sable Island, Canada, from October of 1985 through October of 1987 were analyzed for CH_3Br using System V. The results plotted in Figure D.5 show seasonal cycles with significantly higher (t-test, 95% level) mean CH_3Br concentration during the months April through June and in November, 11.6±1.0 pptv as compared to the mean value during rest of the year 10.1±0.8 pptv.

Seasonal Variations of CH_3Br at Cape Kumukahi, Hawaii

Samples collected at Cape Kumukahi, Hawaii, from February of 1983 through October of 1987 were analyzed for CH_3Br using Systems II through V. The results plotted in Figure D.6 show seasonal cycles with significantly higher (t-test, 95% level) mean CH_3Br concentration during the months September and October, 10.6±1.1 pptv, as compared to the mean value during rest of the year, 9.7±0.8 pptv. The elevated levels of CH_3Br at Cape Kumukahi in September and October may be due to long range transport of air from the Los Angeles area, which is believed to occur during this time of the year.

Seasonal Variations of CH_3Br at Cape Matatula, Samoa

Samples collected at Cape Matatula, Samoa, from December 1982 through October 1987 were analyzed for CH_3Br using Systems II - V. The results indicated a significantly lower mean CH_3Br concentration, 7.1±0.8 pptv, during November than the mean CH_3Br concentration during rest of the year, 8.1±1.1 pptv (t-test, 95% level). These results are plotted in figure D.7.

Seasonal Variations of CH_3Br at Cape Grim, Tasmania

Samples collected at Cape Grim, Tasmania, from September of 1982 through October of 1987 were analyzed for CH_3Br using Systems II through V. The results indicated significantly higher mean CH_3Br concentration, 8.3±1.4 pptv, during November and significantly lower average CH_3Br concentration, 6.2±1.1 pptv, as compared to the average CH_3Br concentration during rest of the year, 7.6±1.0 pptv (t-test, 95% level). These differences are shown in Figure D.8 where the monthly mean CH_3Br concentrations are plotted over twelve months.

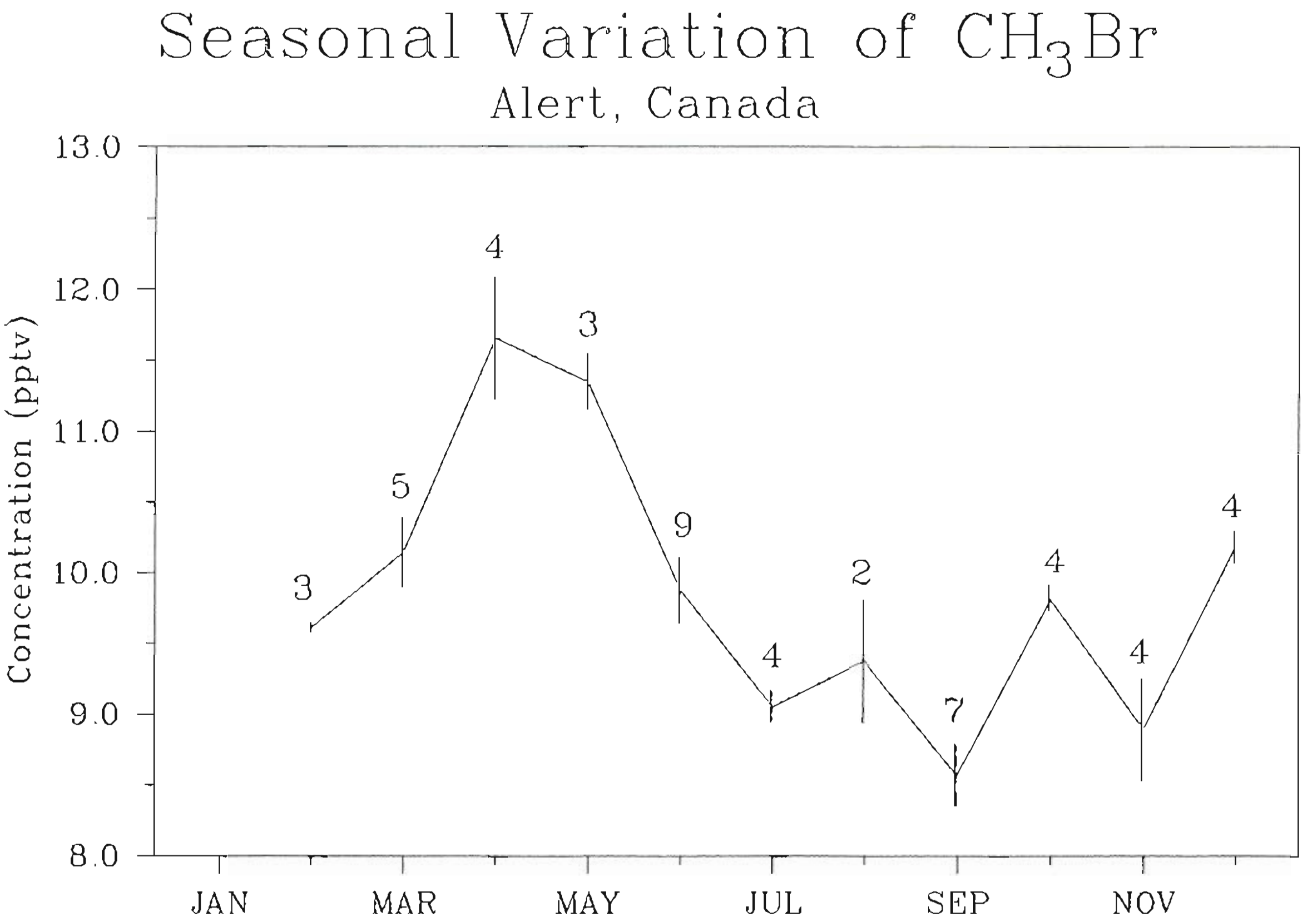


Figure D.1 : Monthly mean CH_3Br concentrations at Alert, Canada
(Error bars are ±1 Standard error)

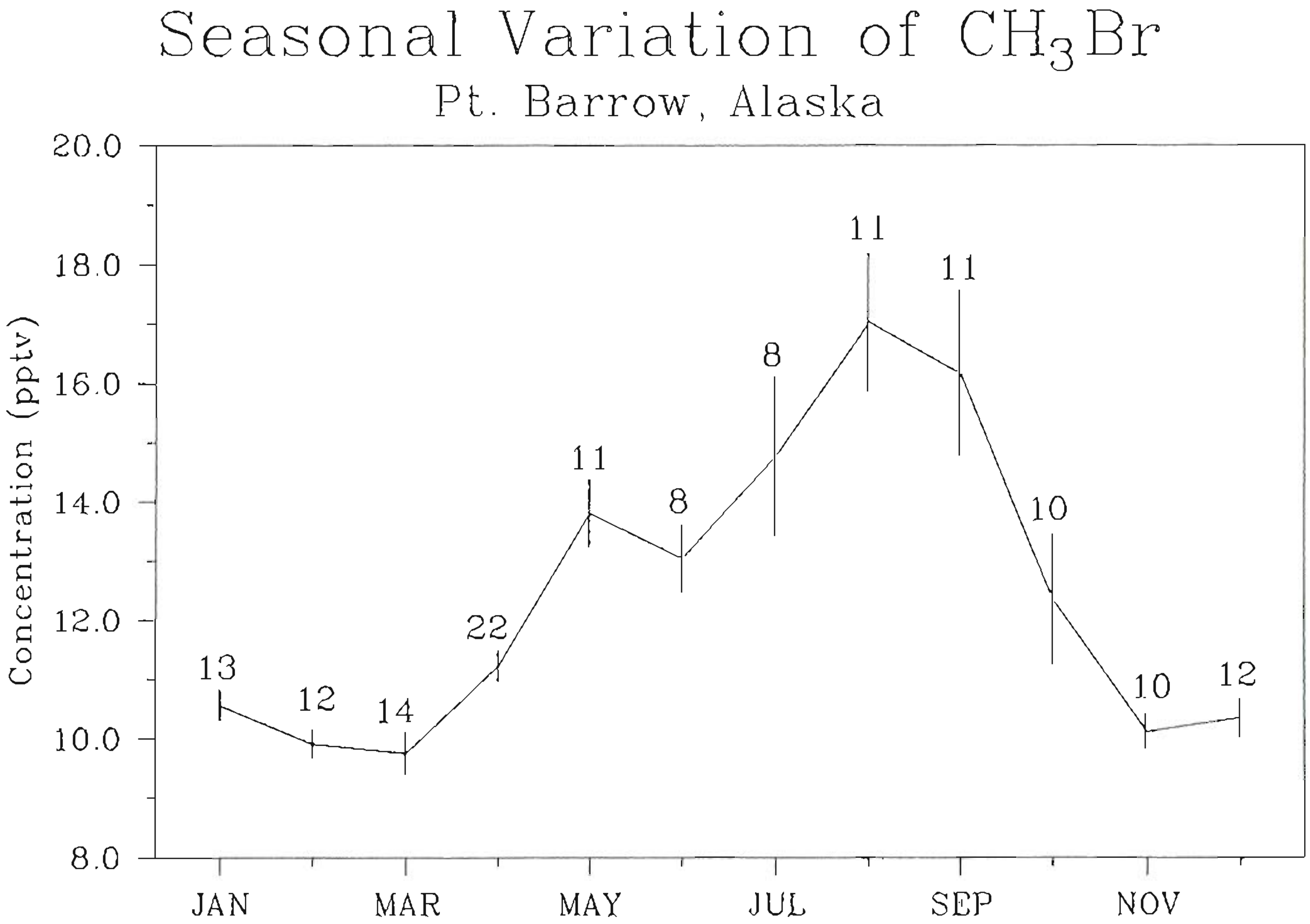


Figure D.2 : Monthly mean CH_3Br concentrations at Pt. Barrow, Alaska
(Error bars are ±1 Standard error)

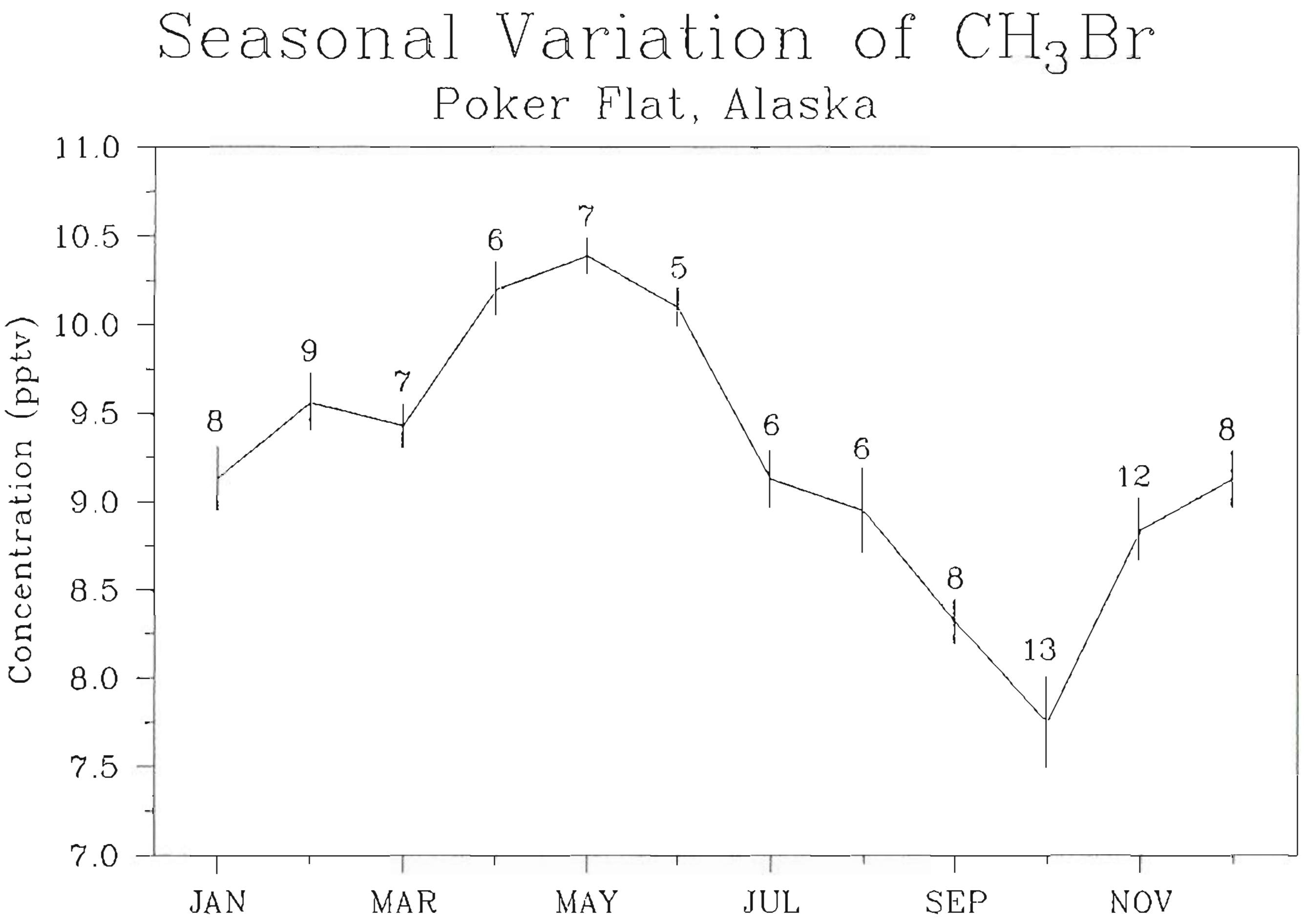


Figure D.3 : Monthly mean CH_3Br concentrations at Poker Flat, Alaska
(Error bars are ±1 Standard error)

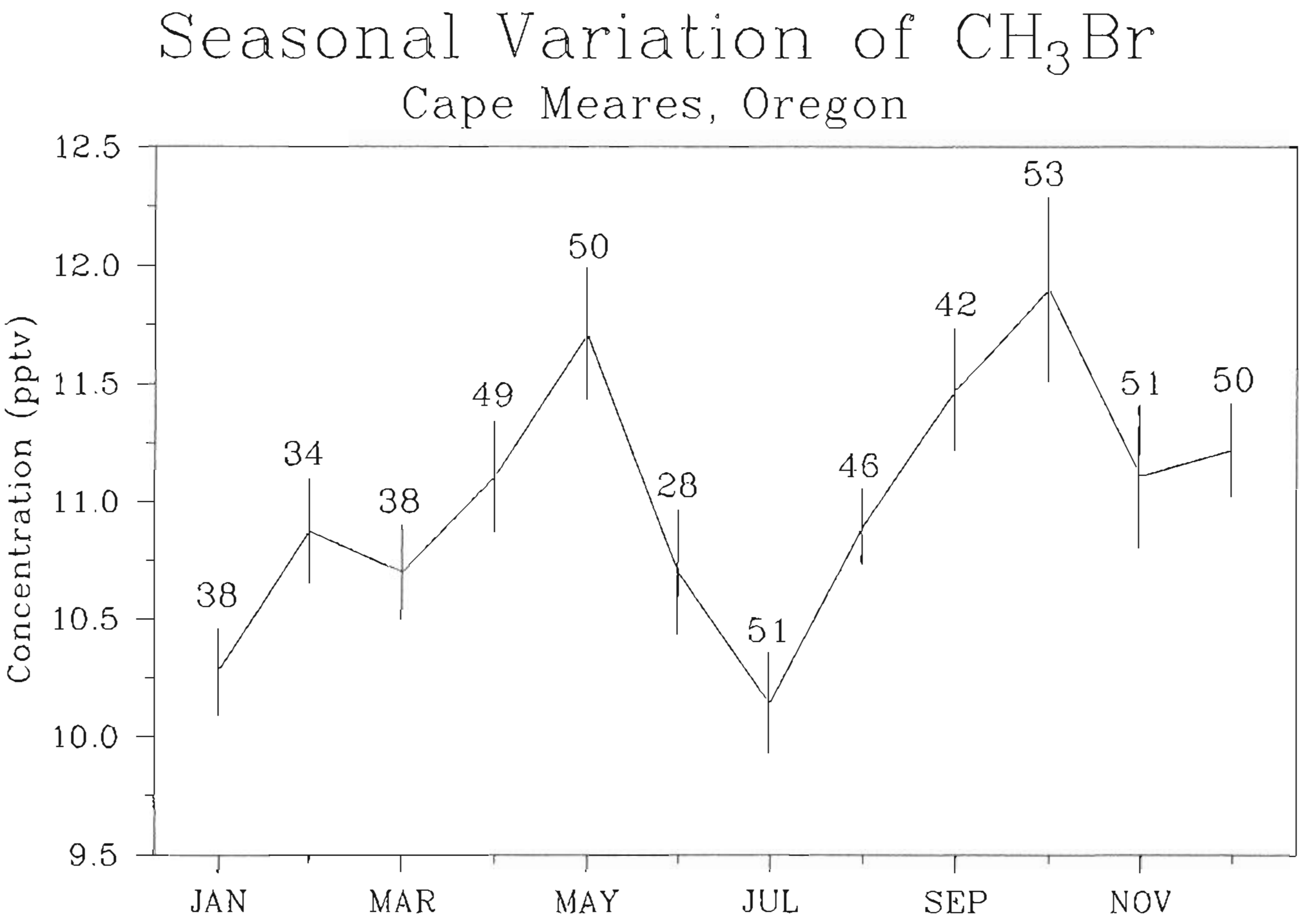


Figure D.4 : Monthly mean CH_3Br concentrations at Cape Meares, Oregon (Error bars are ±1 Standard error)

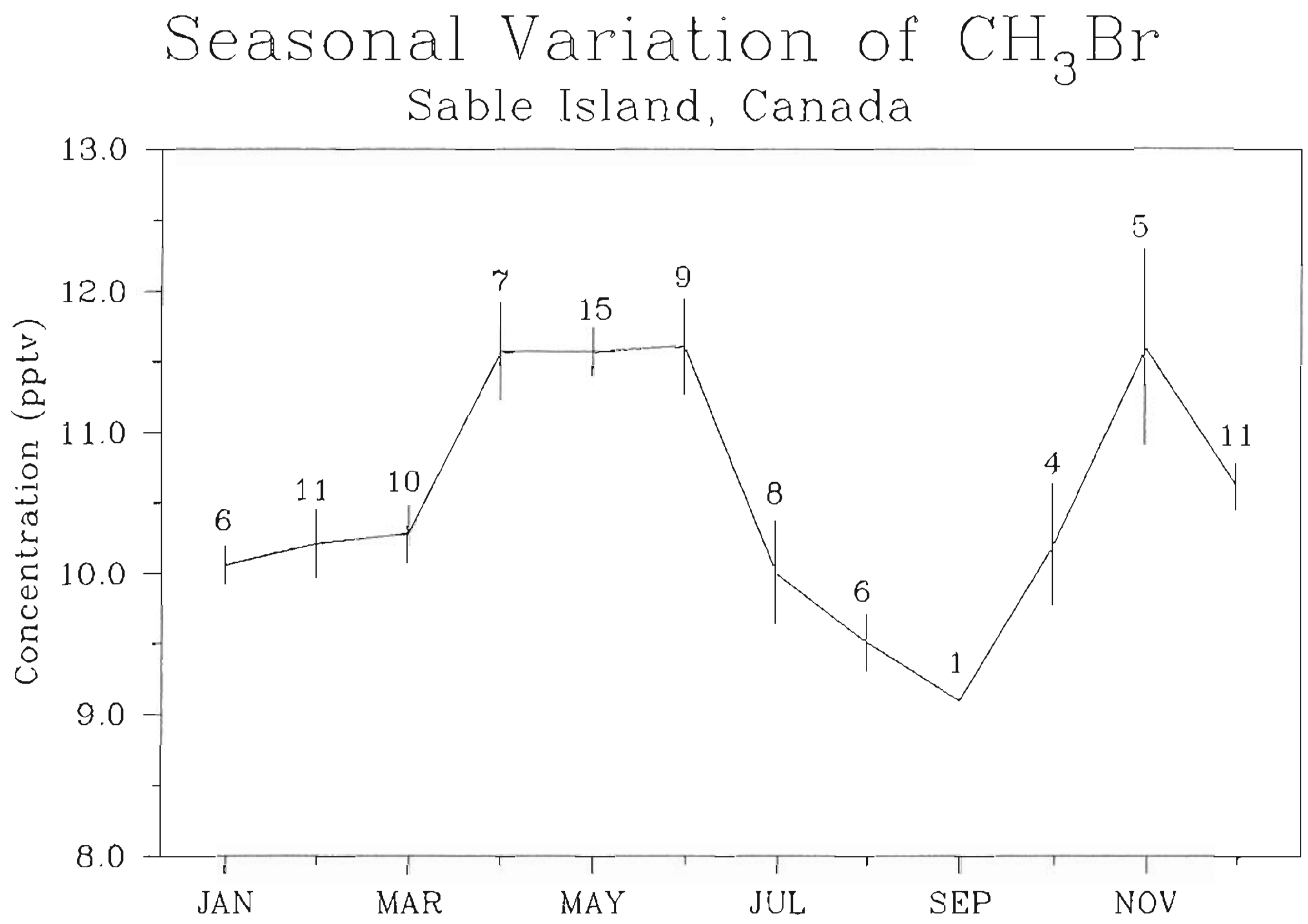


Figure D.5 : Monthly mean CH_3Br concentrations at Sable Island, Canada (Error bars are ±1 Standard error)

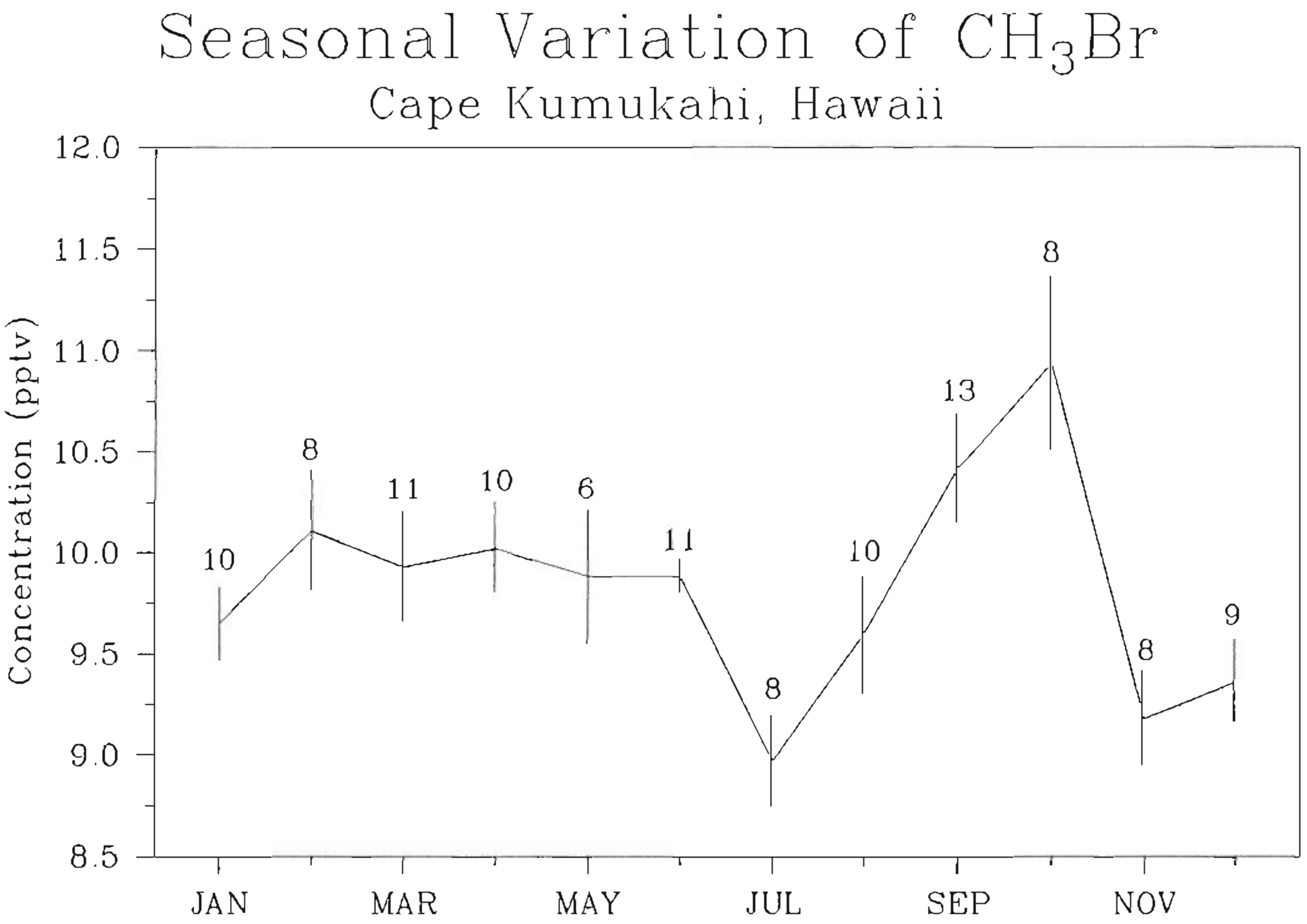


Figure D.6 : Monthly mean CH_3Br concentrations at Cape Kumukahi, Hawaii
(Error bars are ±1 Standard error)

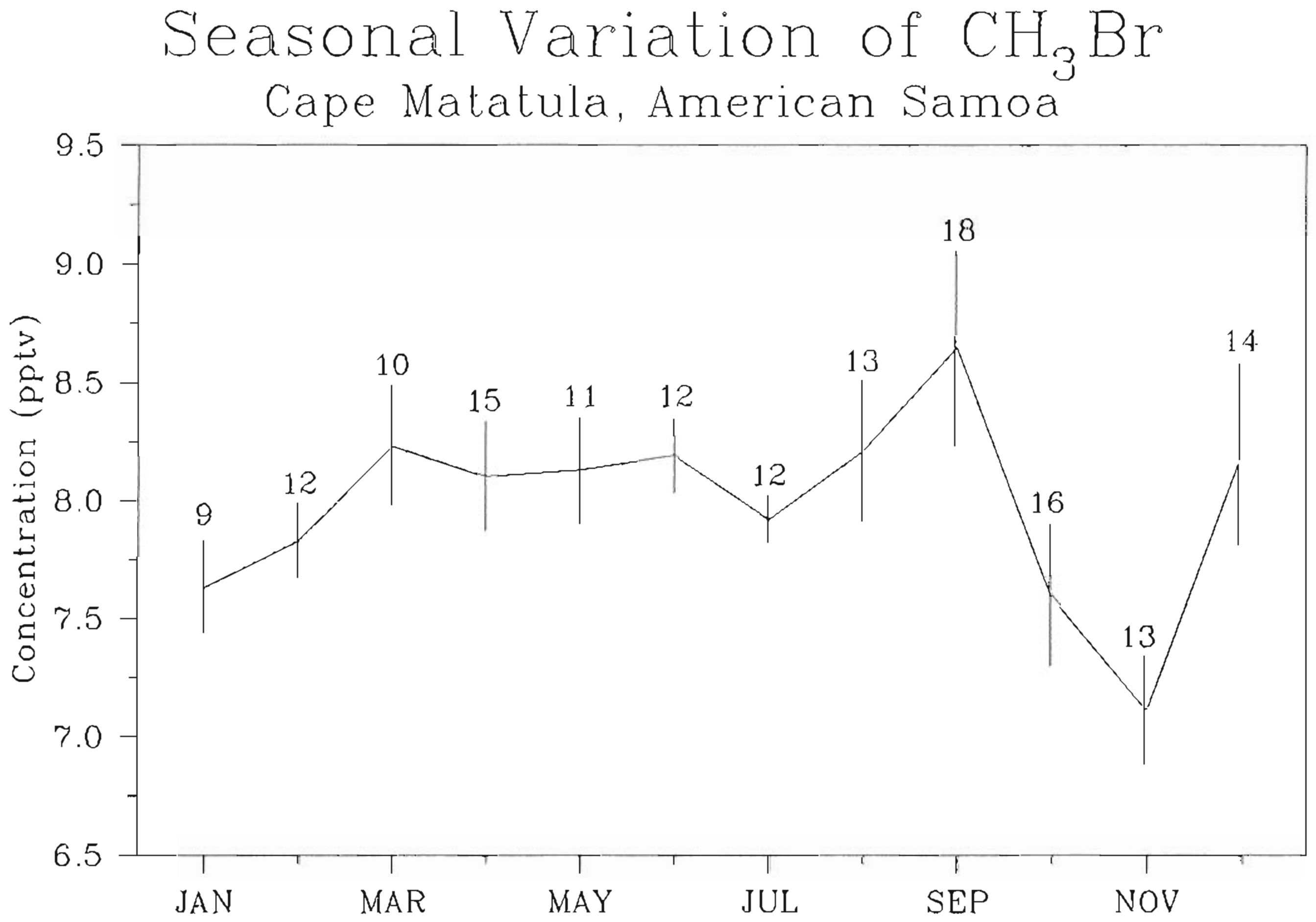


Figure D.7 : Monthly mean CH_3Br concentrations at Cape Matatula, Samoa
(Error bars are ±1 Standard error)

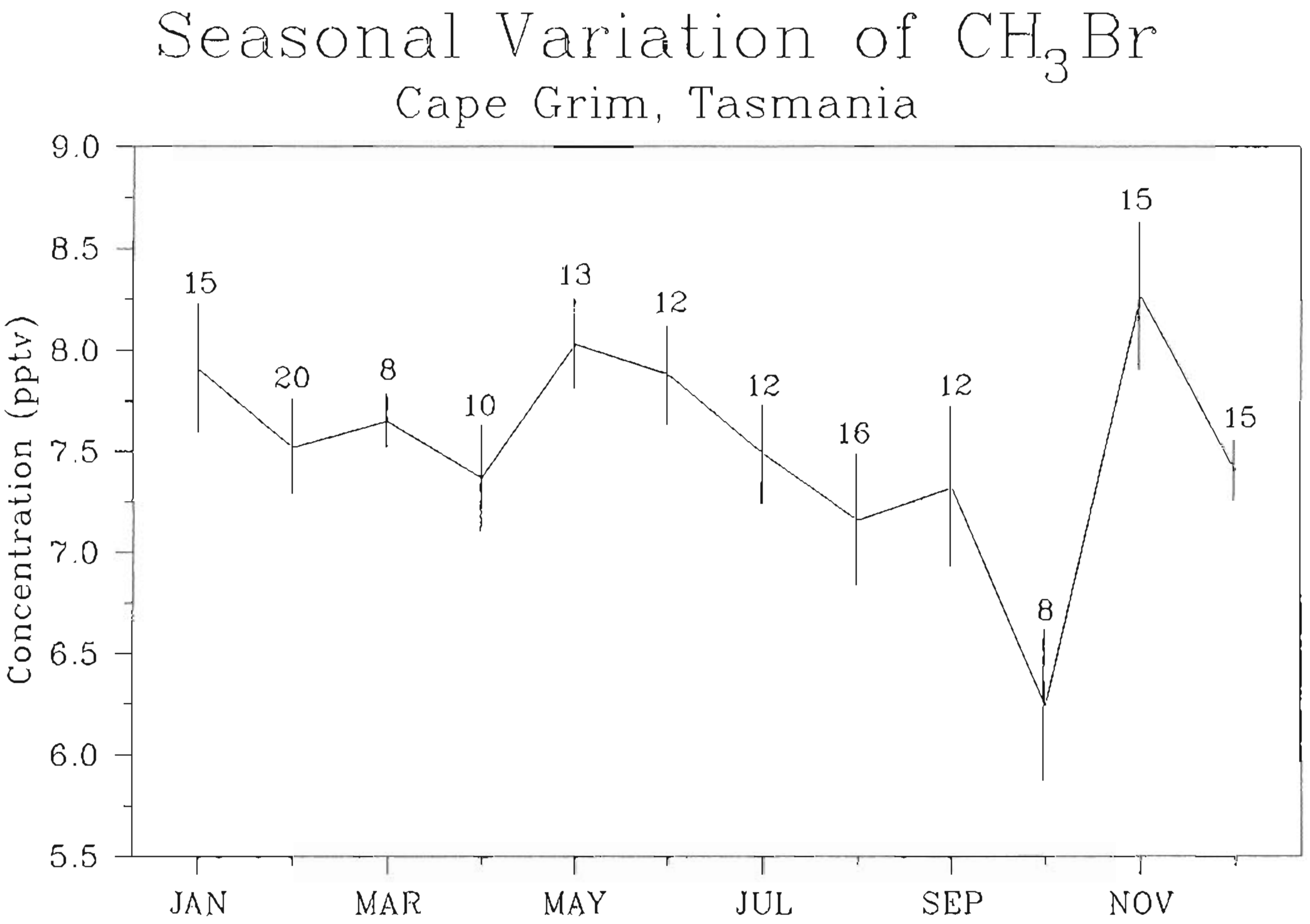


Figure D.8 : Monthly mean CH_3Br concentrations at Cape Grim, Tasmania (Error bars are ±1 Standard error)

Seasonal Variations of CH_3-CH_2Br at Alert, Canada

Air samples collected at Alert from November 1985 through October were analyzed for CH_3-CH_2Br using System V. The results showed a seasonal cycle for CH_3-CH_2Br with a significantly higher (t-test, 95% level) mean concentration 1.3±0.4 pptv during the months of March through May as compared to the mean CH_3-CH_2Br concentration during rest of the year 0.7±0.2 pptv. See Figure D.9.

Seasonal Variations of CH_3-CH_2Br at Pt. Barrow, Alaska

Air samples collected at Point Barrow from September 1984 through November 1987 were analyzed for CH_3-CH_2Br using Systems IV and V. The results showed significantly higher mean CH_3-CH_2Br concentration from May through October 3.3±1.5 pptv than the value during rest of the year 1.9±0.9 pptv. See Figure D.10.

Seasonal Variations of CH_3-CH_2Br at Poker Flat, Alaska

Samples from Poker Flat collected between February 1985 through October 1987 were analyzed for CH_3-CH_2Br using System V. The results plotted in Figure D.11 indicate a strong seasonal cycle in its concentration with significantly higher mean concentration during June through August 1.6±0.6 pptv than the mean value 0.8±0.2 pptv (t-test, 95% level).

Seasonal Variations of CH_3-CH_2Br at Mace Head, Ireland

Samples collected at Mace Head were analyzed for CH_3-CH_2Br using System V. The results showed significantly higher average CH_3-CH_2Br concentration, 2.0±1.0 pptv, during the months of April through August as compared to the average CH_3-CH_2Br concentration during rest of the year, 1.0±0.4 pptv (t-test, 95% level). The results are plotted in Figure D.12.

Seasonal Variations of CH_3-CH_2Br at Cape Meares, Oregon

Samples from Cape Meares collected between September 1984 through December 1987 were analyzed for CH_3-CH_2Br using Systems IV and V. The data are plotted in Figure D.13. This figure showed significantly lower average CH_3-CH_2Br concentration from November through March, 0.9±0.3 pptv, than the average CH_3-CH_2Br concentration during the months of April through October, 1.6±0.8 pptv (t-test, 95% level).

Seasonal Variations of CH_3-CH_2Br at Sable Island, Canada

Sable Island samples collected from October 1985 through October 1987 were analyzed for CH_3-CH_2Br using System V. The results showed significantly higher mean CH_3-CH_2Br concentrations for the months of March through July, 2.6±1.3 pptv, than the average value during rest of the year, 0.9±0.4 pptv (t-test, 95% level). The results are plotted in Figure D.14.

Seasonal Variations of CH_3-CH_2Br at Cape Grim, Tasmania

Cape Grim samples collected between September of 1984 and October of 1987 were analyzed for CH_3-CH_2Br using Systems IV and V. The results plotted in Figure D.15 indicated significantly higher average CH_3-CH_2Br concentration in January, 2.1±0.5 pptv, than during rest of the year, 0.7±0.3 pptv.

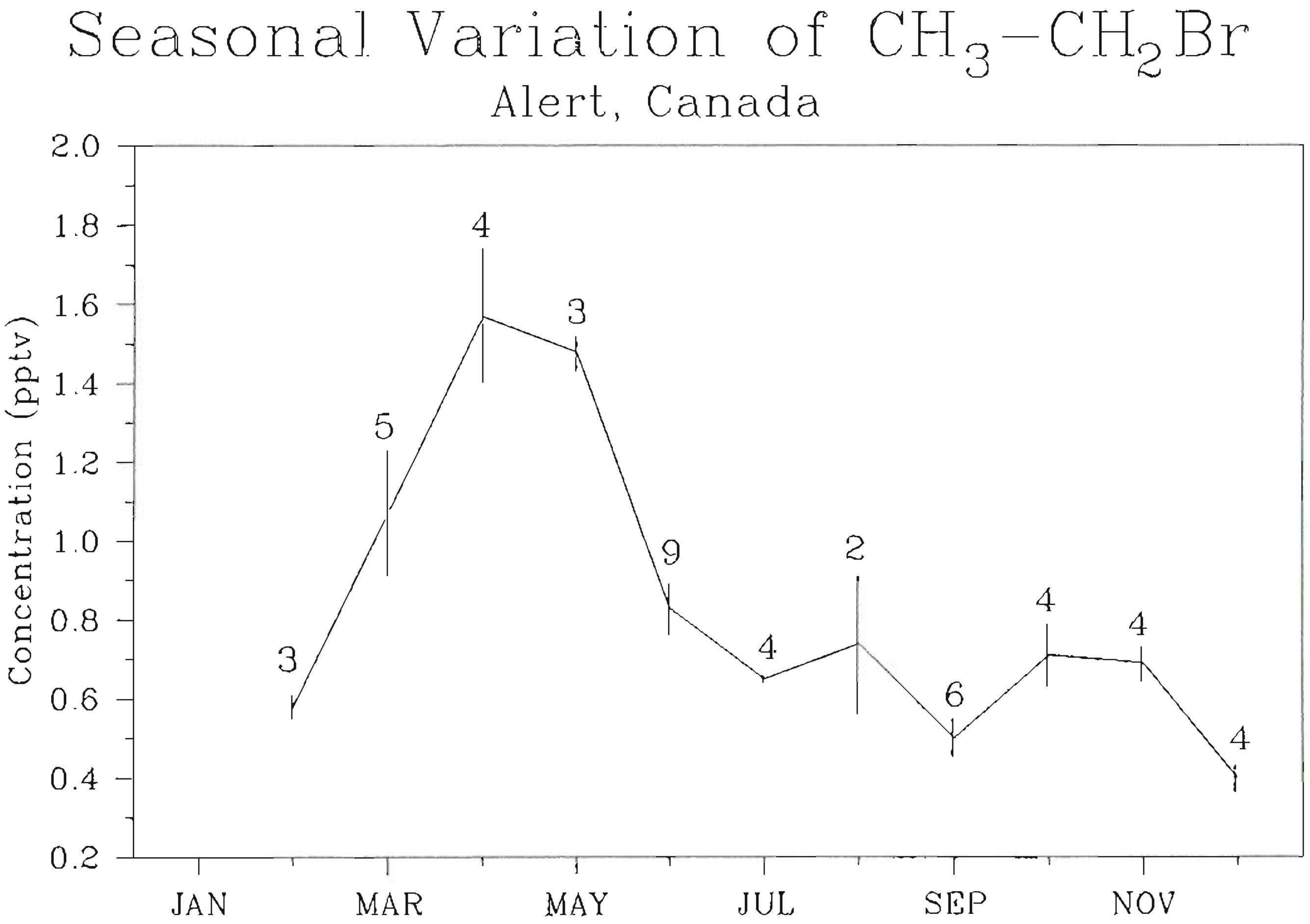


Figure D.9 : Monthly mean CH_3-CH_2Br concentrations at Alert, Canada (Error bars are ±1 Standard error)

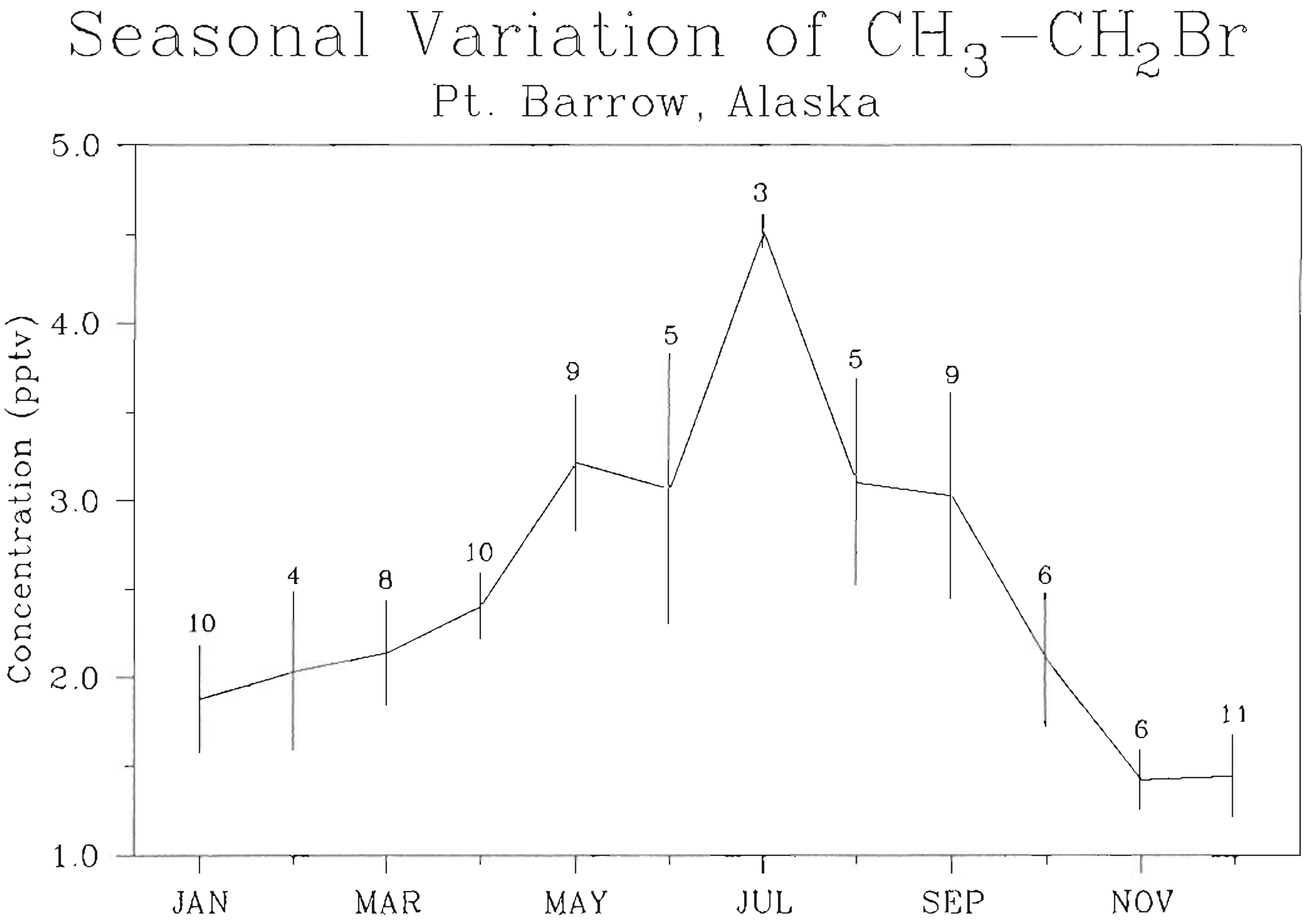


Figure D.10 : Monthly mean CH_3-CH_2Br concentrations at Pt. Barrow, Alaska
(Error bars are ±1 Standard error)

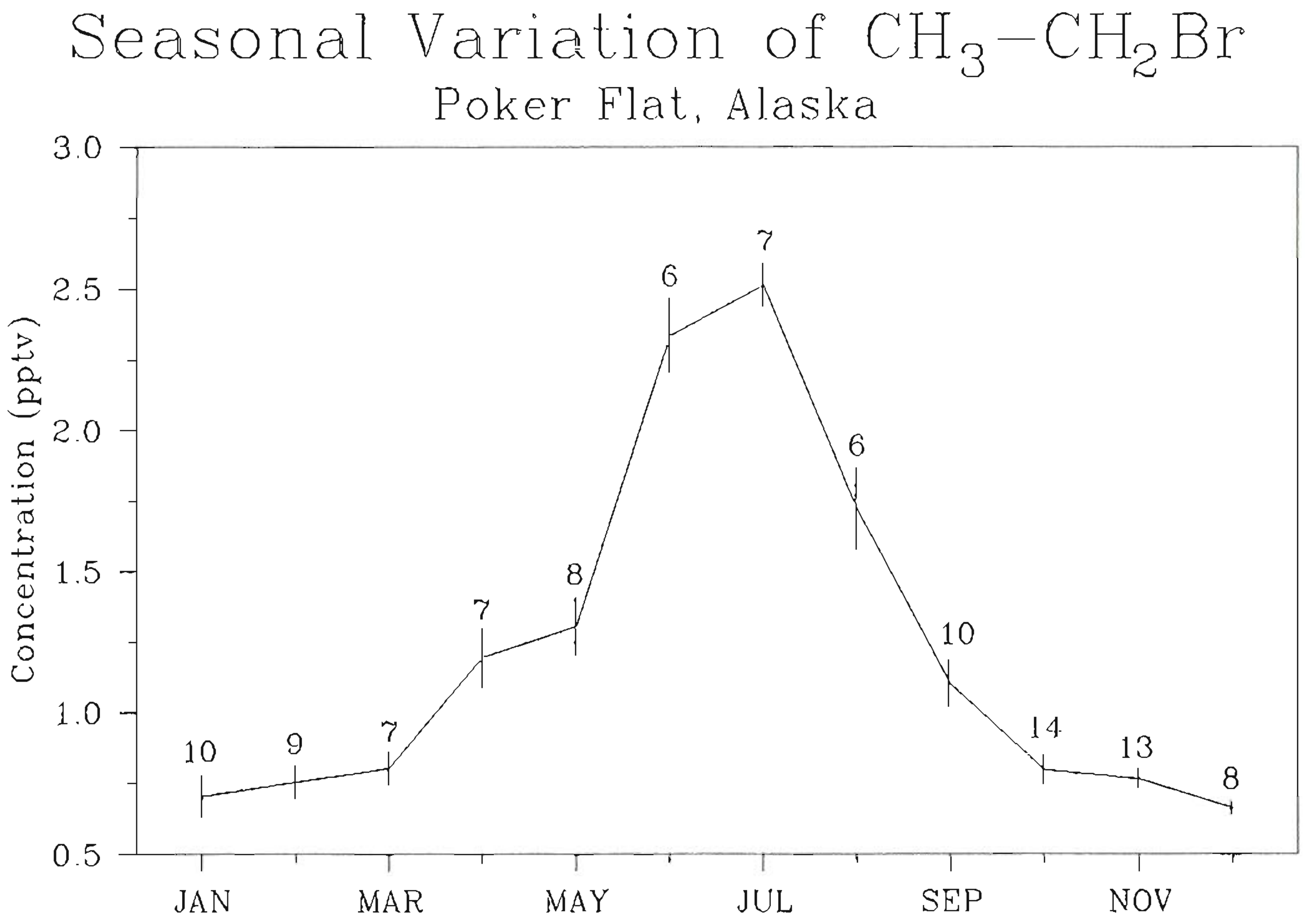


Figure D.11 : Monthly mean CH_3-CH_2Br concentrations at Poker Flat, Alaska (Error bars are ±1 Standard error)

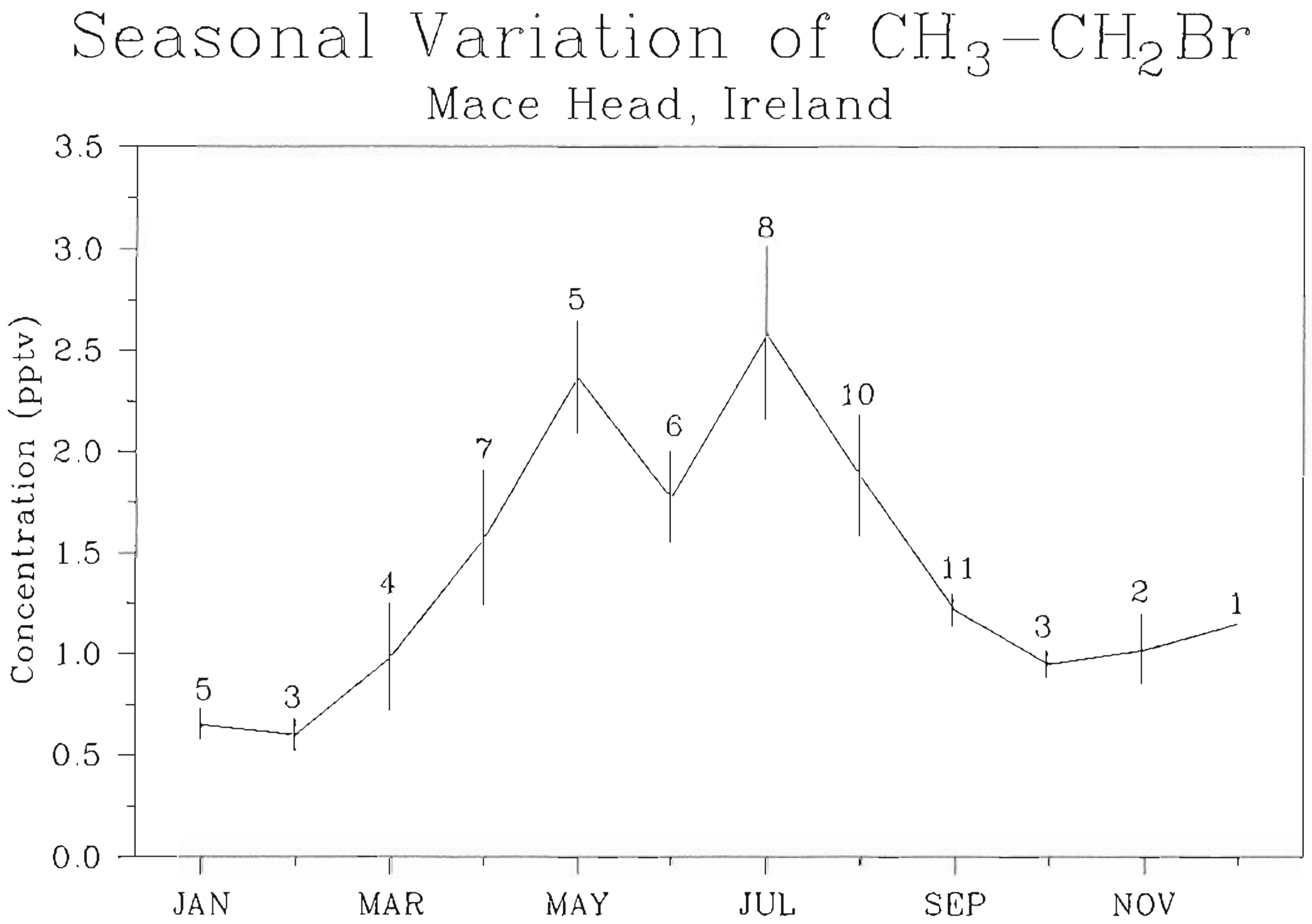


Figure D.12 : Monthly mean CH_3-CH_2Br concentrations at Mace Head, Ireland (Error bars are ±1 Standard error)

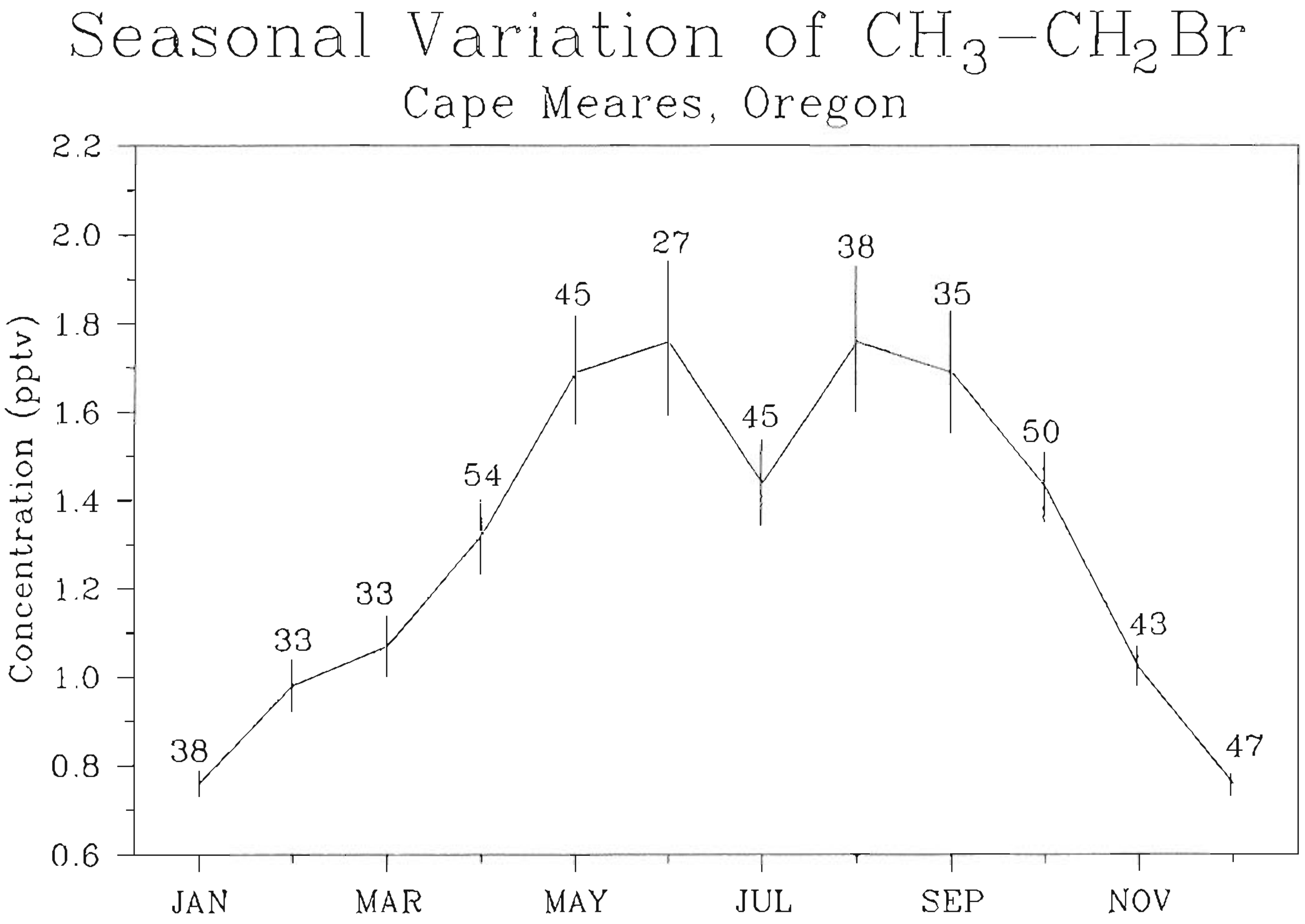


Figure D.13 : Monthly mean CH_3-CH_2Br concentrations at Cape Meares, Oregon (Error bars are ±1 Standard error)

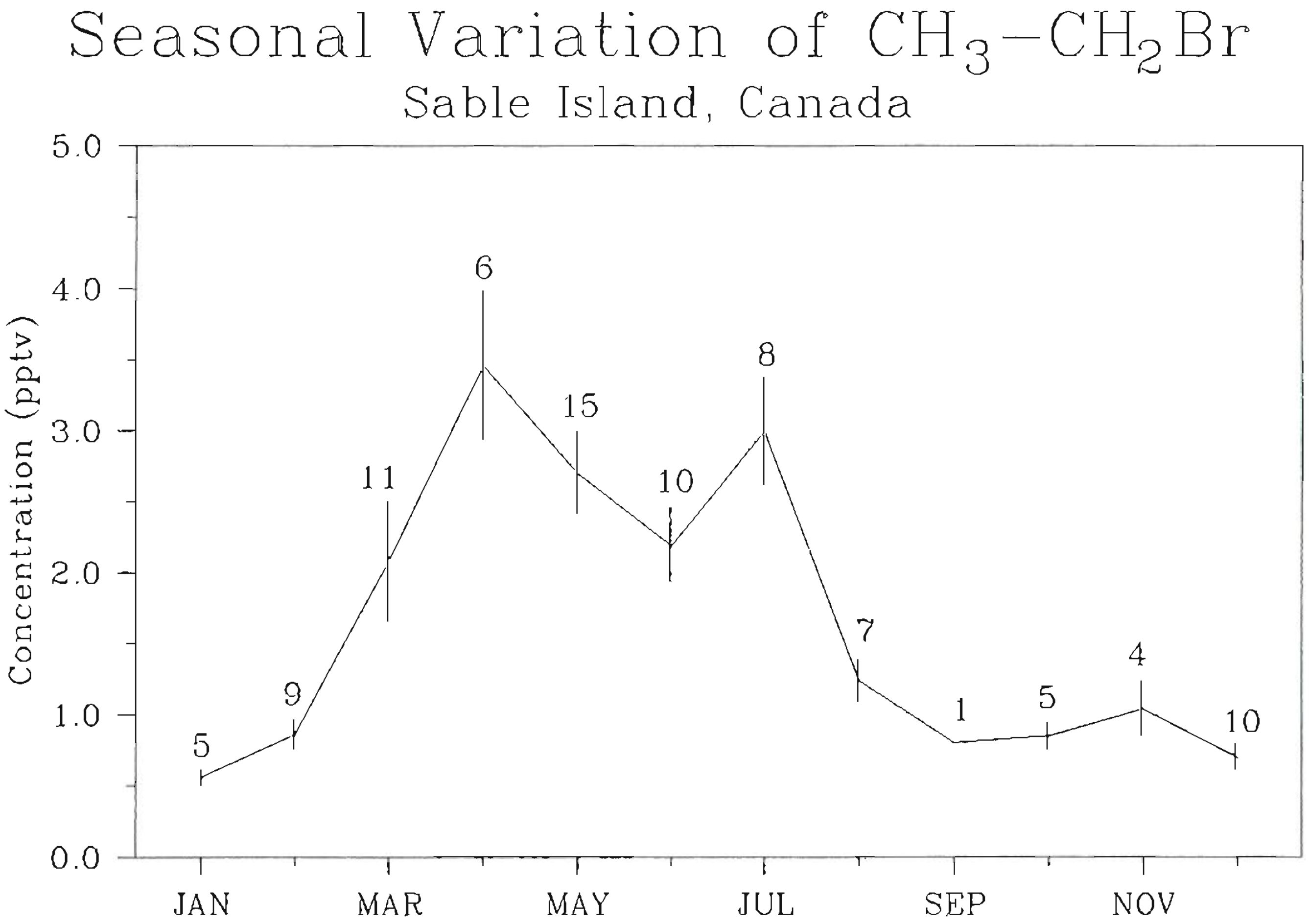


Figure D.14 : Monthly mean CH_3-CH_2Br concentrations at Sable Island, Canada (Error bars are ±1 Standard error)

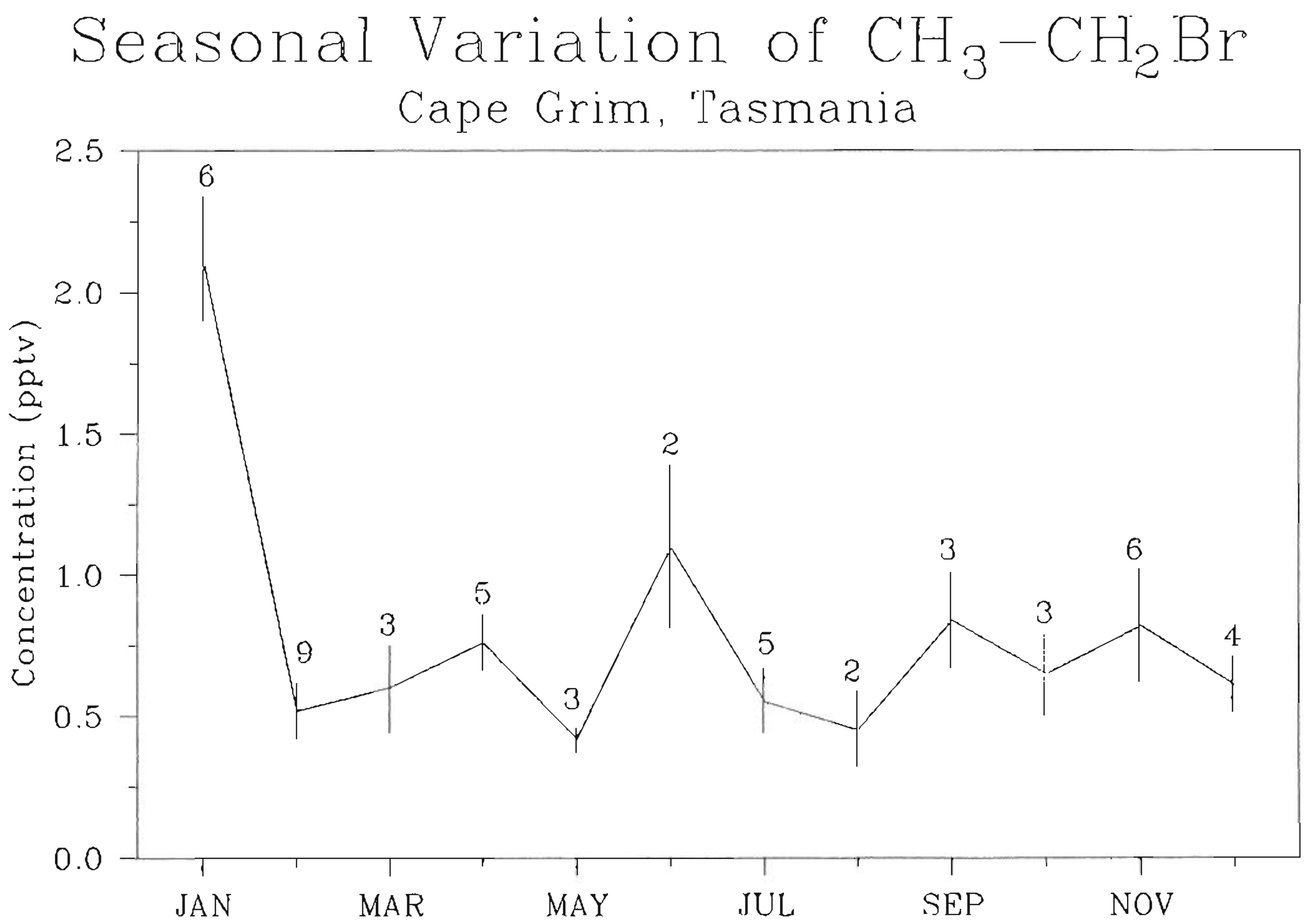


Figure D.15 : Monthly mean CH_3-CH_2Br concentrations at Cape Grim, Tasmania (Error bars are ±1 Standard error)

Seasonal Variations of CH_2BrCl at Cape Meares, Oregon

Samples collected at Cape Meares from September 1984 through December 1987 were analyzed for CH_2BrCl using Systems III, IV and V. The results plotted in Figure D.16 showed a significantly lower mean CH_2BrCl concentration, 1.3±0.5 pptv, during the time period August to October than the average CH_2BrCl concentration during rest of the year, 1.6±0.5 pptv (t-test, 95% level)

Seasonal Variations of CH_2BrCl at St. Croix, U.S. Virgin Islands

Samples collected at St. Croix were analyzed for CH_2BrCl using System V. The results showed significantly higher mean CH_2BrCl concentration during the month of March, 2.0±0.1 pptv, than during rest of the year, 1.4±0.4 pptv (t-test, 95% level). The results are plotted in Figure D.17.

Seasonal Variations of CH_2BrCl at Cape Grim, Tasmania

Samples from Cape Grim collected September of 1984 through October of 1987 were analyzed for CH_2BrCl using Systems III, IV and V. The results plotted in Figure D.18 showed significantly higher average CH_2BrCl concentration in October and November, 1.6±0.7 pptv, than the average CH_2BrCl concentration during rest of the year 1.0±0.4 pptv (t-test, 95% level).

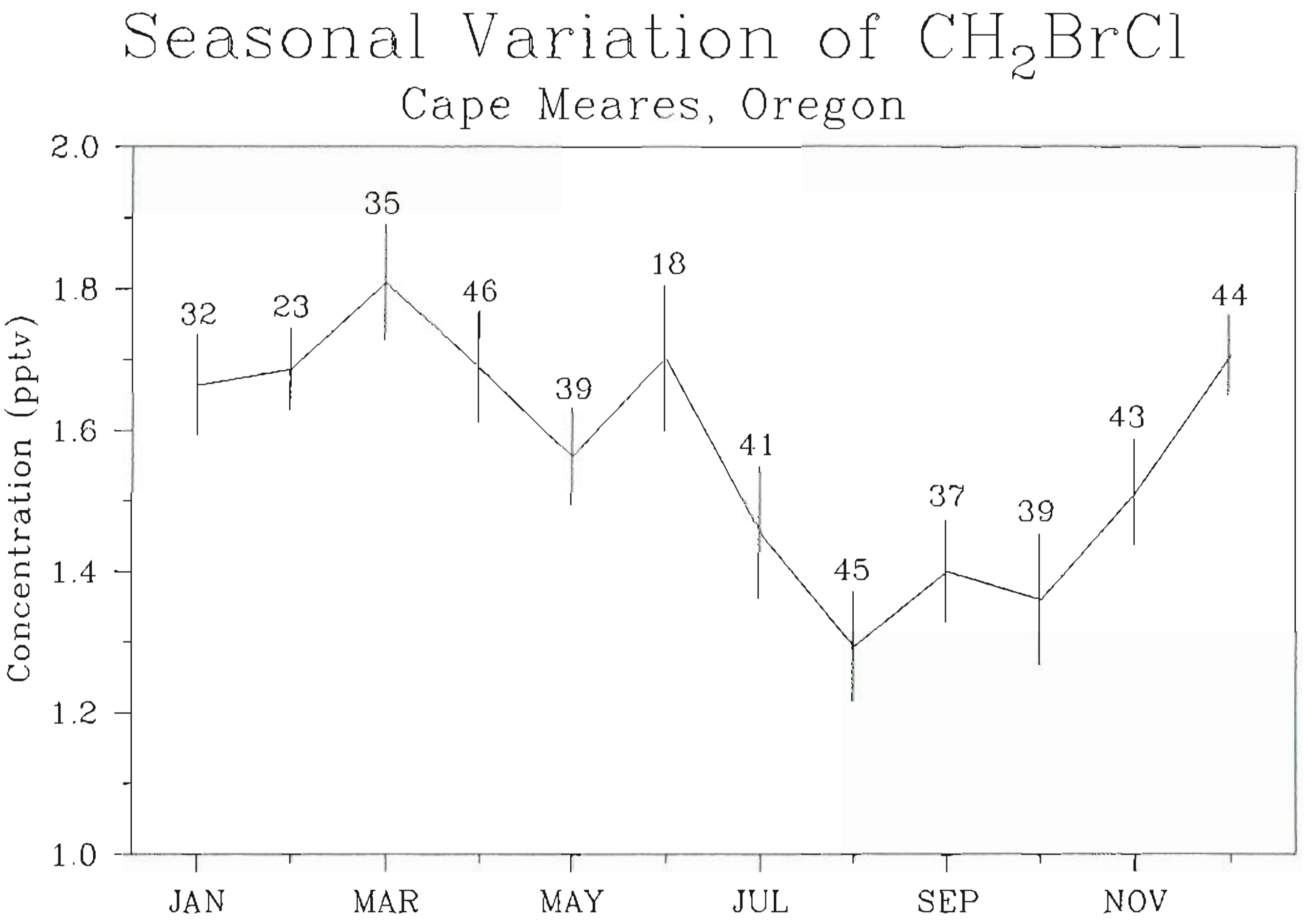


Figure D.16 : Monthly mean CH_2BrCl concentrations at Cape Meares, Oregon (Error bars are ±1 Standard error)

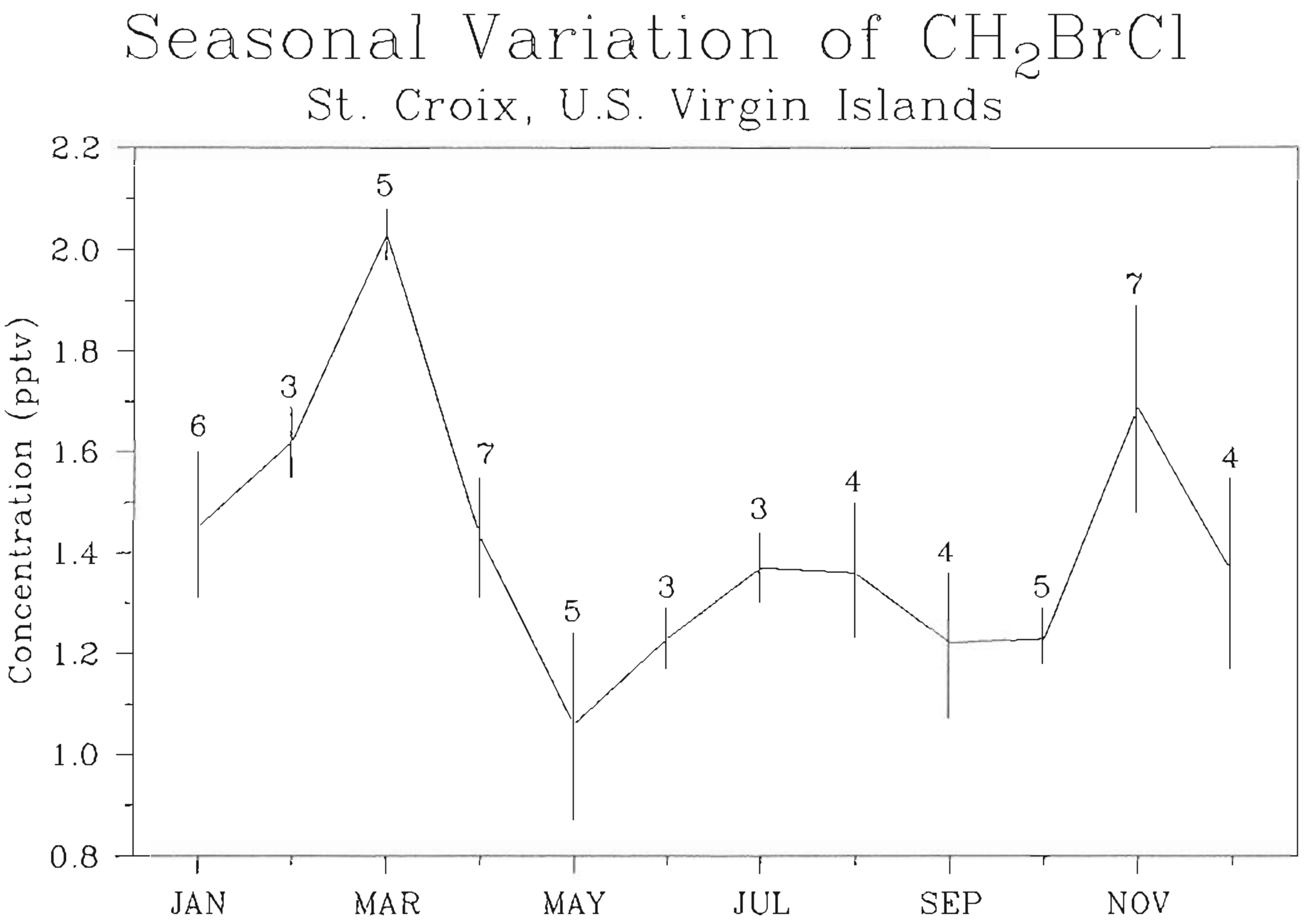


Figure D.17 : Monthly mean CH_2BrCl concentrations at St. Croix, U.S. Virgin Islands (Error bars are ±1 Standard error)

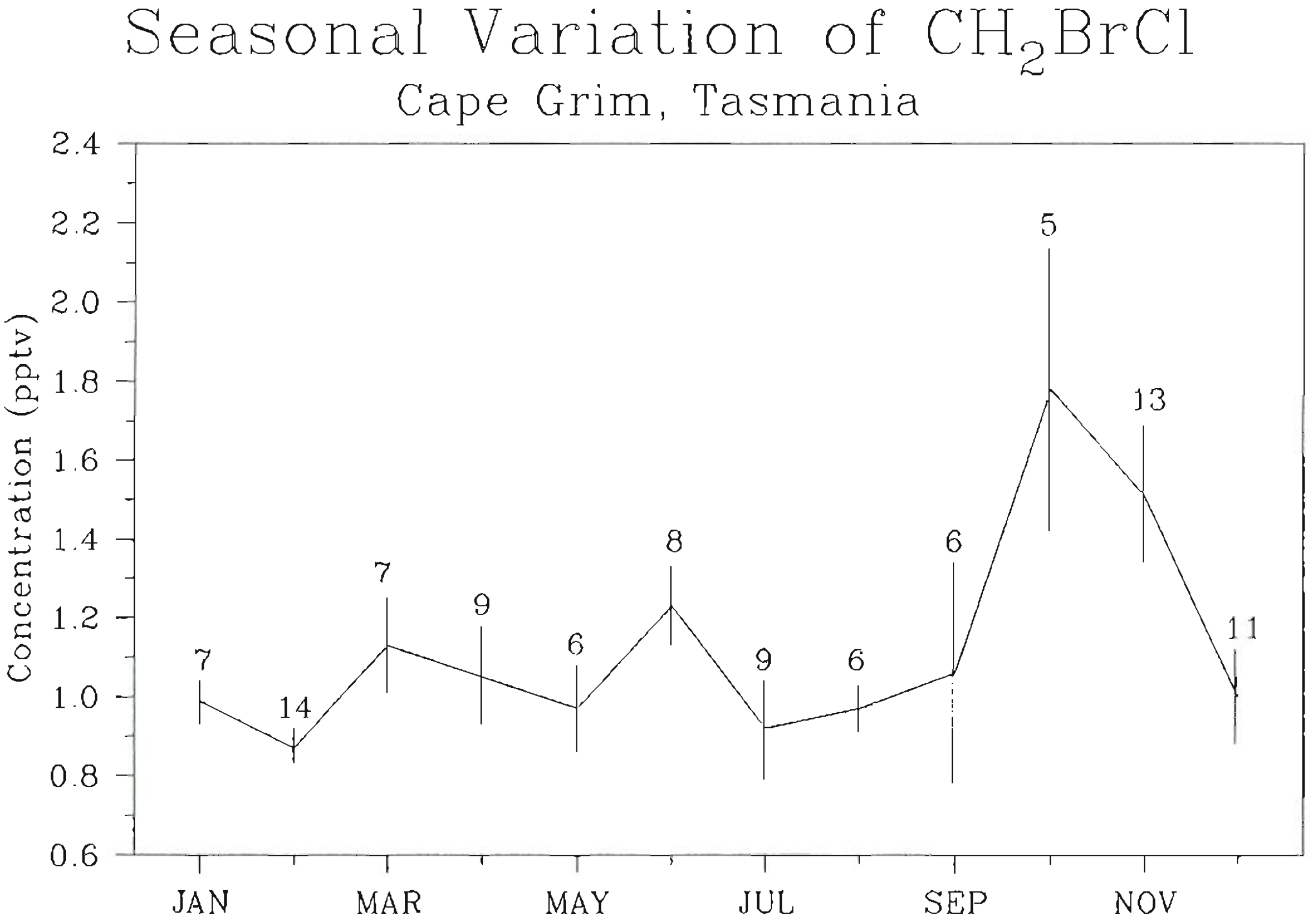


Figure D.18 : Monthly mean CH_2BrCl concentrations at Cape Grim, Tasmania
(Error bars are ±1 Standard error)

Seasonal Variations of CH_2Br_2 at Alert, Canada

Samples collected at Alert were analyzed for CH_2Br_2 using System V. The results showed a significantly higher mean CH_2Br_2 concentration in July, 9.1±0.2 pptv, than the value during rest of the year, 4.0±1.0 pptv (t-test, 95% level). The results are plotted in Figure D.19.

Seasonal Variations of CH_2Br_2 at Pt. Barrow, Alaska

Samples collected at Point Barrow from December 1982 through November 1987 were analyzed for CH_2Br_2 using Systems II - V. The results were plotted as monthly mean concentrations over twelve months in Figure D.20. This figure showed a mean CH_2Br_2 concentration in May (6.1±3.3 pptv) that was higher than the value during the rest of the year (4.4±1.4). This difference was not statistically significant at the 95% level. At the 90% level, the difference was significant.

Seasonal Variations of CH_2Br_2 at Poker Flat, Alaska

Samples collected at Poker Flat from 1985 through 1987 were analyzed using Systems IV and V. The results plotted in Figure D.21 showed higher mean CH_2Br_2 concentration in August (5.3±1.9 pptv) and lower mean CH_2Br_2 value during October and November (3.1±0.8 pptv) than the CH_2Br_2 value during rest of the year (4.1±0.8 pptv). These differences were statistically significant (t-test, 95% level).

Seasonal Variations of CH_2Br_2 at Mace Head, Ireland

Samples collected at Mace Head from May 1986 through October 1987 were analyzed using System V. The results indicated significantly higher (t-test, 95% level) mean CH_2Br_2 concentration (7.4±1.8 pptv) during the months November through May than the mean CH_2Br_2 concentration during June through October (5.2±0.7 pptv). This is shown in Figure D.22.

Seasonal Variations of CH_2Br_2 at Sable Island, Canada

Samples from Sable Island collected from October 1985 through 1987 were analyzed using System V. The results indicated significantly higher mean CH_2Br_2 concentration (8.7±2.5 pptv) during June through November than the mean CH_2Br_2 value during rest of the year (5.8±1.5 pptv). The elevated CH_2Br_2 levels during June through October can be seen in Figure D.23 (t-test, 95% level).

Seasonal Variations of CH_2Br_2 at Cape Matatula, Samoa

Samples collected in Samoa from December 1982 through November 1987 were analyzed using Systems II - V. The results plotted in Figure D.24 showed significantly lower (t-test, 95% level) mean CH_2Br_2 concentration during the month of February (2.8±0.3 pptv) as compared to the mean CH_2Br_2 value during rest of the year (3.9±1.3 pptv).

Seasonal Variations of CH_2Br_2 at Cape Grim, Tasmania

Samples collected at Cape Grim from September 1982 through October 1987 were analyzed using Systems II - V. The results were plotted as monthly mean CH_2Br_2 concentrations over twelve months in Figure D.25. This figure showed higher mean CH_2Br_2 concentration (9.0 ± 2.9 pptv) in October than during rest of the year (4.3 ± 1.3 pptv). This difference was statistically significant (t-test, 95% level).

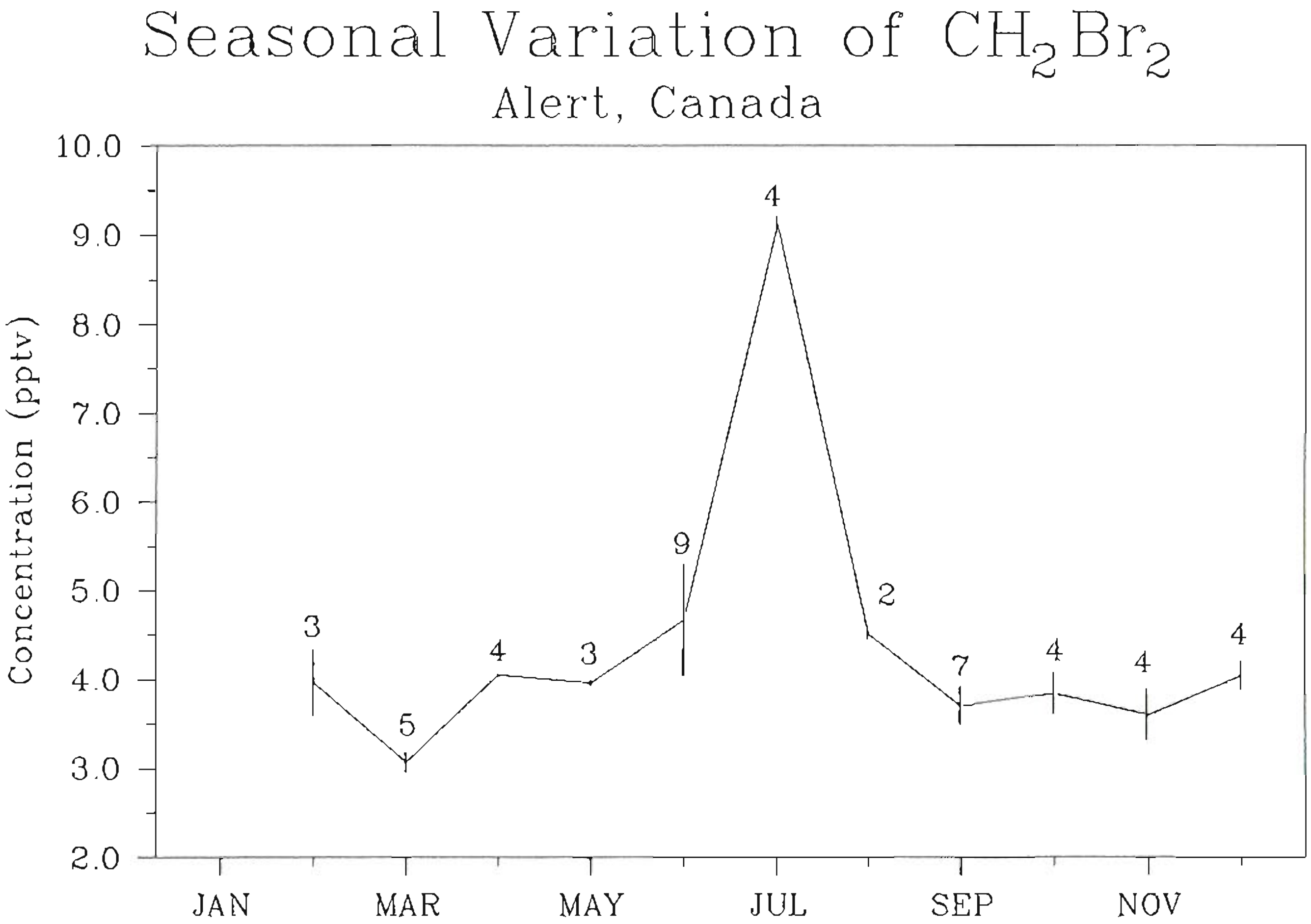


Figure D.19 : Monthly mean CH_2Br_2 concentrations at Alert, Canada
(Error bars are ±1 Standard error)

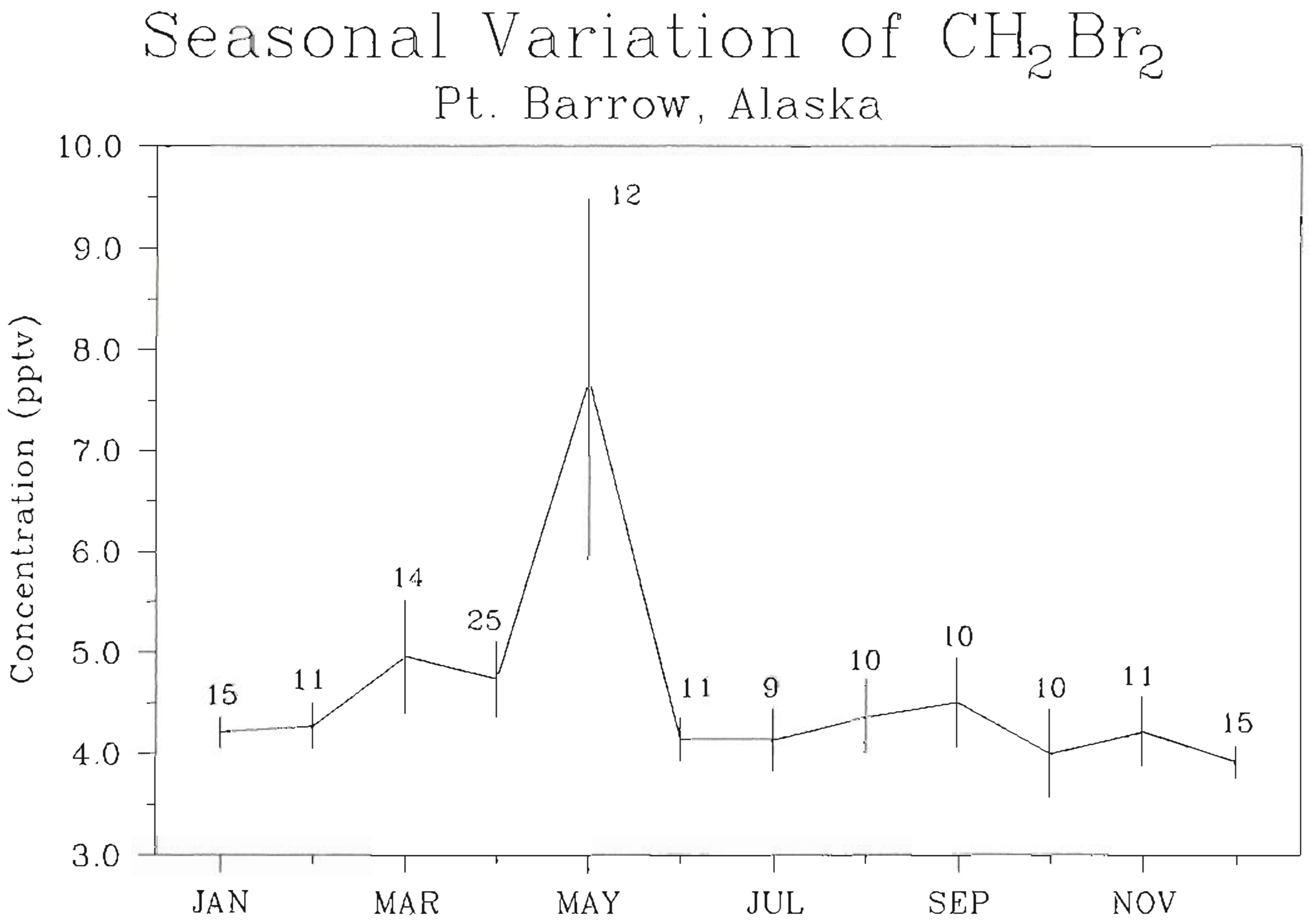


Figure D.20 : Monthly mean CH_2Br_2 concentrations at Pt. Barrow, Alaska
(Error bars are ±1 Standard error)

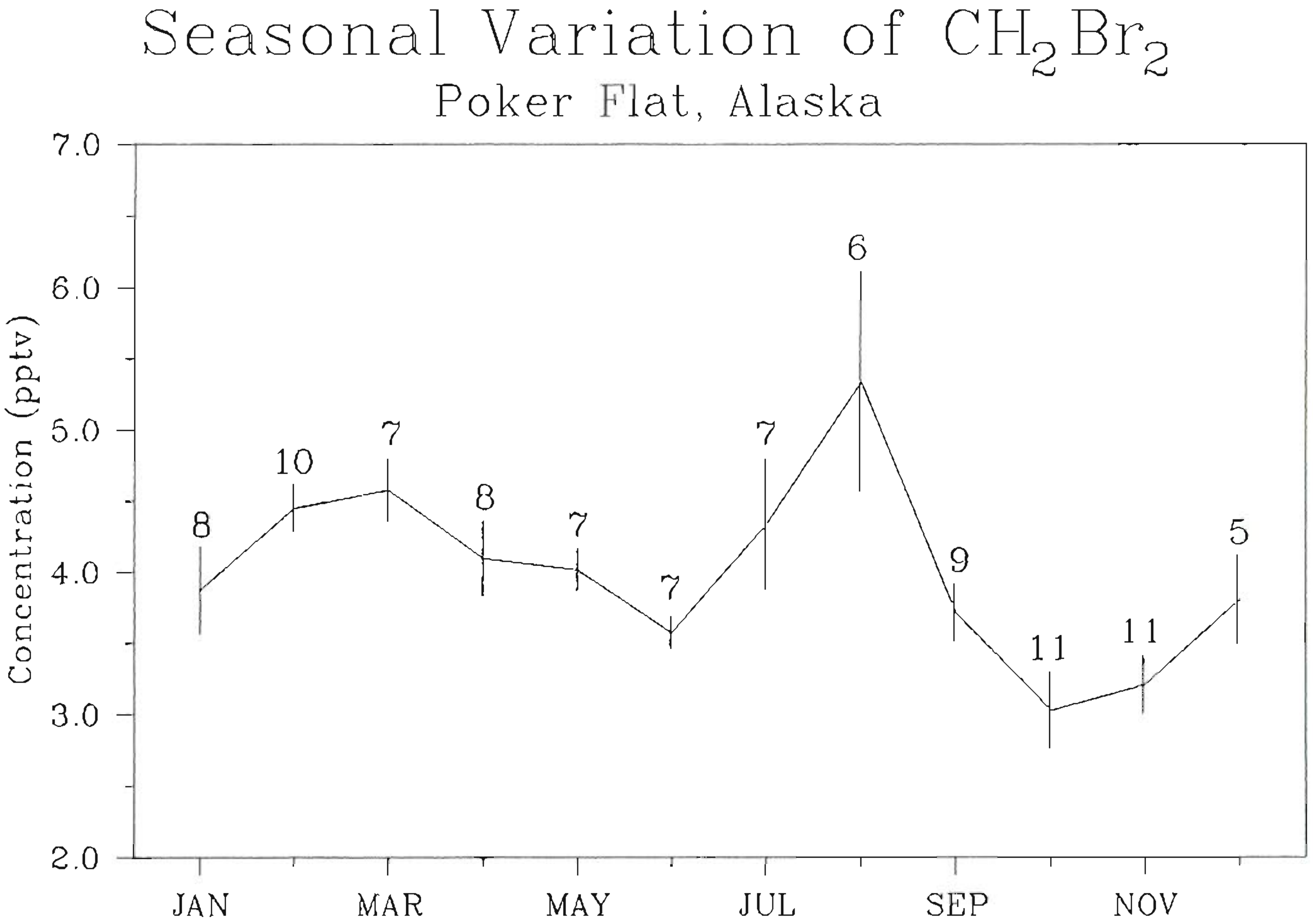


Figure D.21 : Monthly mean CH_2Br_2 concentrations at Poker Flat, Alaska (Error bars are ±1 Standard error)

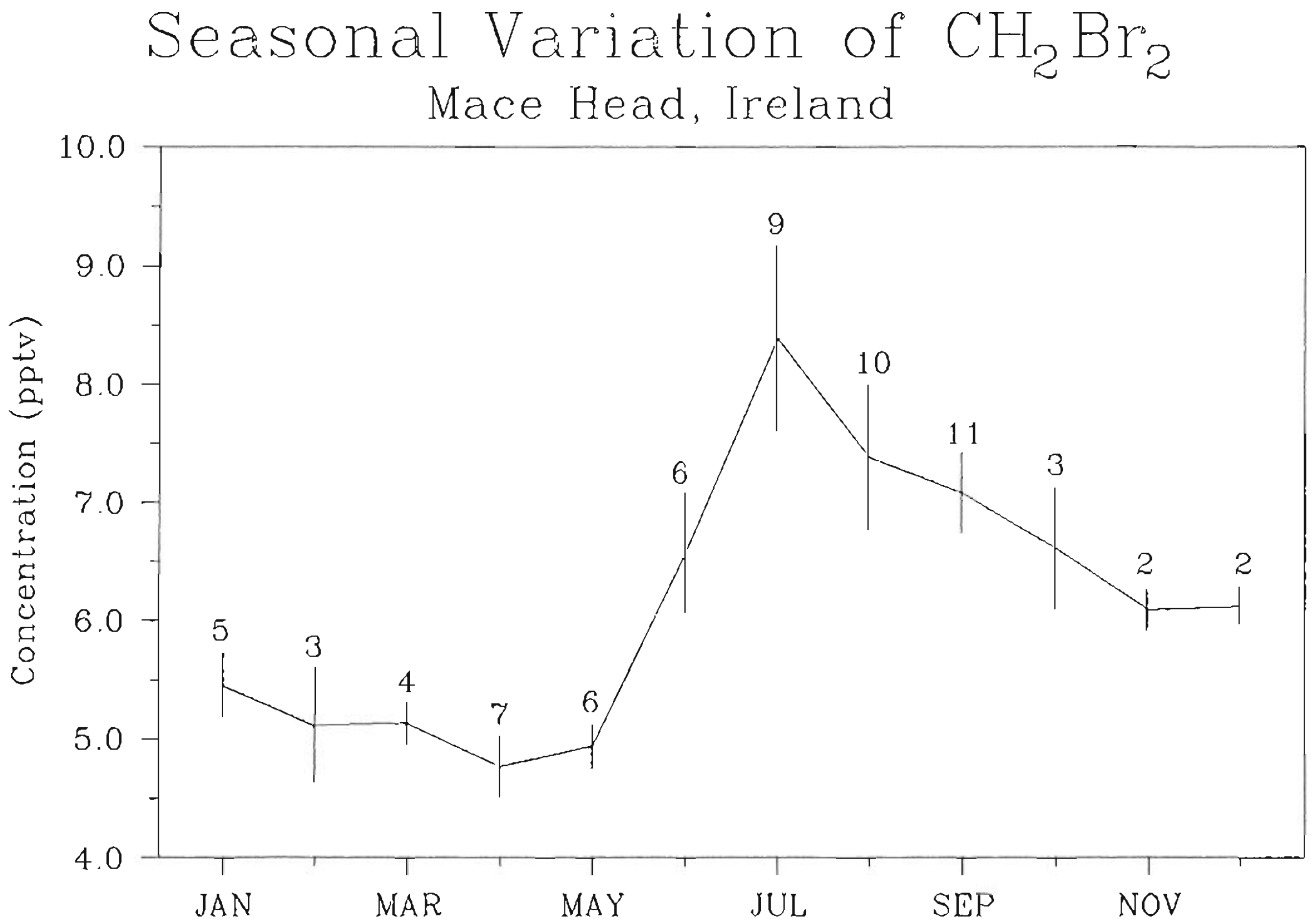


Figure D.22 : Monthly mean CH_2Br_2 concentrations at Mace Head, Ireland (Error bars are ±1 Standard error)

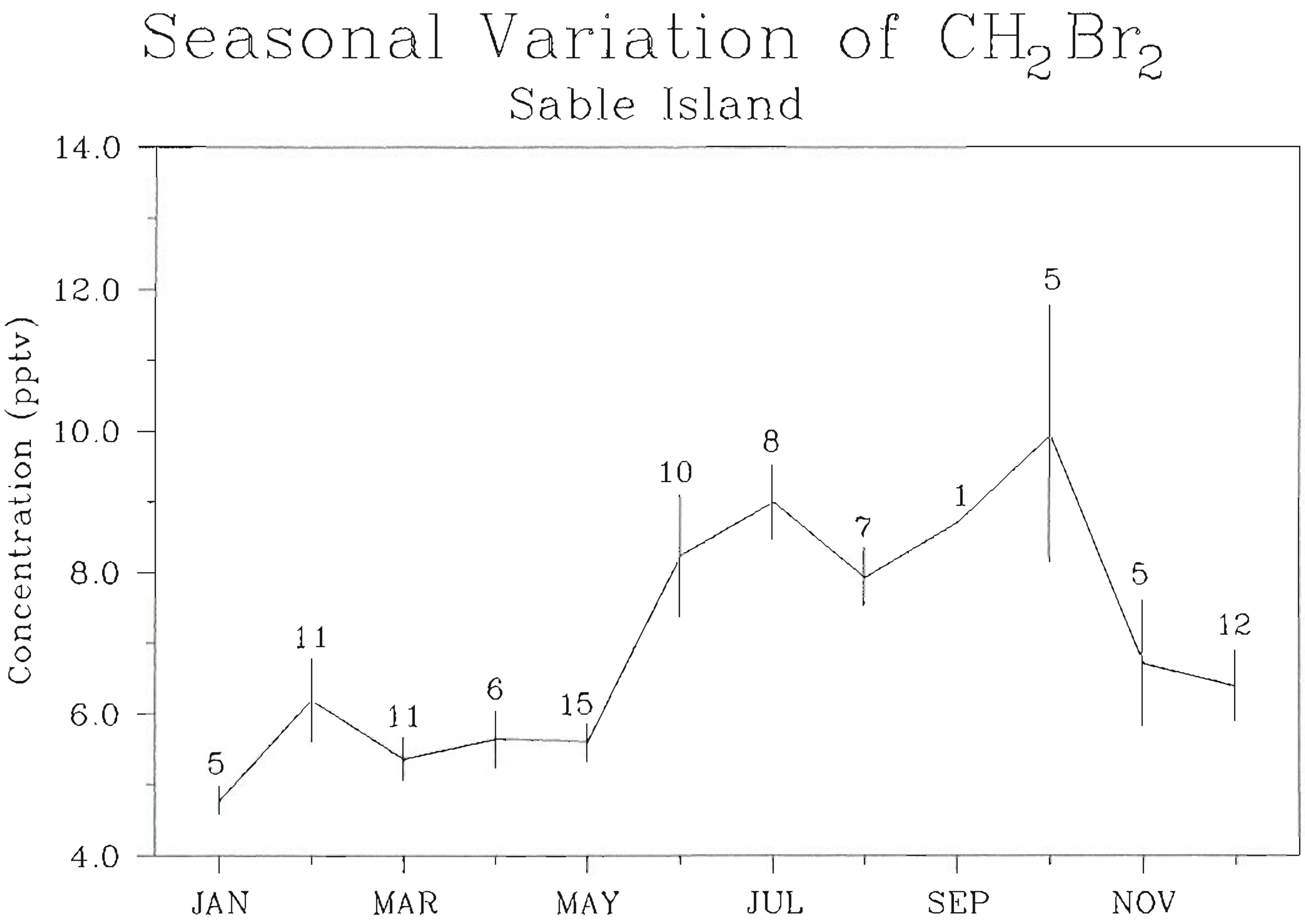


Figure D.23 : Monthly mean CH_2Br_2 concentrations at Sable Island, Canada (Error bars are ±1 Standard error)

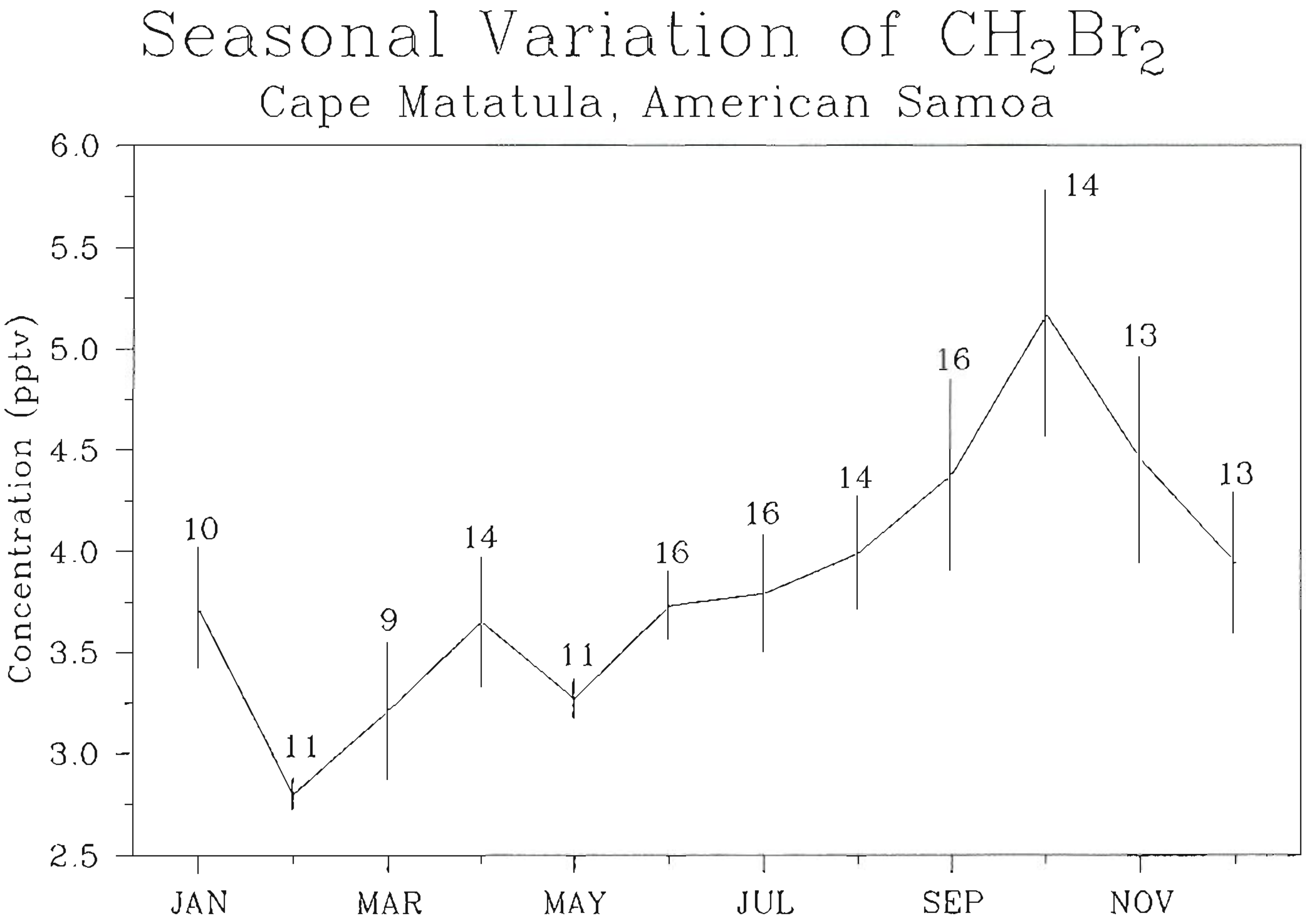


Figure D.24 : Monthly mean CH_2Br_2 concentrations at Cape Matatula, Samoa (Error bars are ±1 Standard error)

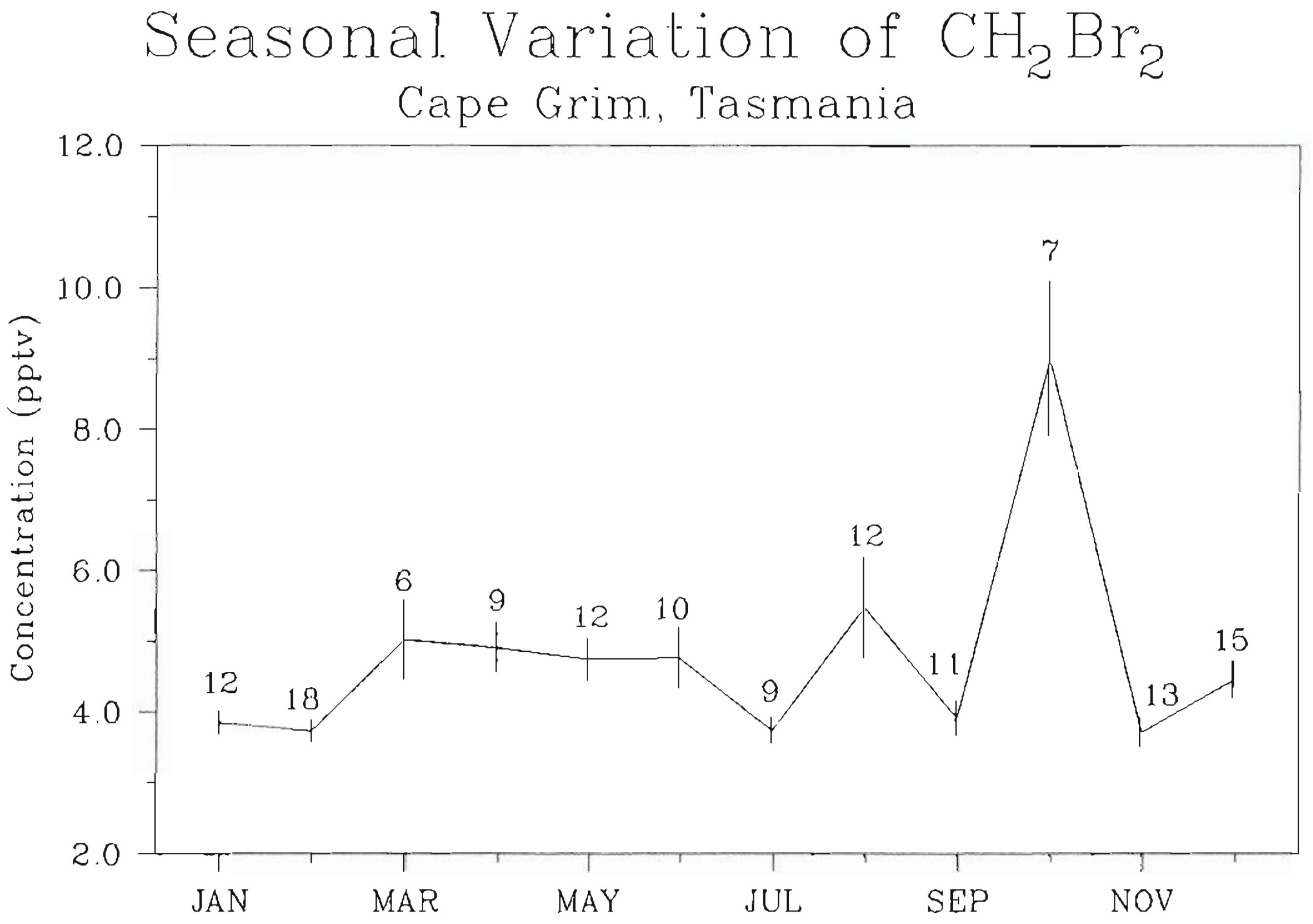


Figure D.25 : Monthly mean CH_2Br_2 concentrations at Cape Grim, Tasmania (Error bars are ±1 Standard error)

Seasonal Variations of $CHBr_2Cl$ at Pt. Barrow, Alaska

Samples collected at Point Barrow from February 1984 through September 1986 were analyzed using Systems III - V. The results showed significantly higher (t-test, 95% level) mean $CHBr_2Cl$ concentration during the months March through May (1.6±0.6 pptv) than the mean value during rest of the year (1.1±0.4 pptv). This difference can be seen in Figure D.26.

Seasonal Variations of $CHBr_2Cl$ at Cape Meares, Oregon

Samples collected at Cape Meares from February 1984 through September 1986 were analyzed using Systems III - V. The results were plotted in Figure D.27. This figure showed depleted levels of $CHBr_2Cl$ (0.8±0.3 pptv) during the months of June through August as compared to rest of the year (1.2±0.3 pptv). The difference was statistically significant (t-test, 95% level).

Seasonal Variations of $CHBr_2Cl$ at Cape Matatula, Samoa

Samples collected in Samoa from February 1984 through July 1986 were analyzed using Systems III - V. The results indicated a significantly higher (t-test, 95% level) mean $CHBr_2Cl$ concentration in May (1.4±0.4 pptv) than the mean value during rest of the year (0.9±0.4 pptv). This is seen in Figure D.28 where the mean monthly $CHBr_2Cl$ concentrations are plotted over twelve months.

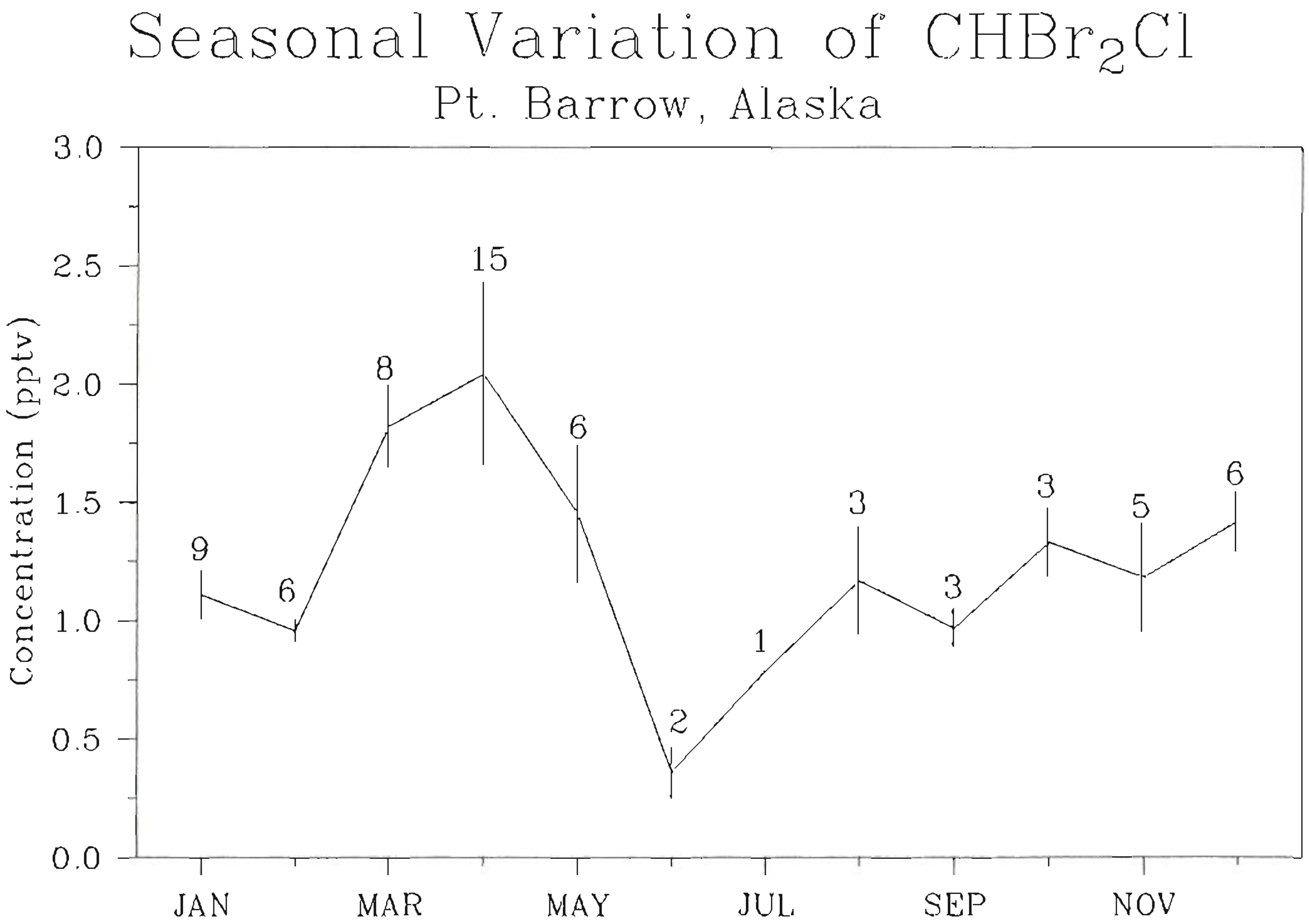


Figure D.26 : Monthly mean $CHBr_2Cl$ concentrations at Pt. Barrow, Alaska
(Error bars are ±1 Standard error)

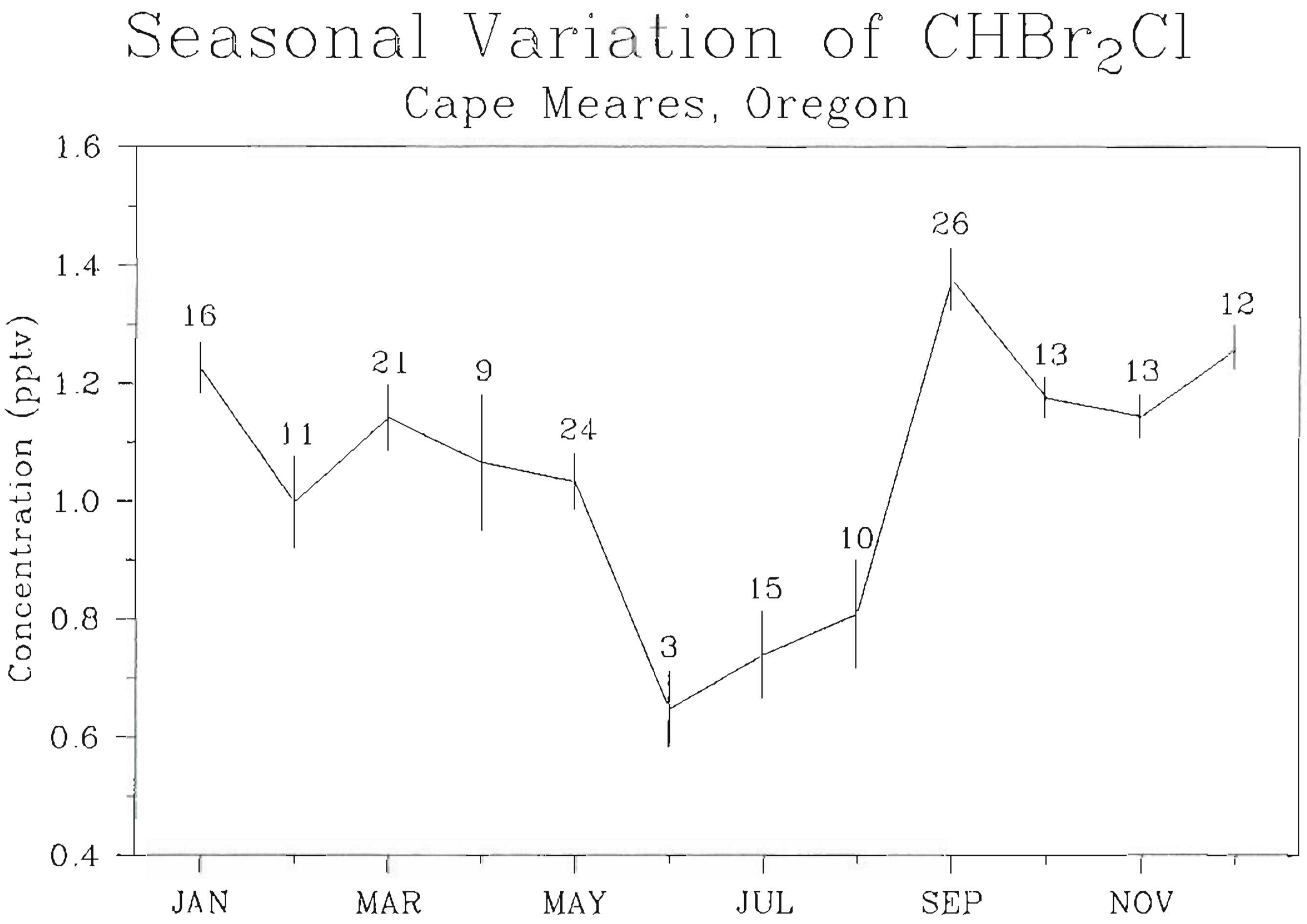


Figure D.27 : Monthly mean $CHBr_2Cl$ concentrations at Cape Meares, Oregon
(Error bars are ±1 Standard error)

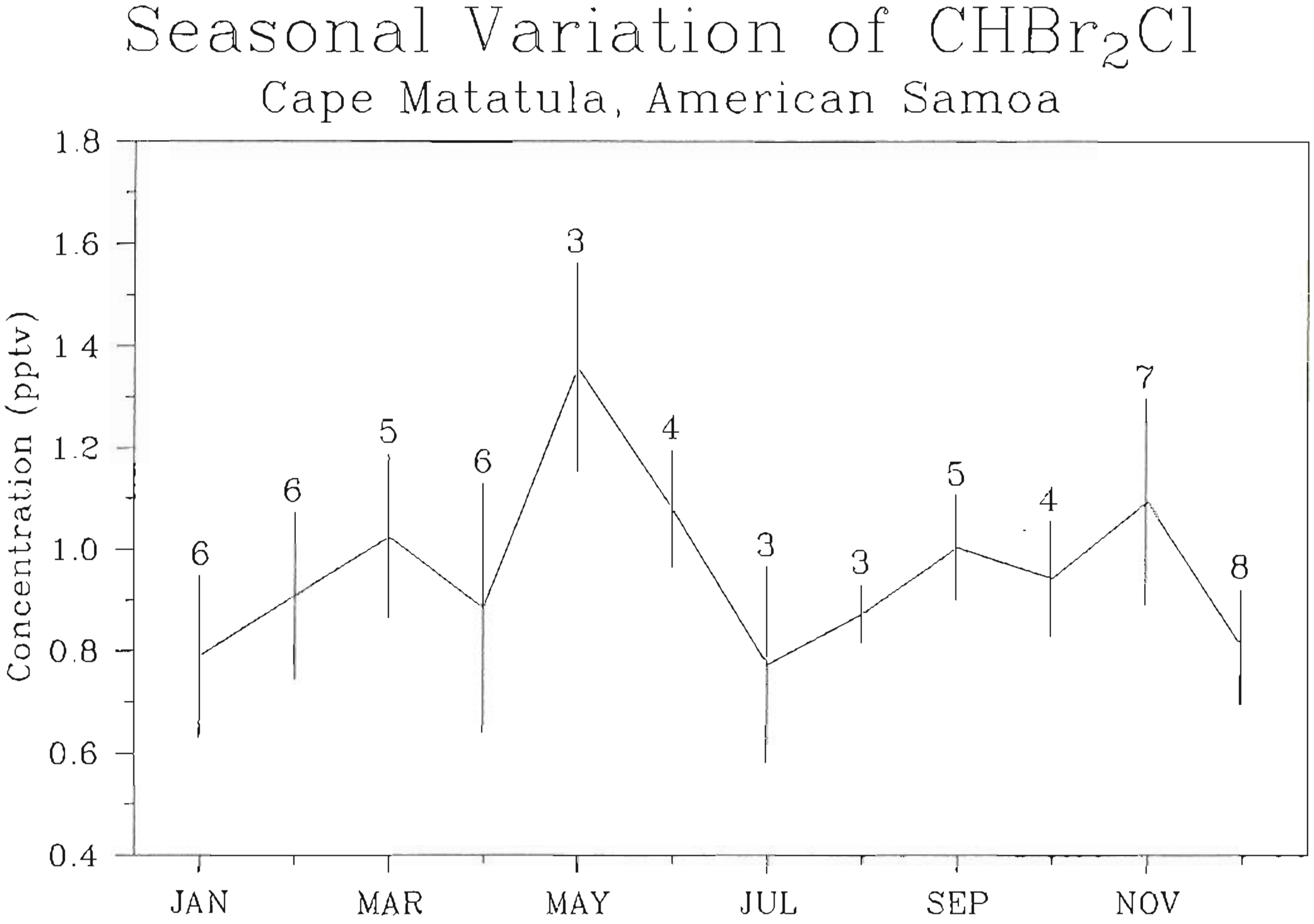


Figure D.28 : Monthly mean $CHBr_2Cl$ concentrations at Cape Matatula, Samoa
(Error bars are ± 1 Standard error)

Seasonal Variations of CH_2Br-CH_2Br at Alert, Canada

Samples collected at Alert from November 1985 through 1987 were analyzed using System V. The results were plotted in Figure D.29. This figure showed higher CH_2Br-CH_2Br concentrations during the months of June through August as compared to rest of the year. The mean concentrations during June through August, 2.4±1.7 pptv, was significantly higher (t-test, 95% level) than the value during rest of the year, 0.4±0.3 pptv.

Seasonal Variations of CH_2Br-CH_2Br at Pt. Barrow, Alaska

Samples collected at Point Barrow from December 1982 through November 1987 were analyzed using System II - V. The results showed a significantly lower mean CH_2Br-CH_2Br concentration, 0.8±0.7 pptv, during the months December through April than during rest of the year, 1.7±1.0 pptv. The monthly mean concentrations are plotted over twelve months are plotted in Figure D.30.

Seasonal Variations of CH_2Br-CH_2Br at Poker Flat, Alaska

Samples collected at Poker Flat from 1985 through 1987 were analyzed using Systems IV - V. The results were plotted in Figure D.31. This figure showed higher CH_2Br-CH_2Br concentrations during the months of June through September as compared to rest of the year. The mean CH_2Br-CH_2Br concentration (2.2±1.0 pptv) was significantly higher (t-test, 95% level) than the mean value during rest of the year (0.5±0.4 pptv). The highest monthly value was observed in August (3.5±0.4).

Seasonal Variations of CH_2Br-CH_2Br at Mace Head, Ireland

Samples collected at Mace Head from May 1986 through 1987 were analyzed using System V. The results showed significantly higher (t-test, 95% level) mean CH_2Br-CH_2Br concentration during the months July through October (3.2±1.2 pptv) than the value during rest of the year (1.9±0.8 pptv). These results are plotted in Figure D.32 as monthly mean concentrations over twelve months.

Seasonal Variations of CH_2Br-CH_2Br at Cape Meares, Oregon

Samples collected at Cape Meares from December 1982 through December 1987 were analyzed using Systems II - V. The results plotted in Figure D.33 showed depleted levels of CH_2Br-CH_2Br during August as compared to rest of the year. The difference between the mean CH_2Br-CH_2Br concentration in August (0.7±0.4 pptv) and during rest of the year (1.0±0.6 pptv) was statistically significant (t-test, 95% level).

Seasonal Variations of CH_2Br-CH_2Br at St. Croix, U.S. Virgin Islands

Samples collected at St. Croix were analyzed using Systems III - V. The data, plotted as monthly mean concentrations over 12 months (Figure D.34) showed a higher average CH_2Br-CH_2Br concentration during the month of May (4.6±0.9 pptv) and a lower value during the month of December (0.5±0.2 pptv) than during rest of the year (1.3±0.8 pptv). These differences were statistically significant (t-test, 95% level).

Seasonal Variations of CH_2Br-CH_2Br at Cape Grim, Tasmania

Samples collected at Cape Grim from September 1982 through October 1987 were analyzed using Systems II - V. The results indicated significantly higher average CH_2Br-CH_2Br concentration during the months of March, June and October (2.2±1.6 pptv) than the mean value during rest of the year (1.0±0.8 pptv). These results are plotted in Figure D.35.

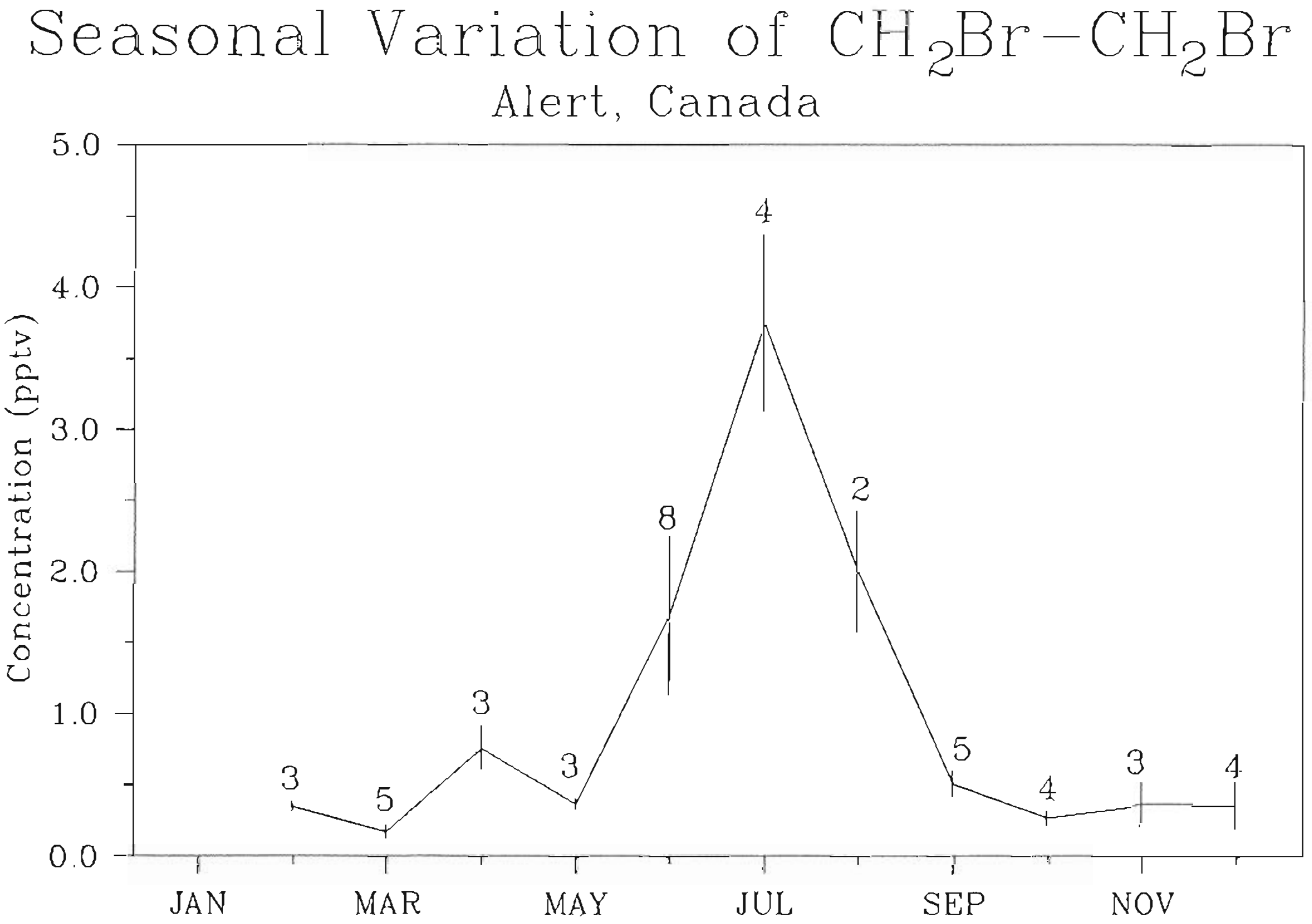


Figure D.29 : Monthly mean CH_2Br-CH_2Br concentrations at Alert, Canada (Error bars are ±1 Standard error)

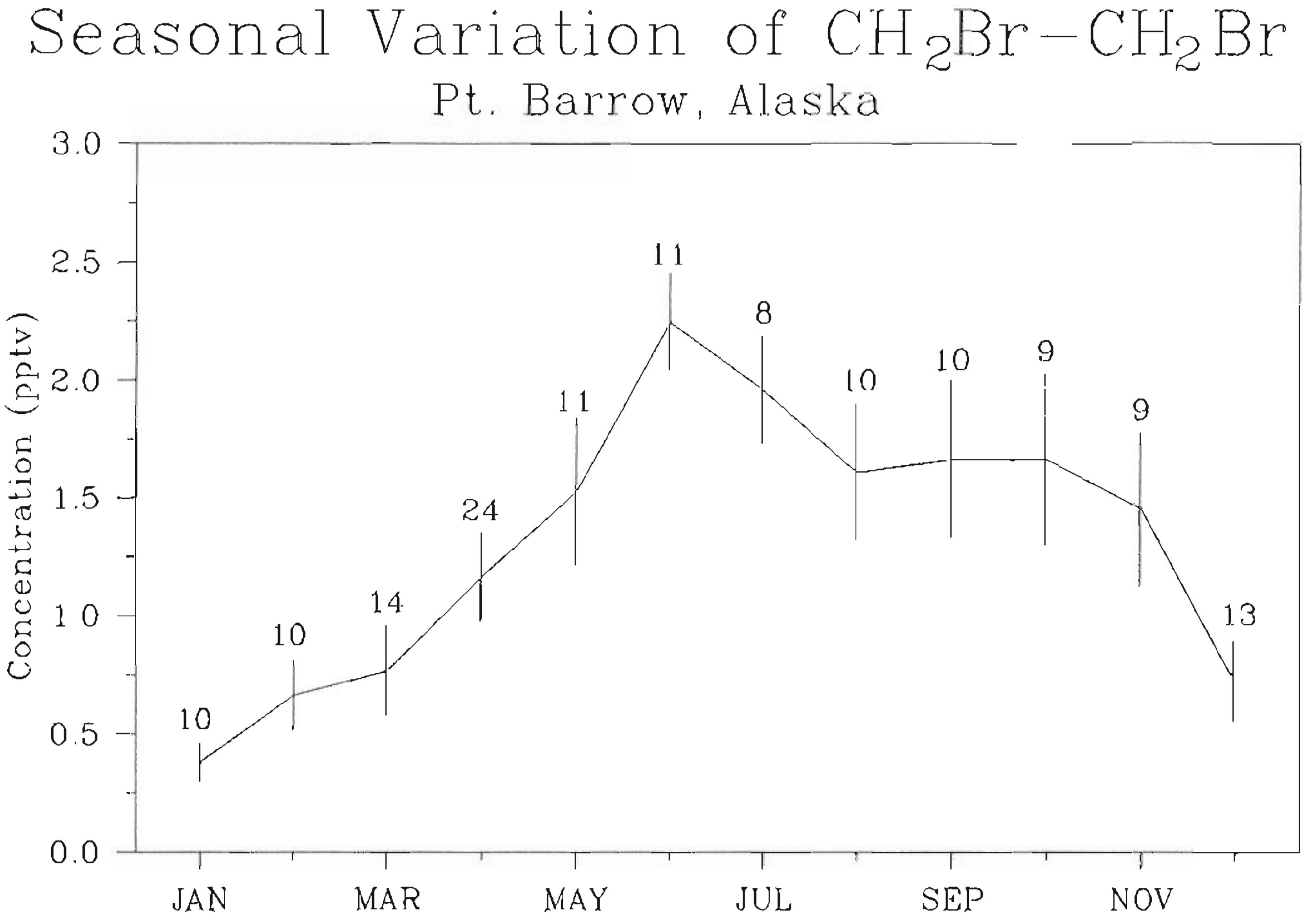


Figure D.30 : Monthly mean CH_2Br-CH_2Br concentrations at Pt. Barrow, Alaska (Error bars are ±1 Standard error)

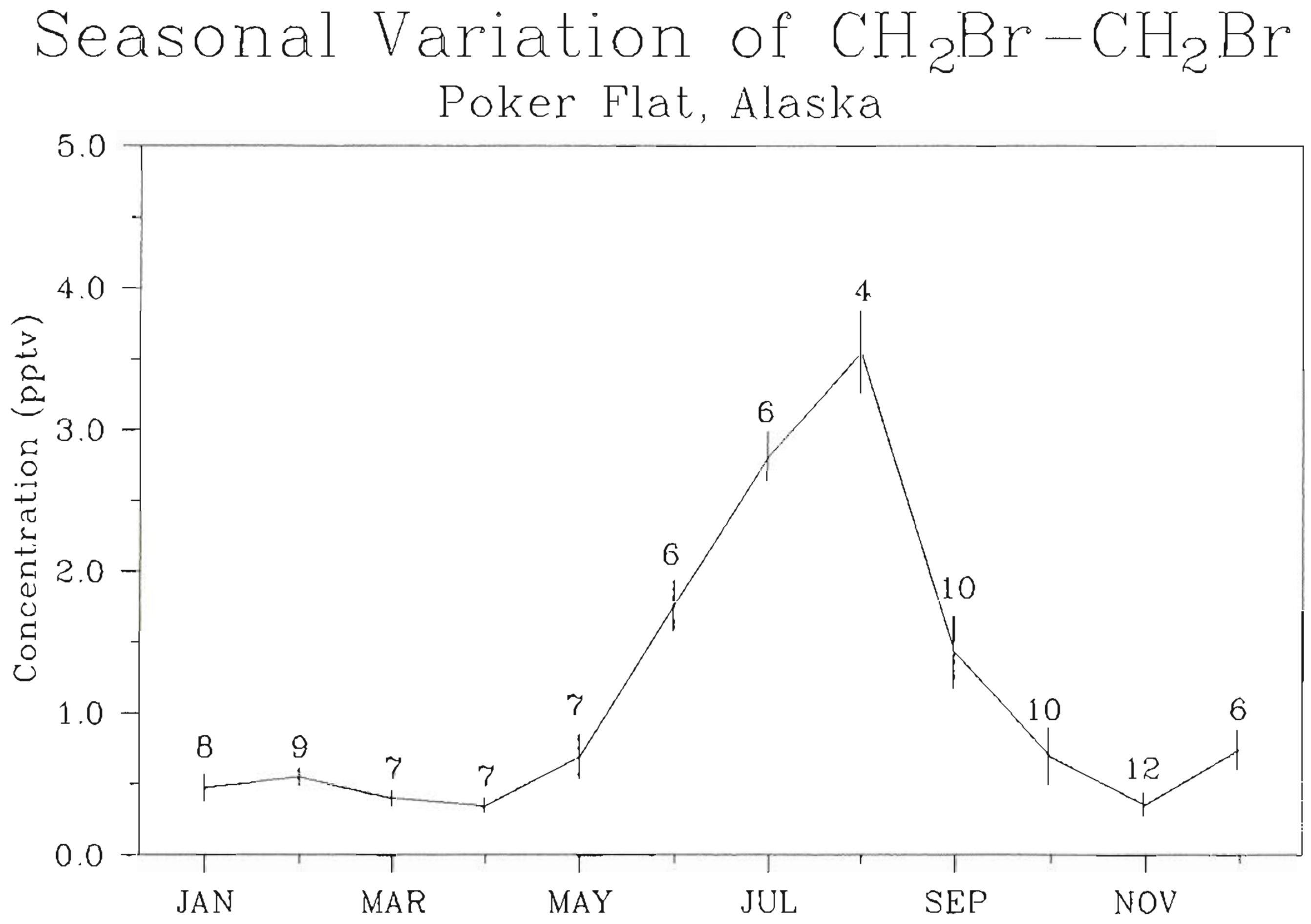


Figure D.31 : Monthly mean CH_2Br-CH_2Br concentrations at Poker Flat, Alaska (Error bars are ±1 Standard error)

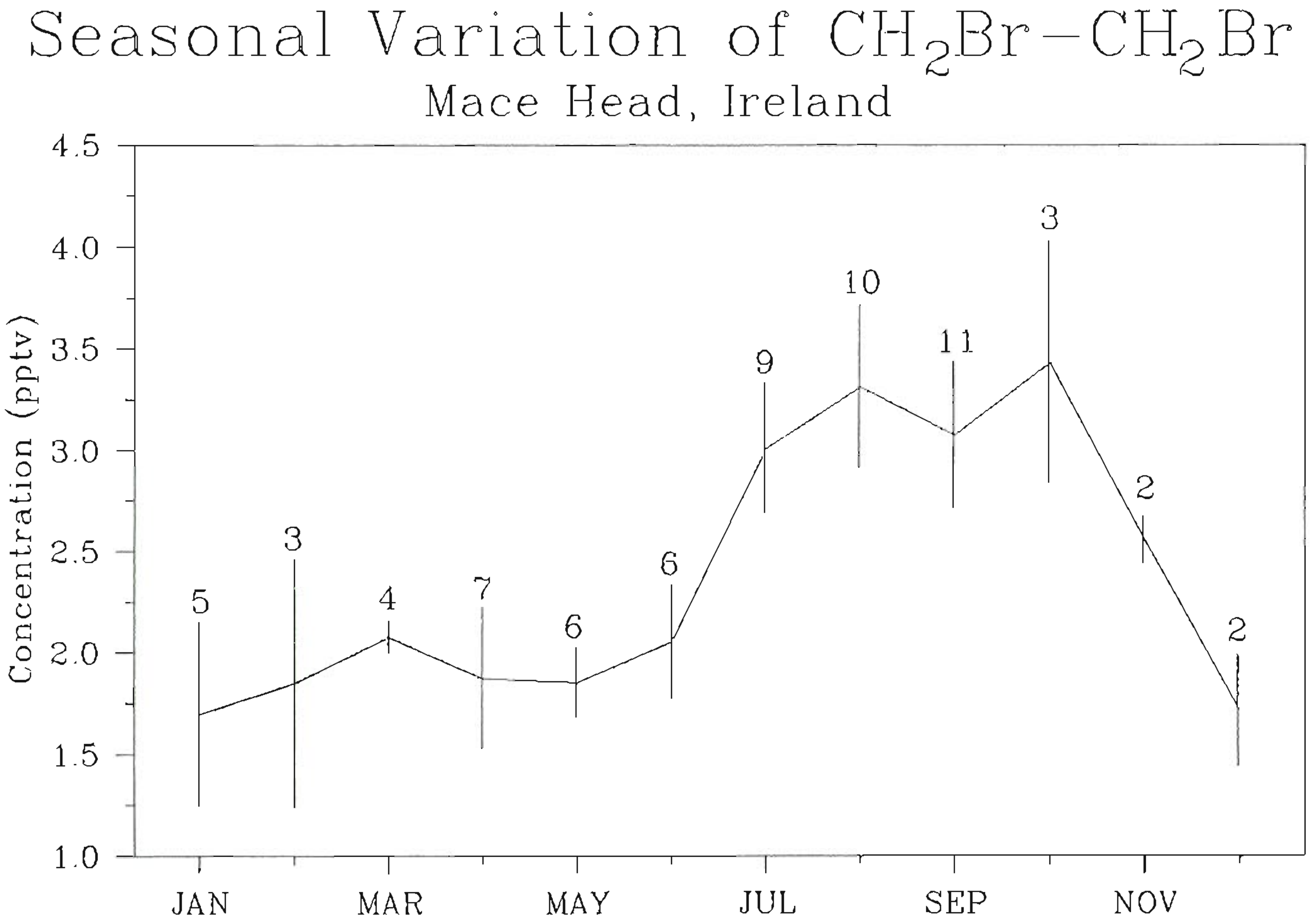


Figure D.32 : Monthly mean CH_2Br-CH_2Br concentrations at Mace Head, Ireland (Error bars are ±1 Standard error)

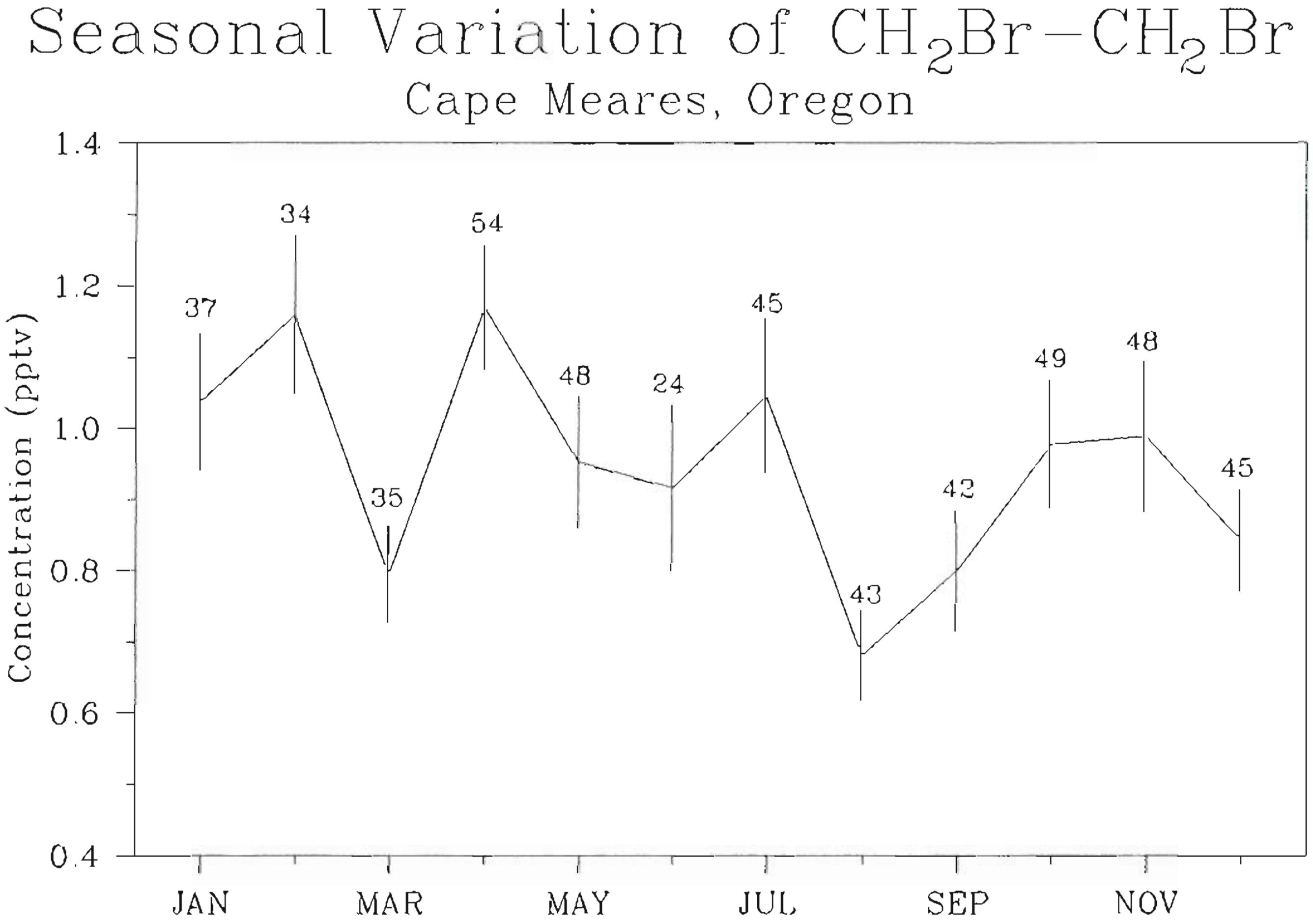


Figure D.33 : Monthly mean CH_2Br-CH_2Br concentrations at Cape Meares, Oregon (Error bars are ±1 Standard error)

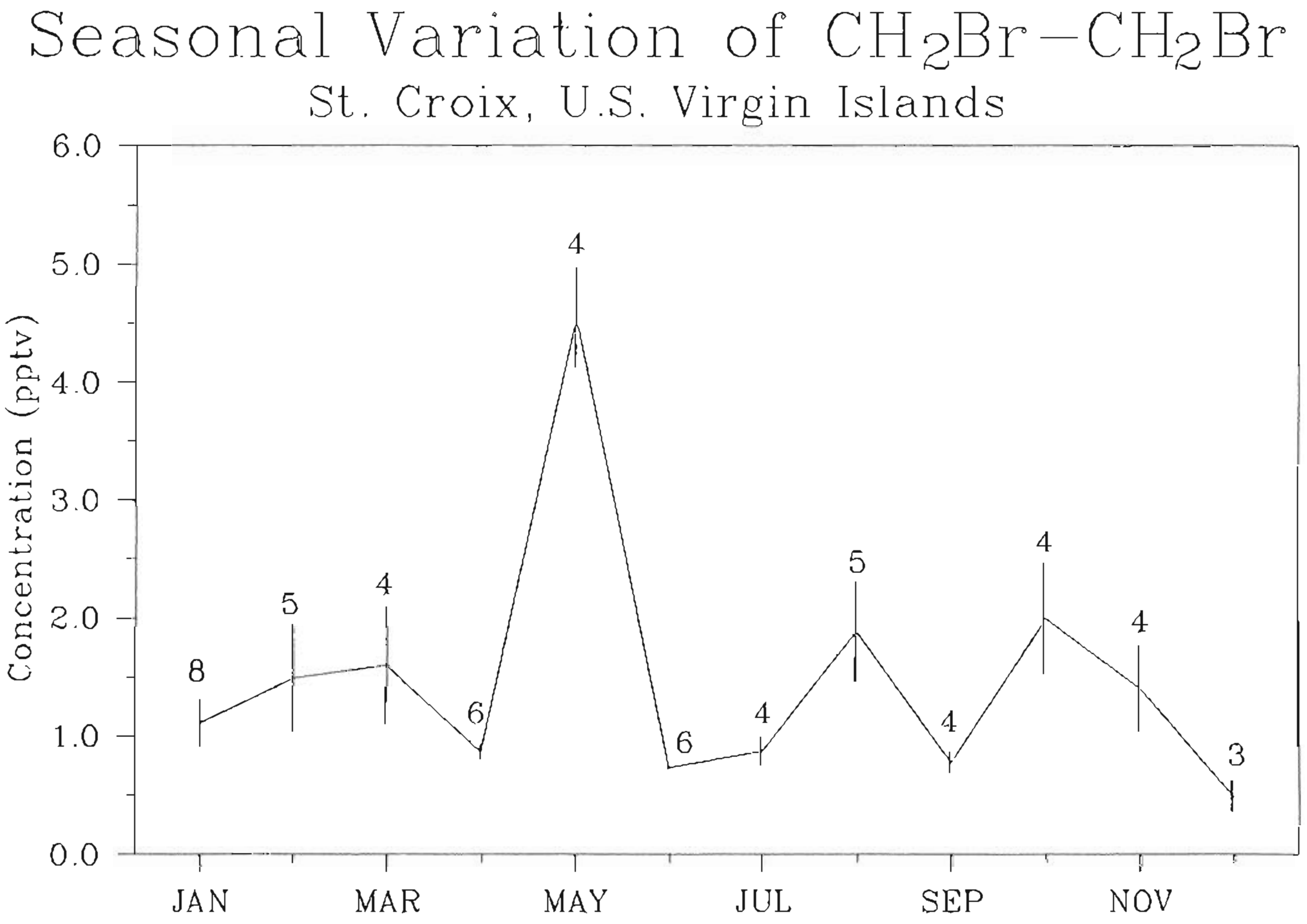


Figure D.34 : Monthly mean CH_2Br-CH_2Br concentrations at St. Croix, (Error bars are ±1 Standard error) U.S. Virgin Islands

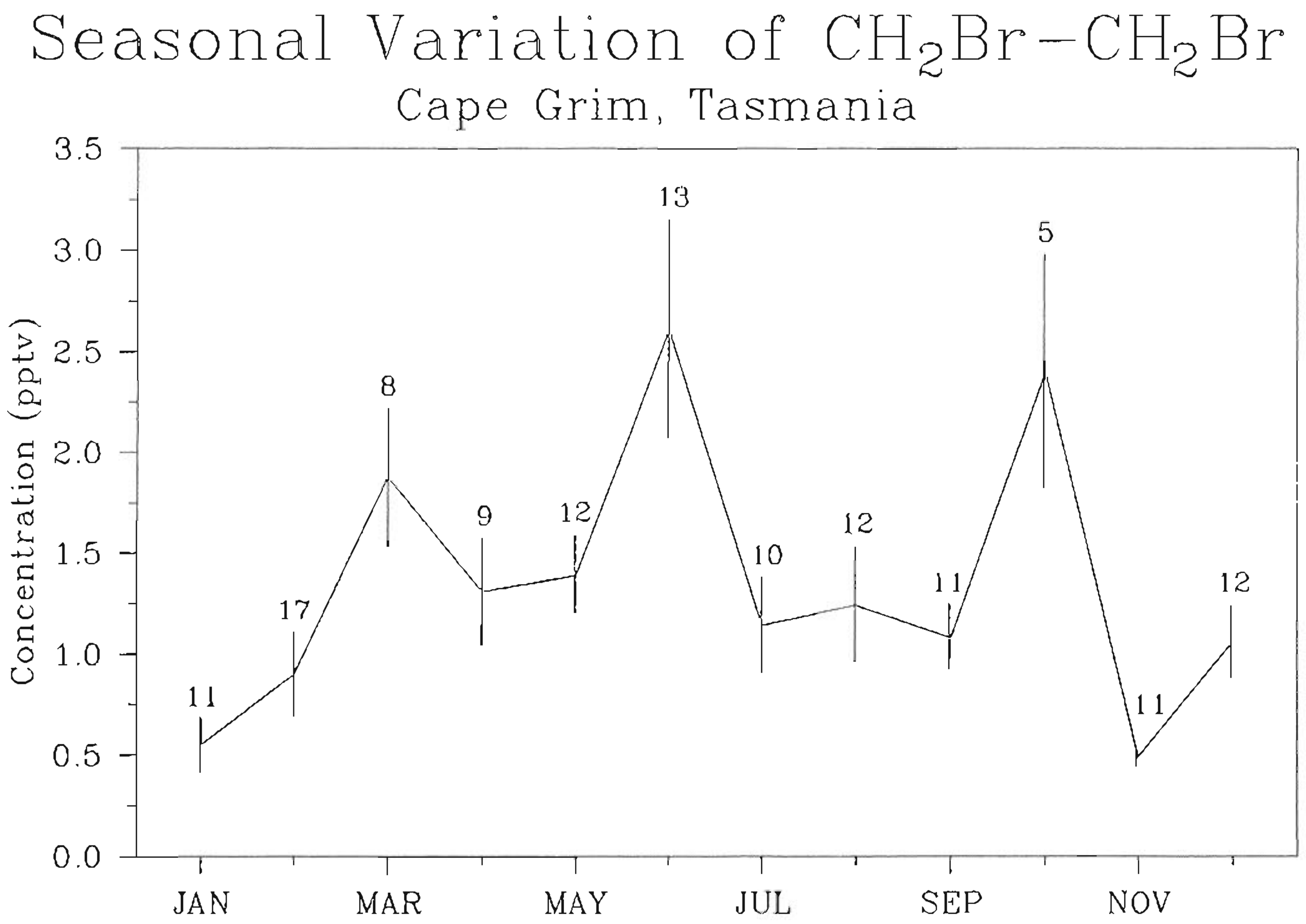


Figure D.35 : Monthly mean CH_2Br-CH_2Br concentrations at Cape Grim, Tasmania (Error bars are ±1 Standard error)

Seasonal Variations of $CHBr_3$ at Alert, Canada

Samples collected at Alert, Canada, from November 1985 through 1987 were analyzed using System V. The results were plotted in Figure D.36. This figure showed depleted levels of $CHBr_3$ during March and April and elevated levels during September and October. The mean $CHBr_3$ concentration during March and April was 2.3±1.8 pptv and the mean value during September and October was 9.5±2.2 pptv. These values were significantly different (t-test, 95% level) than the mean concentration during rest of the year (5.6±2.4 pptv).

Seasonal Variations of $CHBr_3$ at Pt. Barrow, Alaska

Systems III - V were used to analyze samples collected at Pt. Barrow, Alaska, from 1984 through 1987. The results were plotted in Figure D.37. This figure showed depleted levels $CHBr_3$ during the months June through November. The mean $CHBr_3$ concentration during these months, 10.3±6.5 pptv, was not significantly different from the value during rest of the year, 14.8±8.1 pptv, (t-test, 95% level). But at the 90% level, the difference was statistically significant.

Seasonal Variations of $CHBr_3$ at Mace Head, Ireland

Samples collected at Mace Head, Ireland, were analyzed using System V. The results, plotted in Figure D.38, showed a seasonal cycle with elevated levels of $CHBr_3$ during July through October. The mean $CHBr_3$ concentration during July through October (37.4±8.7 pptv) was not significantly higher (t-test, 95% level) than the mean value during rest of the year

(22.7±8.4 pptv). This difference was significant only at the 90% level.

Seasonal Variations of $CHBr_3$ at Cape Meares, Oregon

Systems III - V were used to analyze the samples collected at Cape Meares, Oregon, from 1984 through 1987. The results, plotted in Figure D.39, showed higher $CHBr_3$ concentrations during the months of June through September as compared to rest of the year. The mean value during June through September (10.1±5.3 pptv) was significantly higher (t-test, 95% level) than the mean $CHBr_3$ concentration during rest of the year (7.1±2.2 pptv).

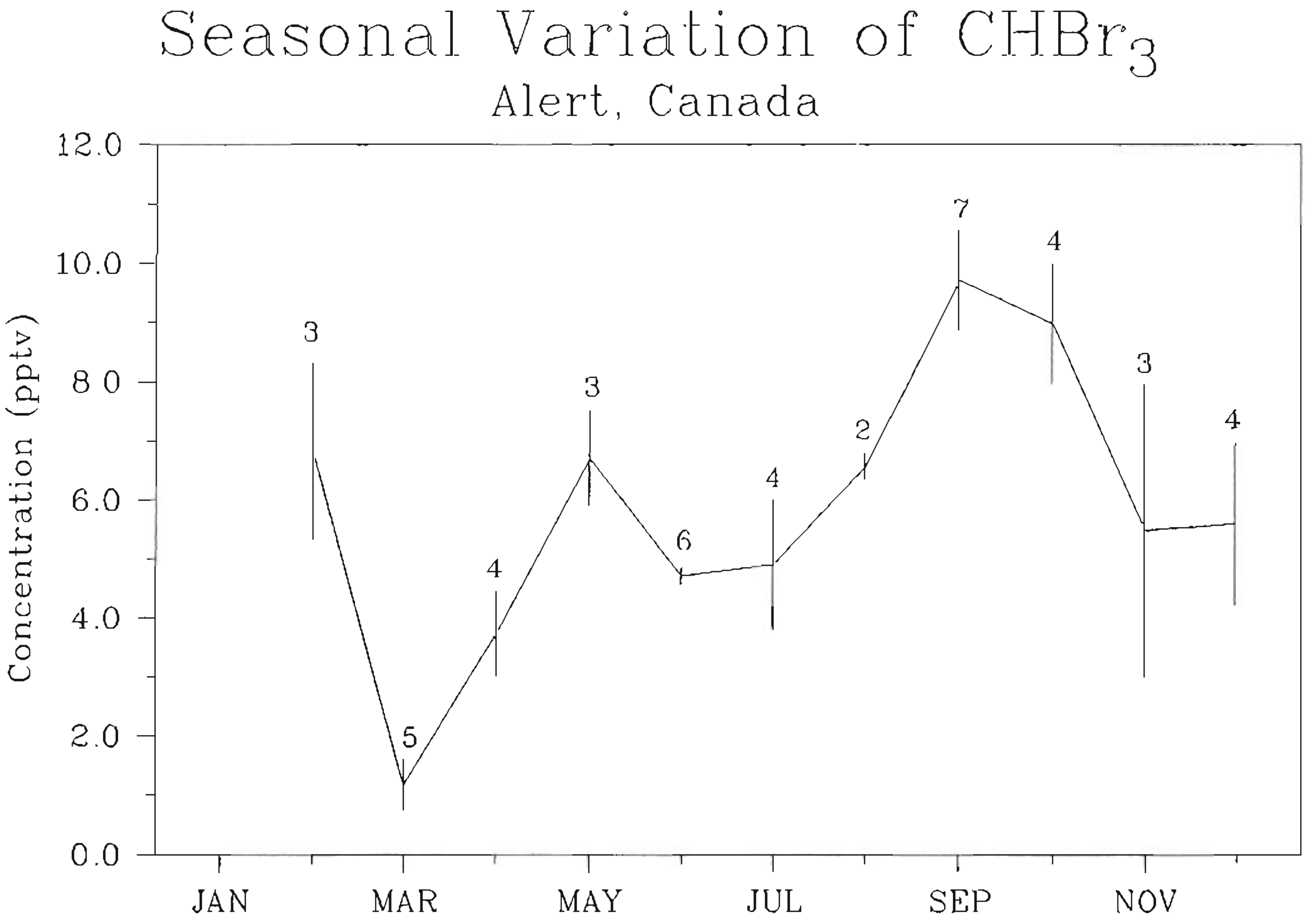
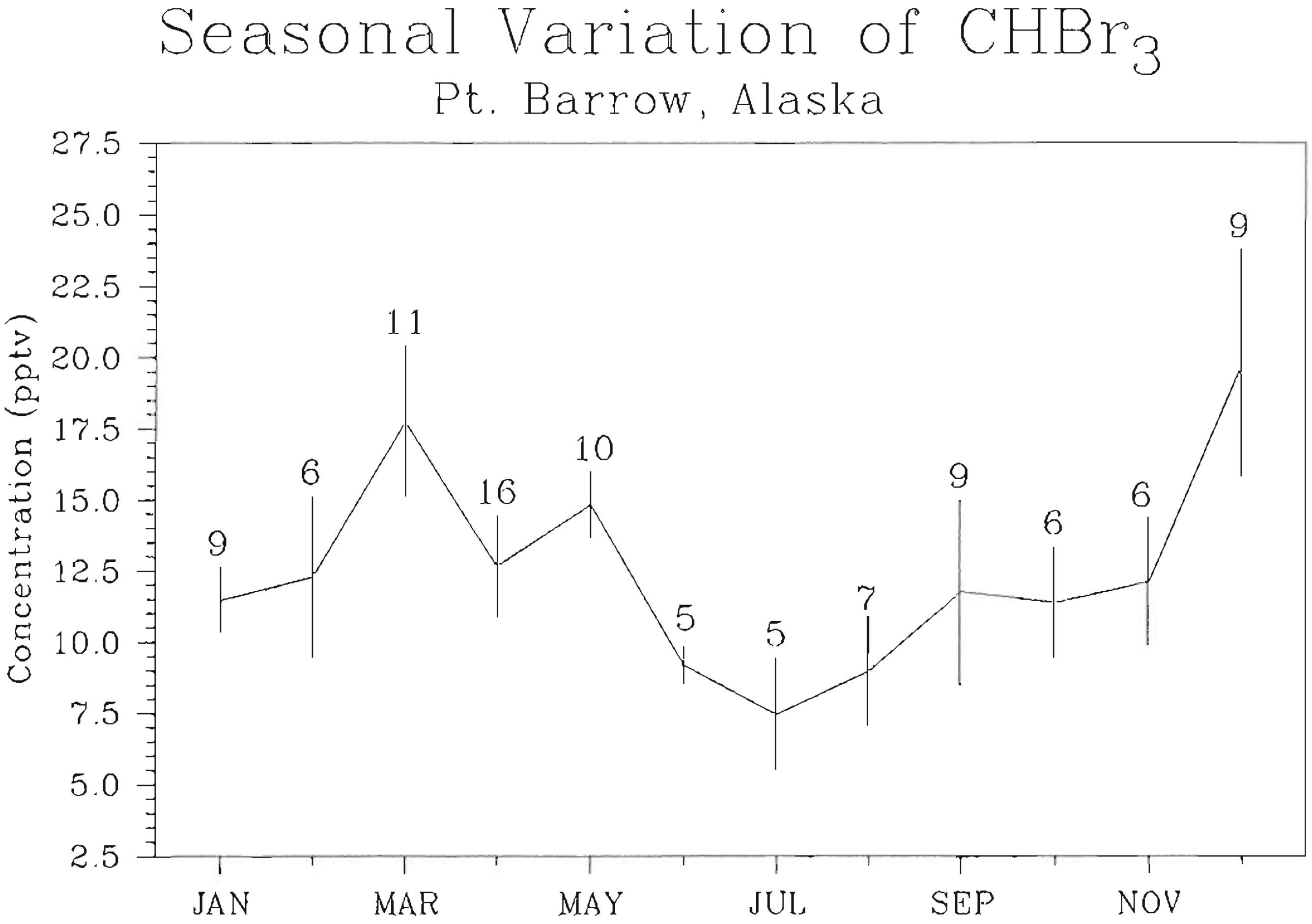
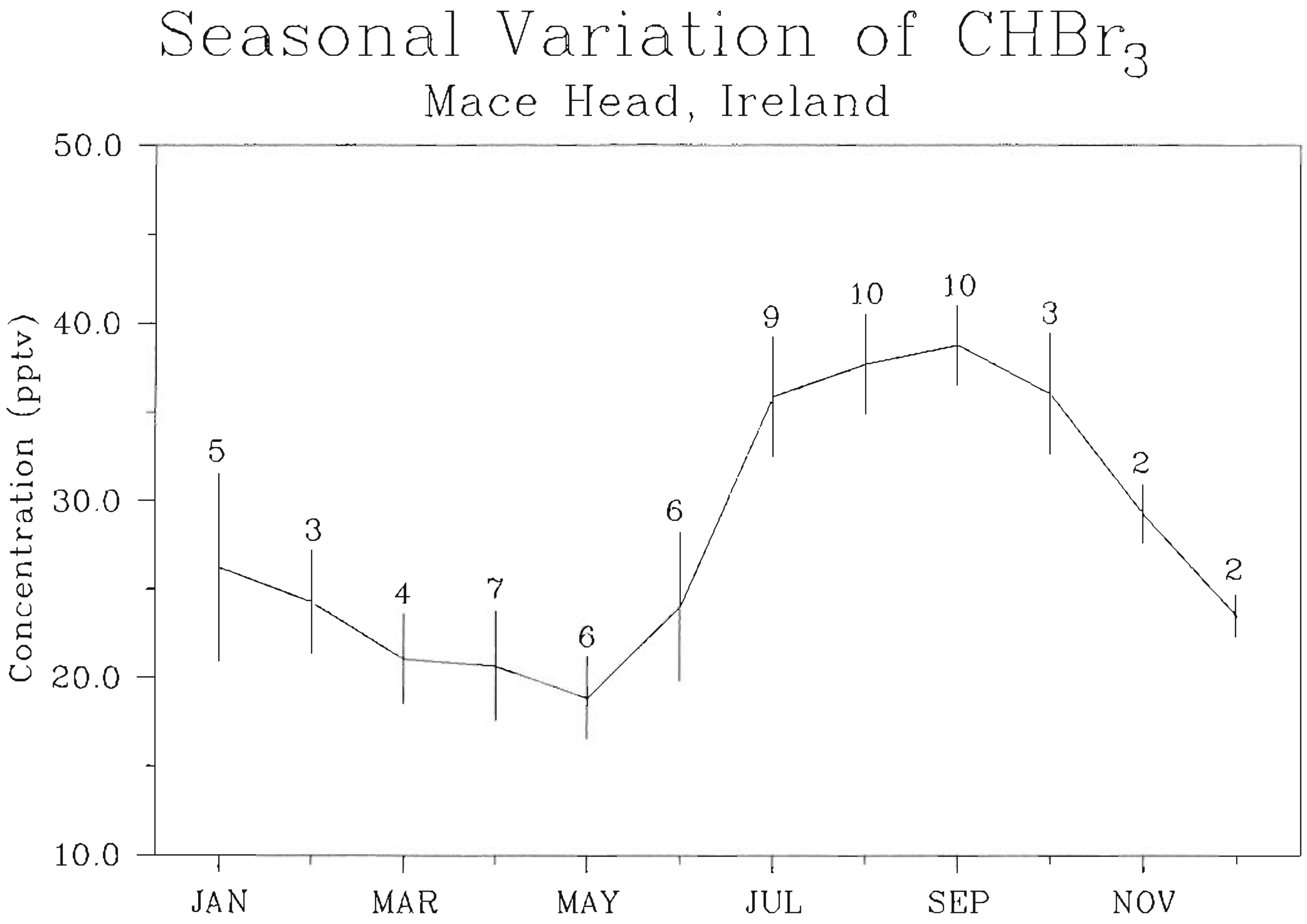


Figure D.36 : Monthly mean $CHBr_3$ concentrations at Alert, Canada (Error bars are ±1 Standard error)


Seasonal Variation of $CHBr_3$

Pt. Barrow, Alaska

Figure D.37 : Monthly mean $CHBr_3$ concentrations at Pt. Barrow, Alaska
(Error bars are ±1 Standard error)



Seasonal Variation of $CHBr_3$

Mace Head, Ireland

Figure D.38 : Monthly mean $CHBr_3$ concentrations at Mace Head, Ireland (Error bars are ±1 Standard error)

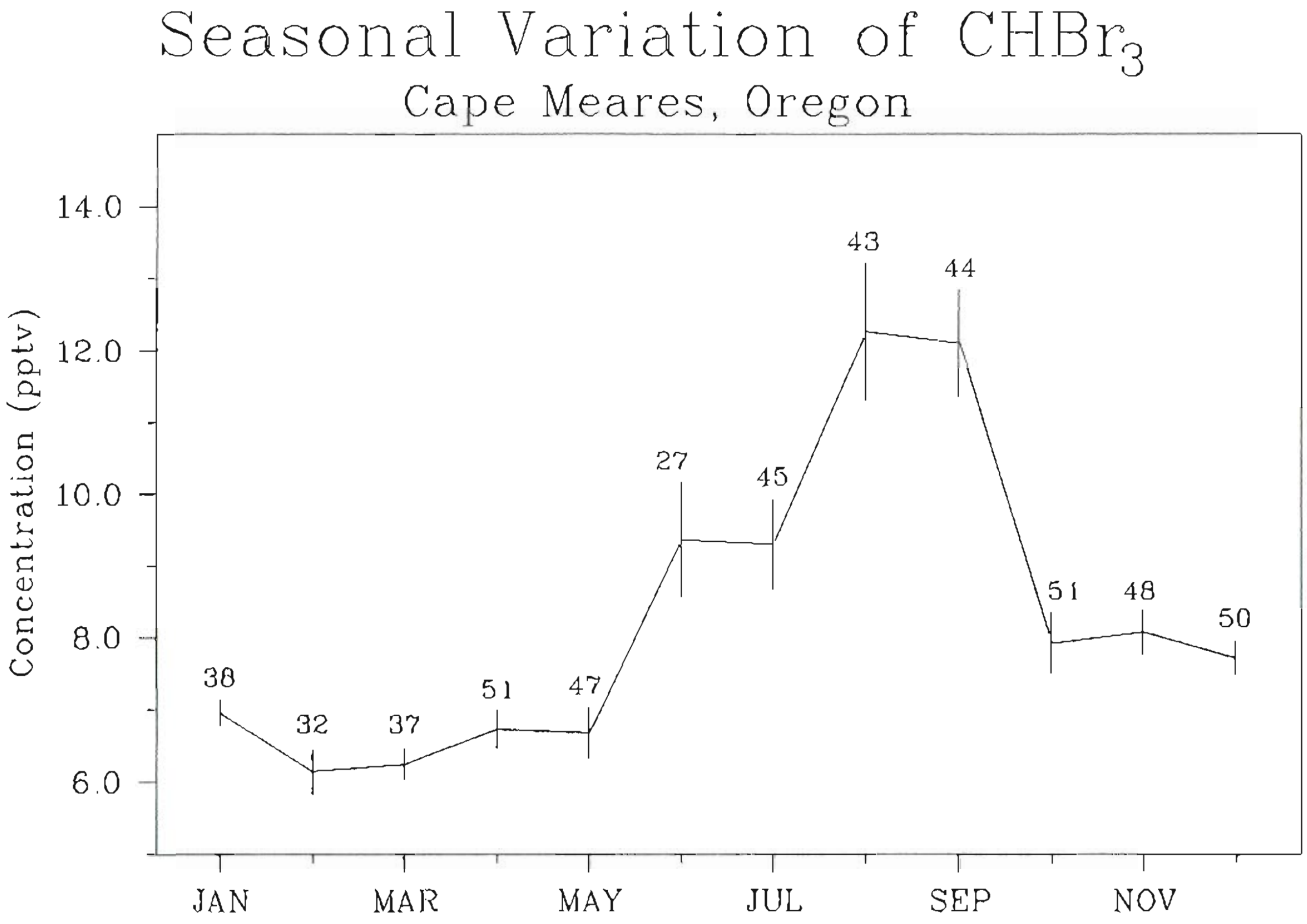


Figure D.39 : Monthly mean $CHBr_3$ concentrations at Cape Meares, Oregon
(Error bars are ±1 Standard error)

VITA

Rohith Gunawardena was born in Colombo, Sri Lanka, on January 3, 1955. He attended Royal Primary School, Royal Junior School and was graduated from Royal College High-school, Colombo in 1974. While at Royal College, he was awarded the H. J. Wijesinghe Prize for Advanced Level Chemistry. He entered University of Sri Lanka (Colombo) in 1975 and obtained a Bachelor of Science degree in Physical Sciences in 1978. After graduation, he worked for one year as a lab instructor in Physics at University of Sri Lanka in Colombo. In the Fall of 1979, he entered the Oregon Graduate Center and completed the requirements for the Master of Science degree in Environmental Sciences in 1985. In April 1989 he completed requirements for the Doctor of Philosophy degree in Atmospheric Sciences.

Rohith has been married to Lalani since 1979 and they have a son, Navindra, aged 7 years, and a daughter, Yoshini, aged 2 years.