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Anthropogenic

sources of
GHG

Table 2 $\text{Pb}_2\text{O}(\text{Pb}_2\text{K}_2)[\text{Si}_8\text{O}_{20}]$: atom coordinates and anisotropic thermal vibration ($\times 10^4$) parameters*

Atom	Cell	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	4	0.0000	0.0000	0.2815(1)	405(4)	405(4)	93(3)	0	0	0
Pb(2)	$8 \times \frac{1}{2}$	0.1508(1)	0.1508(1)	0.0000	116(3)	116(3)	229(5)	0	0	-32(5)
K	$8 \times \frac{1}{2}$	0.1860(5)	0.1860(5)	0.0000	210(23)	210(23)	165(29)	0	0	57(30)
Si	16	0.3197(2)	0.0000	0.3006(3)	99(11)	298(14)	121(10)	0	-14(9)	0
O(1)	2	0.0000	0.0000	0.0000	645(119)	645(119)	148(106)	0	0	0
O(2)	16	0.2028(5)	0.0000	0.2057(7)	134(29)	277(34)	224(31)	0	-61(27)	0
O(3)	16	0.1113(5)	-0.3887(5)	0.2500	292(25)	292(25)	1,095(78)	-42(37)	42(37)	185(36)
O(4)	8	0.3031(12)	0.0000	0.5000	287(75)	2,970(273)	106(51)	0	0	0

The polyhedron of interest is $[\text{Pb}^{2+}\text{O}_4\text{Cl}_4]$ which is a distorted square antiprism. There exist $4\text{Pb}-\text{OH}=2.48$ and $4\text{Pb}-\text{Cl}=3.32$ Å averages. Electing $r=1.40$ Å for $^{[6]}\text{O}^{2-}$, $r=1.81$ Å for $^{[6]}\text{Cl}^-$ and $r=1.29$ Å for $^{[8]}\text{Pb}^{2+}$, the calculated averages are $\text{Pb}^{2+}-\text{O}=2.69$ Å and $\text{Pb}^{2+}-\text{Cl}=3.10$ Å, effective averages larger and smaller, respectively, than the experimental averages for diabolite. This was noted in the earlier study which further supports the interaction between the $6s^2$ Pb^{2+} lone pair with the enveloping bond pairs. It requires that the centroid of the lone electron pair is towards the direction of the plane of the Cl^- ions, foreshortening the opposing $\text{Pb}^{2+}-\text{OH}^-$ distances and lengthening the adjacent $\text{Pb}^{2+}-\text{Cl}^-$ distances with respect to the effective averages. An analogous relation can be found for $\text{Pb(1)O}_5\psi$ in KPS where $4\text{Pb(1)}-\text{O(2)}=2.47$ Å and $1\text{Pb(1)}-\text{O(1)}=2.23$ Å. If the centroid of the lone pair is postulated to oppose O(1) in KPS; then the short $\text{Pb(1)}-\text{O(1)}$ distance and the absence of $\text{Pb}^{2+}-\text{O}$ bonds on its opposing side can be understood. It is immediately apparent that the average for the Pb ion stripped of all its valence electrons, $^{[6]}\text{Pb}^{4+}-\text{O}=2.18$ Å from the same tables⁷, is not far removed from $\text{Pb(1)}-\text{O(1)}$ in KPS. Increase in average distances for coordination polyhedra of increasing order has been explained adequately elsewhere⁸. Similarly, displacement of a metal with a lone electron pair from the equator of a coordination polyhedron has electrostatic origins in the interaction implicit on a cation with a lone pair of electrons and the circumjacent bond pairs⁹.

The remaining polyhedron in the second region is a distorted monocapped cube, or Pb(2)O_6 . The average distance is $\text{Pb(2)}-\text{O}=2.93$ Å, but the range in polyhedral distances is considerable, from $\text{Pb(2)}-\text{O(2)}=2.49$ Å to $\text{Pb(2)}-\text{O(3)}=3.47$ Å. We propose that the locus of the lone pair is on Pb(2) opposite the $\text{Pb(2)}-\text{O(1)}$ bond, the considerable distortion in polyhedron and bond distances being due to the effect from interaction of a lone pair with the surrounding bond pairs. Further evidence for this interaction can be obtained from the same structure by selecting the site centroid of the KO_6 polyhedron associated with the purported $[\text{K}, \text{Pb(2)}]$ solid solution. The distances range from $\text{K}-\text{O(2)}=2.74$ Å to $\text{K}-\text{O(3)}=3.23$ Å with an average $\text{K}-\text{O}=3.00$ Å, a range of only 0.49 Å compared with a range of 0.98 Å for $\text{Pb(2)}-\text{O}$. This is a rare case where a cation with a lone pair of electrons in the valence shell can be directly compared with a cation where all valence electrons are stripped away in the same polyhedral environment which, in effect, constitutes a structural solid solution (compare with isostructural $\text{Pb}_2\text{Pb}_4\text{Si}_6\text{Al}_2\text{O}_{21}$).

Another feature is the similarity of the cluster in the second region to the structure of hyalotekite, a complex lead-barium-calcium-borosilicate-fluoride¹⁰. This compound is triclinic, but its cell is pseudo-tetragonal, with $a \sim 11.1$ Å, $c \sim 10.3$ Å and possesses two formula units in the cell. A weak structural relationship occurs between KPS and hyalotekite. Writing the formulae in sequence hints at this relationship.

KPS $\text{Pb}_2\text{O}(\text{Pb}_2\text{K}_2)$ $[\text{Si}_8\text{O}_{20}]$ $\text{Pb}-\text{K}=0.59$ Å
Hyalotekite $\text{Ca}_2\text{F}(\text{Pb}_2\text{Ba}_2)$ $[\text{Be}_{0.5}\text{B}_2\text{Si}_{0.5}\text{O}_{28}]$ $\text{Pb}-\text{Ba}=0.46$ Å

In both structures, an apparent solid solution exists between a cation possessing a lone pair and a cation with a closed shell.

The KPS structure invites a simple experiment. The effect on a solid solution from interaction of a lone pair and neighbouring bond pairs with respect to temperature is unknown. Even the problem of solid solution between a cation possessing a lone pair (such as Pb^{2+}) and a cation stripped of all its valence electrons (such as K^{1+}) is not understood. We plan to study the crystal structure of KPS at elevated subsolidus temperatures to explore in more detail the bond distances and behaviour of the anisotropic thermal vibration ellipsoids through the thermal effect on the $\text{Pb(2)}-\text{K}$ site separation. Finally, since the lone electron pairs about Pb^{2+} are evidently circumjacent to the second aforementioned structural region and since the first region is a silicate tube, the curious appearance of fluffy fibrous material on grinding clear crystals suggests a pressure effect on the interaction between a lone pair and circumjacent bond pairs. Bond length, bond angle and solid solution dependencies on temperature and pressure would be most informative.

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An interhemispheric comparison of the concentrations of bromine compounds in the atmosphere

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At least seven organic bromine compounds have been positively identified in the atmosphere^{1,2} (CH_3Br , CH_2Br_2 , CHBr_3 , CH_2BrCl , CF_3Br , CF_2BrCl and $\text{C}_2\text{H}_4\text{Br}_2$) and others have been observed in coastal seawater samples ($\text{C}_2\text{H}_5\text{Br}$, $\text{C}_3\text{H}_7\text{Br}$ and CHBr_2Cl) (S. A. P. and R. A. Rasmussen, unpublished data). The atmospheric chemistry of bromine compounds has considerable consequence in the stratosphere, where bromine acts as a more efficient catalyst than chlorine in removing ozone^{3,4}. Several

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bromine compounds also fulfil an important role in the geochemical cycling of the element through the troposphere⁵. Here we present measurements of four bromine compounds (CF_3Br , CH_3Br , CH_2Br_2 and CHBr_3) over a large latitudinal range (40°N to 75°S). These data suggest that the major source of bromine in the atmosphere could be bromoform (CHBr_3), probably emitted from the ocean and with a short lifetime due to photolysis. Our data also suggest that the major emission of methyl bromide (CH_3Br), and hence most bromine entering the stratosphere, will be anthropogenic.

The specific sources of many bromine compounds are unknown, but are either anthropogenic or natural, with ocean chemistry and volcanic activity being obvious choices for the latter. The atmospheric lifetimes of the individual molecular species are likely to differ by many orders of magnitude, depending on the reaction rate with hydroxyl radicals or the photolytic destruction rate.

One way to categorize the source type and reactivity is to collect information on the latitudinal and longitudinal variation of the concentration of these compounds, in particular, to determine whether there is a substantial difference in concentration between Northern and Southern Hemispheric air samples. This is because the vast majority of anthropogenic sources are situated in the Northern Hemisphere and the interhemispheric transfer time is quite long (1–4 yr)^{6,7}.

Measurements of this type have been made at Harwell on air samples collected by the British Antarctic Survey (BAS) whose ships regularly traverse the Atlantic and Southern Oceans from about 50°N to 75°S on route from the UK to Antarctica. The samples were collected using a cryogenic trapping technique originally devised by Rasmussen⁸. Air was sampled on the bow of the BAS ships RRS *Bransfield* through a 10-ft length of steel pipe, which protruded out from the plating, and the sampling time was typically 10 min. The samples were only collected when the wind was on the bow or from a non-contaminating quarter, so the potential for contamination from the ship was very small. Typically 50 l of air were collected in each of the stainless steel sample bottles (volume 1.6 l), which were made to high specifications by Rasmussen. The properties of these containers with respect to contamination and decay of many trace gases have been studied extensively. Almost all trace gases were found to be stable at the high pressures (~ 450 p.s.i.) resulting from the sample collection process, when the air contained amounts of water vapour typical of surface samples. The wind direction was recorded at the time of sampling. No air mass trajectory calculations have been made due to difficulty in obtaining meteorological data.

In 1982, the ship sailed from Southampton to Cape Town, South Africa, passing the Canary and Ascension Islands along standard steamship routes and then to Antarctica. In 1983, the ship sailed from Southampton to Rio, Brazil, passing the Canary Islands and about 100 km east of the Cape Verde Islands along the steamship route and then on to Antarctica. The samples collected as far as Cape Town and Rio were air-freighted to London and analysed at Harwell within 6 weeks of collection. The samples collected farther south arrived back in England up to 6 months after collection. No marked difference in trace gas concentrations could be observed due to the different storage times.

The samples were analysed at Harwell for a large range of trace gases including halocarbons, hydrocarbons and sulphur compounds. In the case of the bromine compounds, which were the subject of this investigation, analysis was made using a highly sensitive gas chromatograph/mass spectrometer (GC/MS) combination developed especially for atmospheric trace gas measurements⁹. Before injection into the GC the air sample was enriched using a procedure very similar to that described previously¹⁰. This requires condensation of the gaseous air to liquid and removal of the permanent diluent gases under vacuum at liquid nitrogen temperature. The calibration procedure involved a static dilution technique which has been described in detail elsewhere¹¹. The detection limit was

~ 0.5 p.p.t.v. (parts per 10^{12} by volume) for CH_3Br , 0.2 p.p.t.v. for CH_2Br_2 and CF_3Br and ~ 0.1 p.p.t.v. for CHBr_3 . The precision of the analysis and sampling procedure was $\sim 10\%$ for all four compounds as the largest error arose in estimating the volume used in the analysis stage.

Data for the variation of concentration with latitude are shown in Fig. 1 for CH_3Br , CH_2Br_2 , CHBr_3 and CF_3Br . In the case of methyl bromide (CH_3Br), (Fig. 1a) there is a clear reduction in concentration between the two hemispheres, such that the average concentration in the Northern Hemisphere (NH) is 15.4 ± 1.9 p.p.t. and that in the Southern Hemisphere (SH) is 10.6 ± 0.9 p.p.t. There is also more scatter in the limited amount of Northern Hemisphere data while the variation in the southern data is very close to the limits of precision for the GC/MS system ($\sim 10\%$). A similar interhemispheric gradient has been observed previously¹² but the concentrations observed in both hemispheres were higher.

Methylene dibromide (CH_2Br_2) (Fig. 1b) also shows a marked hemispheric difference in concentration (NH = 2.70 ± 0.59 p.p.t.v., SH = 1.58 ± 0.26 p.p.t.v.) with again less variation in the Southern Hemisphere. The bromoform (CHBr_3) data (Fig. 1c) are much more scattered than either the CH_3Br or the CH_2Br_2 data. Although there is a tendency for the Northern Hemisphere concentrations to be higher, the mean interhemispheric difference is within the scatter of the data. The values for the mean and standard deviation are NH = 0.85 ± 0.44 p.p.t.v., when the value of 5.96 p.p.t.v. at 20°N is omitted, and SH = 0.58 ± 0.30 p.p.t.v. with the inclusion of the equatorial value of 0.88 p.p.t.v. These are both valid procedures since; first, the CHBr_3 concentration in the 20°N sample was elevated far above the average whereas none of the other trace gases measured showed such an elevation, and second, other trace gases such as ethane and some saturated hydrocarbons in the equatorial sample gave results typical of the Southern Hemisphere. There is no evidence that the high value at 20°N was associated with long-range transport of a plume of anthropogenic pollutants, because other trace gases indicative of pollution were present at levels similar to the average for the Northern Hemisphere samples. The slightly higher concentrations of CHBr_3 at 75°S in 1982 and 50°S in 1983 cannot be explained in terms of anthropogenic emissions. These data could mean that CHBr_3 has oceanic sources in both hemispheres and that it is more reactive in the atmosphere than are the mono- and di-bromo-substituted methanes. The CHBr_3 data contrast with those for CF_3Br (Fig. 1d) which show a very small gradient north and south on the 1982–83 voyage and a variability well within the limits of precision of the measurements (NH = 1.15 ± 0.05 p.p.t.v., SH = 1.06 ± 0.09 p.p.t.v.). CHBr_3 and CH_2Br_2 have been identified in coastal seawater (S. A. P. and R. A. Rasmussen, unpublished data).

The different variability in the concentration of the four molecules is associated with different source distributions and reactivity. The simplest behaviour is that of CF_3Br (CFC13B1) which is used as a flame retardant and is unlikely to have any natural sources. The molecule is mostly emitted into the atmosphere in the Northern Hemisphere and it has no significant tropospheric sinks. However, it is removed in the stratosphere by photolysis, as shown by measurements of its vertical profile up to 25 km (ref. 13). The small interhemispheric gradient is very similar to that of CFC 11 and 12, which have been growing in concentration at a rate close to $5\% \text{ yr}^{-1}$. A similar growth rate is therefore anticipated for CF_3Br . This compound was originally detected in the atmosphere in 1980 and its concentration then was estimated to be about 0.7 p.p.t.v. (ref. 10). Unfortunately, this was not a precise estimate and thus no absolute growth rate can be ascertained from our data at present.

CH_3Br is extensively used as a fumigant and annual production in 1972 was estimated to be about 300,000 tons, a quarter of which (75,000 tons) was probably emitted to the atmosphere³. It has also been proposed that the ocean is a major source, as in the case of methyl chloride and methyl iodide^{13,14}.

If it is assumed that CH_3Br is mostly removed from the

atmosphere by reaction with hydroxyl radicals in the troposphere, then the present data can be used to estimate the size of the annual input. A recently calculated value of the global average hydroxyl concentration is 4×10^5 molecules cm^{-3} (ref. 15); the atmospheric burden of CH_3Br is about 2.26×10^5 tons according to our data. These data require an annual input of 90,000 tons assuming removal only by hydroxyl radical chemistry with a rate constant of 3.2×10^{-14} cm^3 per molecule per s at 280 K (ref. 15). This is only slightly higher than the estimate³ of anthropogenic atmospheric emission made in 1972 of 75,000 tons, suggesting either that the ocean makes a relatively small contribution to the atmospheric burden of CH_3Br or that our rather simple chemistry is incorrect. An independent check on the chemistry can be made by comparing the methyl bromide levels in the two hemispheres. Assuming only a Northern Hemisphere source for CH_3Br which is transferred to the Southern Hemisphere with a relaxation time of 400 days, then the global average hydroxyl concentration required to account for the data is 3.6×10^5 molecules cm^{-3} , assuming all reactions take place at 280 K. The chemistry, therefore seems to be consistent and this leaves a problem with the oceanic source of CH_3Br . An estimate made recently¹² suggests that 300,000 tons of CH_3Br are emitted annually from the ocean. This would far outweigh the anthropogenic emission of CH_3Br and would argue for the globally-even distribution in concentration, observed for CH_3Cl (ref. 12), which has a similar removal rate from the atmosphere by hydroxyl radicals¹⁶. The global average hydroxyl concentration is an uncertain quantity and a larger total emission of methyl bromide into the atmosphere can be allowed, but the weight of evidence does not favour a large natural source.

Our interpretation of the data, therefore, suggests that the predominant source of CH_3Br in the atmosphere is anthropogenic rather than natural. This has important consequences for stratospheric ozone chemistry. It has been assumed previously that the stratospheric burden of bromine was mainly natural in origin and that any reduction in ozone produced by its presence was not a recent phenomenon¹⁰. This assumption is now questionable, and we suggest that stratospheric bromine chemistry should be examined more carefully in the context of possible effects of increased anthropogenic emissions.

The degree of variation in concentration suggests that both CH_2Br_2 and CHBr_3 are quite reactive in the troposphere, more so than CH_3Br and much more so than CF_3Br . They may have a mixture of sources since the CH_2Br_2 and CHBr_3 concentrations have been observed to increase during pollution incidents in the Arctic¹. Also, GC/MS studies of sea water containing different types of seaweed collected at a coastal site in southern England, show evidence for the presence of many different bromine compounds. These included $\text{C}_2\text{H}_5\text{Br}$, $\text{C}_3\text{H}_8\text{Br}$, CH_2BrCl , CHBr_2Cl and at least an order of magnitude greater quantities of CH_2Br_2 and CHBr_3 (S. A. P. and R. A. Rasmussen, unpublished data). It seems possible from the following calculations that CHBr_3 is the most important natural vector for gaseous bromine in the atmosphere and that CH_2Br_2 also has substantial natural sources. Their chemical lifetimes are unknown at present because of lack of published data either on rates of removal by hydroxyl radicals or on their photochemistry. However, the rates of reaction of the bromine compounds CH_3Br and $\text{BrCH}_2\text{CH}_2\text{Br}$ with hydroxyl radicals are very similar to those for their chlorine analogues. It is not unreasonable to assume, therefore, that to a first approximation, the rates for CH_2Br_2 and CHBr_3 are also similar to those for their chlorine analogues, for which published data exist: $k_{280\text{K}} = 1.128 \times 10^{-13}$ cm^3 per molecule per s for CH_2Cl_2 and 8.28×10^{-14} cm^3 per molecule per s for CHCl_3 (ref. 16). These rates should lead to a substantial interhemispheric gradient such as that observed for CH_2Cl_2 in our own unpublished data, where Southern Hemisphere values are only a quarter of the Northern Hemisphere values. The concentration distribution shown in Fig. 1 thus argues strongly for substantial sources of both CH_2Br_2 and CHBr_3 in the Southern Hemisphere, which must surely be natural rather than anthropogenic.

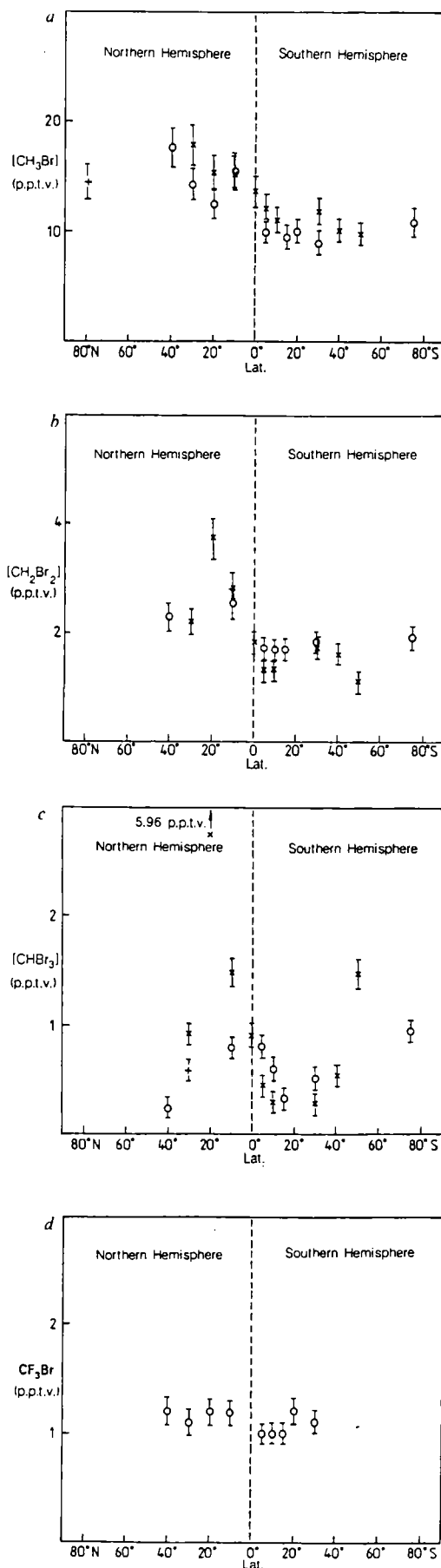


Fig. 1 Longitudinal transects of the concentrations of four bromine compounds: a, CH_3Br ; b, CH_2Br_2 ; c, CHBr_3 ; d, CF_3Br . $\circ$, 1982 voyage via Cape Town; $\times$, 1983 voyage via Rio; $+$, values collected on other experiments.

The case for natural sources of CHBr_3 is emphasized when a consideration is made of its potential atmosphere photochemistry. No published absorption spectrum could be found but some preliminary measurements were made at Harwell using a diode array spectrometer in conjunction with R. A. Cox. The absorption maximum occurs at a wavelength of 221 nm, where $\sigma = 5.51 \times 10^{-18} \text{ cm}^2$ per molecule and a significant overlap occurs in the region of tropospheric solar flux (305–320 nm). Assuming a quantum yield of unity, the atmospheric lifetime of CHBr_3 due to tropospheric photolysis could be as low as 2 weeks. This would require an annual emission in the region of 10^6 tons, which almost certainly exceeds the anthropogenic emissions many times over and makes CHBr_3 the most significant source of bromide released into the atmosphere. It is unlikely, though, that much CHBr_3 would penetrate into the stratosphere with a tropospheric lifetime this short.

Finally, there appear to be a substantial number of bromine compounds present in sea-surface waters that can find their way into the atmosphere. This indicates the presence of a rich bromine chemistry and mixed chlorobromo chemistry in the ocean that merit investigation in detail. The chemical behaviour of the bromine atoms released in both the troposphere and the stratosphere also needs study.

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Pyroxene solid solution in garnets included in diamond

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In what proved to be a temporary phase of trial mining of the Monastery Mine kimberlite pipe, South Africa, we recently had a brief opportunity to characterize the mineral inclusions in diamonds from this locality. The usefulness of such studies in elucidating mantle processes has already been demonstrated^{1–3}. We describe here garnets included in diamonds which have a unique range of compositions. They are interpreted as representing the first natural occurrence of garnet hosting a component of pyroxene in solid solution. Their discovery fulfils predictions based on successful laboratory experiments in which pyroxene was dissolved in garnet at very high pressures (50–180 kbar)^{4–6}. As this solid solution is accompanied by an increase in density, such results have both geophysical and chemical implications for the structure

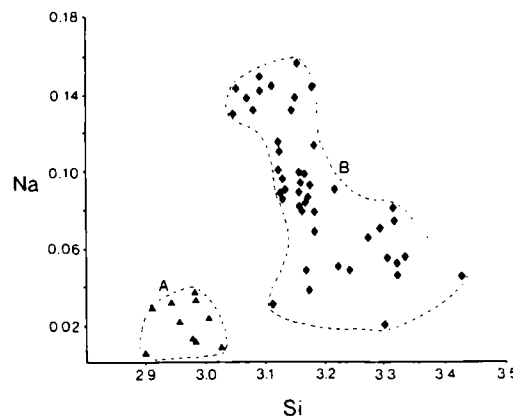


Fig. 1 Plot of atomic Na against atomic Si for 12 oxygens. Group A represents garnets of similar composition to eclogitic diamond inclusion garnets worldwide^{1–3,12–16}. Group B represents garnets interpreted to host a component of pyroxene in solid solution. Δ , Group A garnets; $\diamond$, group B garnets.

of the mantle. In addition, the pressures inferred are higher than generally proposed for mantle minerals sampled by kimberlites. Recent work has demonstrated that at least some inclusion-bearing diamonds have been derived from Archaean lithosphere⁷. The Monastery garnets in diamonds may indicate that the old lithosphere was very thick^{8,9}. Alternatively, if they have an asthenospheric origin, they may prove particularly interesting because of their different source.

Monastery Mine is situated near the border between South Africa and Lesotho, close to the inferred eastern margin of the Kaapvaal Craton. It was an inviting target for a study of mineral inclusions in diamonds because it is geographically well separated from the established kimberlite diamond mines in southern Africa and because it is a kimberlite with an abundance of fresh xenoliths and xenocrysts of mantle rocks and minerals to which the inclusions and hence the diamonds might be related. The general geology of Monastery has been described elsewhere¹⁰.

In this study, 131 inclusion-bearing diamonds in the size range $-9+5$ (ref. 11) were selected from 4,600 carats of general production. The diamonds are <3 mm in largest dimension and average ~ 0.12 carats per stone. After careful visual inspection and rigorous cleaning, the inclusions were liberated from the diamonds by mechanical crushing in an enclosed steel cracker. The individual inclusions, usually between 75 and 250 μm in longest dimension were mounted in epoxy resin on glass slides and polished. Mineral compositions were determined by means of a Cameca Camebax microanalyser, using standards of essentially similar composition to the unknowns and an on-line ZAF correction procedure. Analyses are believed to be accurate to $\pm 1\%$ relative and have been checked at two independent microprobe laboratories.

The minerals found as inclusions in diamonds from the Monastery Mine kimberlite are almost entirely of an eclogitic paragenesis. Fifty-six eclogitic garnets have been analysed. Each analysis represents an average of at least five individual spots either on a single inclusion or several inclusions from the same diamond. Two distinct populations of eclogitic garnets are present in the diamonds (Fig. 1). One group (termed group A) consists of 10 garnets which have compositions similar to those described from diamonds worldwide^{1–3,12–16}. They have Na_2O concentrations which range from 0.04 to 0.25 wt% Na_2O , variable quantities of FeO, MgO and CaO typical of eclogitic garnets included in diamond, and SiO_2 and Al_2O_3 present in normal stoichiometric proportions, namely 39.0–42.2 wt% SiO_2 and 20.19–23.06 wt% Al_2O_3 (Fig. 2). The second group (group B) consists of 46 garnets that form a related suite of compositions which have never been reported before. Particularly extreme concentrations of Si and Al range to as high as 47.43 wt% SiO_2 and as low as 11.29 wt% Al_2O_3 (Fig. 2). Note that the low Al_2O_3 values are not supported by high Cr_2O_3 concentrations as occurs for peridotitic garnets, the maximum chrome concentration in

Atmospheric Chemistry of Toxic Contaminants. 4. Saturated Halogenated Aliphatics: Methyl Bromide, Epichlorhydrin, Phosgene

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Mechanisms are outlined for the reactions that contribute to in-situ formation and atmospheric removal of the saturated halogenated aliphatic contaminants methyl bromide, epichlorhydrin, and phosgene. In-situ formation is important only for phosgene and involves the reaction of OH with chloroethenes and other chlorinated hydrocarbons. A ranking of these phosgene precursors is given using data for precursor ambient concentrations and chemical reactivity. The three toxic compounds studied are long-lived in the atmosphere, where removal of phosgene and methyl bromide by chemical reactions is negligibly slow. Epichlorhydrin is removed slowly by reaction with OH, leading to formaldehyde, chloroacetaldehyde, and the chlorinated peroxyacyl nitrate $\text{CH}_2\text{ClC}(\text{O})\text{OONO}_2$.

While toxic compounds are released in substantial quantities in urban air, little data exist regarding the chemical reaction pathways by which these toxic compounds are produced in-situ and concurrently removed from the atmosphere. This information, however, is essential when attempting to assess the risk associated with population exposure to toxic compounds.

In a preceding article,¹ quantitative estimates have been presented regarding the atmospheric persistence of aliphatic, unsaturated, and aromatic toxic air contaminants. In this article, we outline the chemical reactions involved in the in-situ formation and atmospheric removal of one category of toxic air contaminants, the saturated halogenated aliphatics. Similar studies of

atmospheric fate have been presented for other air toxics including saturated aliphatic,² unsaturated aliphatic,³ and unsaturated halogenated aliphatic compounds.⁴

The three compounds selected for study are methyl bromide (CH_3Br), epichlorhydrin ($\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{Cl}$), and phosgene (COCl_2). These toxic compounds may be emitted into the atmosphere by a number of anthropogenic sources. Methyl bromide is mainly used as a soil fumigant (agricultural pest control). Other uses include industrial applications as a disinfectant, fumigant, methylating agent, and degreaser.⁵ For example, recent estimates of methyl bromide emissions to the atmosphere in California are 3,200 metric tons per year.⁵ The oceans are a major natural source of methyl bromide.⁶ Epichlorhydrin's major use is as an intermediate in the production of epoxy resins and synthetic glycerin; it is also used as an intermediate in the production of elastomers, rubber for automobile parts, adhesives, rubber coating fabrics, polyamide resins, flame retardants, pharmaceuticals, and pesticides.⁵ Phosgene is an intermediate in the production of toluene diisocyanate, isocyanates, and polycarbonate resins. These products account for 55, 30, and 7 percent, respectively, of the total use of phosgene as an intermediate in chemical manufacturing.⁵

In the following sections of this article, we describe chemical reaction pathways that are responsible for the in-situ formation and removal of methyl bromide, epichlorhydrin, and phos-

gene in the atmosphere. This information, while contributing to a better understanding of the atmospheric fate of the three contaminants studied, can also serve as a guide to assess the persistence and fate of structural homologues, that is, other saturated halogenated aliphatic toxics, in urban and industrial atmospheres.

Ambient Concentrations

To our knowledge, no data are available regarding ambient levels of epichlorhydrin. For methyl bromide, a substantial body of information exists, see Table I. The data compiled by Brodzinsky and Singh⁷ from earlier work of Singh and coworkers⁸ indicate mean urban values of 30-250 ppt and maxima of 100-900 ppt. Yearly averages (year 1980) of Guicherit and Schulting⁹ for three sites in the Netherlands are consistent with these values. "Background" methyl bromide concentrations at remote continental sites are 5 ppt. Higher values are recorded at coastal locations and may reflect oceanic sources, transport of urban CH_3Br , or both.

Shikiya et al.¹⁰ collected 24 hour-integrated samples at four sites in the Southern California Air Basin. Samples were collected every 2-5 days, yielding 6-20 data points per month per site. The stated detection limit for methyl bromide was 200 ppt, which is higher than most mean values reported by Brodzinsky and Singh⁷ and by Guicherit and Schulting.⁹ With this high detection limit, methyl bromide was not detected at three of the four sites, and was detected in only 8 percent of the samples collected at the remaining site, El Monte. During the November 1982-December 1983 study period, the reported maximum value, highest monthly mean and composite mean at the El Monte site were 1,300, 560, and 450 ppt, respectively. A strong seasonal variation was observed, with winter

Implications

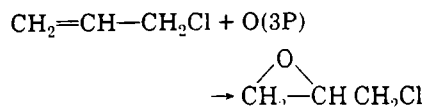
A number of countries and states have begun to implement control programs to regulate air emissions of toxic chemicals. These programs include, as a critically important component, the gathering and evaluation of data on atmospheric persistence, from which an assessment of public exposure can be made. In this article, reaction mechanisms are outlined for one category of toxic contaminants, the saturated halogenated aliphatics. These mechanisms describe in-situ formation, in-situ removal, and the corresponding reaction products in the atmosphere.

maxima of 360–560 ppt (monthly averages) and summer minima of less than 200 ppt (the detection limit).

Ambient levels of phosgene have been seldom measured (Table II). Urban concentrations measured at several locations in California and in Phoenix, Arizona were in the range 30–60 ppt^{7,8,11} and were less than 20 ppt at three sites in the Netherlands.⁹ Phosgene concentrations at more rural and remote locations were about 15 ppt.^{7,8,11}

In-Situ Formation

There are no reactions by which methyl bromide may form in the atmosphere. The reaction of bromine atoms with methane does not involve substitution to yield CH₃Br but proceeds by H-atom abstraction to form hydrogen bromide and methyl radicals (i.e., Br + CH₄ → HBr + CH₃). Epoxides are formed in the reaction of atomic oxygen with olefins. Accordingly, epichlorohydrin may form by reaction of atomic oxygen with 3-chloropropene (allyl chloride):



This reaction is not, however, expected to be of importance in ambient air. Allyl chloride also reacts rapidly with OH and with ozone,⁴ and concentrations of O(3P) in the atmosphere, relative to those of OH and O₃, are too low for the allyl chloride-O(3P) reaction to compete with the allyl chloride-OH and allyl chloride-O₃ reactions.

In contrast, in-situ formation is believed to be a major source of atmospheric phosgene. In the atmosphere, phosgene may be produced by the following reactions:

- The reaction of the hydroxyl radical with chloroethenes: vinylidene chloride,^{12,13} trichloroethylene,^{12,13} and tetrachloroethylene.^{12–16}
- The reaction of ozone with chloroethenes: vinylidene chloride,¹⁷ trichloroethylene (no data available), and tetrachloroethylene.¹⁸
- The reaction of chlorine atoms with chloroethenes: vinylidene chloride (no data available), trichloroethylene (no data available), and tetrachloroethylene.¹⁸
- The OH-initiated oxidation of chloromethanes: while no data are available for this reaction, all hydrocarbons containing a CCl₂ group, including methylene chloride and chloroform, may yield phosgene.
- The reaction of chlorine atoms with chloromethanes: methylene chloride^{19,20} and chloroform.^{19,20}

Table I. Ambient levels of methyl bromide.

Reference	Location	CH ₃ Br (ppt)	
		mean	max
Singh et al. ⁸	Los Angeles, CA	244	894
	Oakland, CA	55	108
	Phoenix, AZ	67	190
Brodzinsky and Singh ^{7,a}	Badger Pass, CA	4.8	8.0
	Denver, CO	120	190
	Houston, TX	100	170
	Jetmore, KA	5.0	5.0
	Los Angeles, CA ^a	150	580
	Menlo Park, CA	16	16
	Mill Valley, CA	25	25
	Oakland, CA ^a	55	78
	Palm Springs, CA	24	24
	Phoenix, AZ ^a	67	120
	Point Arena, CA	17	20
	Point Reyes, CA	93	93
	Reese River, NV	5.0	5.0
Guicherit and Schulting ⁹	Riverside, CA	250	560
	San Jose, CA	31	31
Shikiya et al. ¹⁰	St. Louis, MO	81	100
	Delft, Vlaardingen and Terschelling, The Netherlands ^b	50–200	100–900
	Dominguez Hills, CA ^c	ND ^d	—
	Riverside, CA ^c	ND	—
	Los Angeles, CA ^c	ND	—
	El Monte, CA ^c	450	1,300 ^e

^a Includes substantial overlap with data reported in Singh et al.⁸

^b 350 samples per site during year 1980.

^c Study period: Nov. 1982–Dec. 1983.

^d None detected with a detection limit of 200 ppt.

^e Only 8 percent of the values were above the detection limit of 200 ppt.

- The photolysis of chloroacetylchlorides: HCl₂CCCl and Cl₃CCCl (no data available).
- The photolysis and reaction with OH of chloroacetaldehydes: Cl₂HCCHO and Cl₃CCHO (no data available).

Mechanisms for phosgene formation in the above reactions are outlined in Figure 1. Detailed reaction mechanisms for phosgene formation from

chloroethenes are presented elsewhere.⁴ Phosgene yields measured in the studies cited above are compiled in Table III.

The relative importance of the several phosgene formation pathways can be estimated from the ambient concentrations of the precursors and the rates of their reactions leading to phosgene. This information is summarized in Table IV. Reaction rate constants are from the literature when available or have been estimated from data for structural analogues and similar reac-

Table II. Ambient levels of phosgene.

Reference	Location	Phosgene (ppt)	
		mean	max.
Singh ¹¹	Los Angeles, CA	31.7 ± 8.3	61.1
	Palm Springs, CA	29.3 ± 6.2	44.4
	Menlo Park, CA	30.3 ± 3.2	38.8
	Badger Pass, CA	21.6 ± 5.1	28.8
Singh et al. ⁸	Phoenix, AZ	49.7 ± 5.1	56.7
Brodzinsky and Singh ⁷	Mill Valley, CA	18 (1 sample)	—
	Point Arena, CA	15 (2 samples)	15
	Riverside, CA	45 (1 sample)	—
	Reese River, CA	15 (1 sample)	—
Guicherit and Schulting ⁹	3 sites, The Netherlands	none detected	(≤20 ppt)

Table III. Phosgene formation yields.

Precursor	Reaction	Phosgene yield ^a	Reference
Vinylidene chloride (CH ₂ =CCl ₂)	OH	0.52 ^b	Tuazon et al., 1988 ¹³
		0.73 ^c	
		0.18	
	O ₃	0.63	Gay et al., 1976 ¹²
Trichloroethylene (CHCl=CCl ₂)	OH	0.63	Hull et al., 1973 ¹⁷
		no data	
		—	
	O ₃	0.27 ^b	Tuazon et al., 1988 ¹³
Tetrachloroethylene (CCl ₂ =CCl ₂)	OH	0.40 ^c	
		0.21	
		no data	
	O ₃	no data	—
Methylene chloride (CH ₂ Cl ₂)	OH	no data	Lillian et al., 1975 ¹⁵
		0.60	
		0.34	
	O ₃	0.49 ^b	Gay et al., 1976 ¹²
Chloroform (CHCl ₃)	OH	0.47 ^c	
		large	
		large	
	O ₃	large	Mathias et al., 1974 ¹⁸
Chloroacetyl chlorides (RCOCl, R=CH ₂ Cl, CHCl ₂ , CCl ₃)	OH	no data	Mathias et al. 1974 ¹⁸
		no data	
		no data	
	Cl	0.05	Spence et al., 1976 ²⁰
Chloroacetaldehydes (CH _{3-x} Cl _x CHO, x = 1,2,3)	OH	no data	—
		no data	
		no data	
	OH	no data	—

^a Molecules of phosgene produced per molecule of precursor reacted.

^b Without excess ethane added to scavenge chlorine atoms formed in the OH-chlorinated reaction.

^c With excess ethane added.

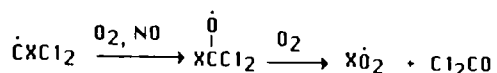
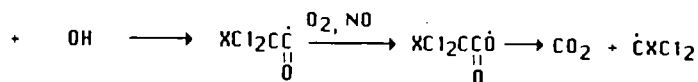
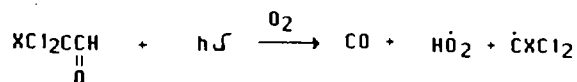
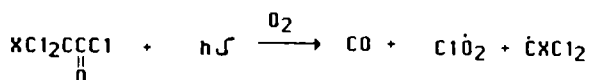
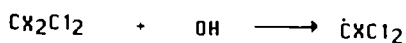
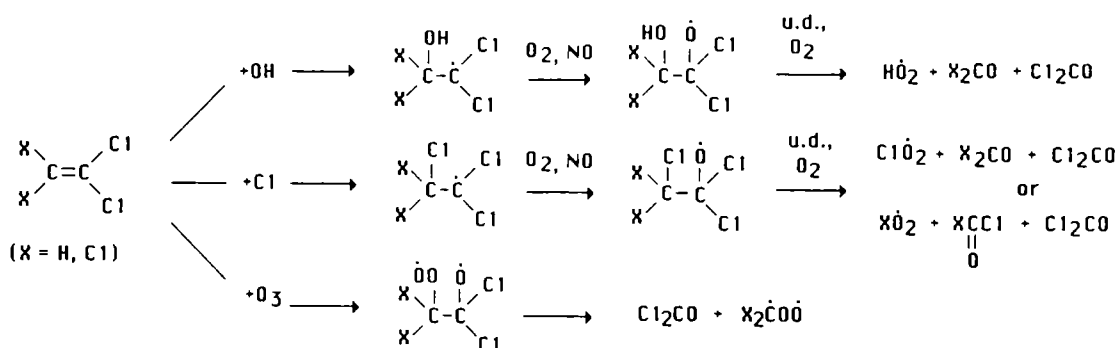


Figure 1. In-situ formation pathways for atmospheric phosgene (u.d. = unimolecular decomposition)

Table IV. Phosgene precursors: kinetic data and ambient concentrations.

Precursor	Ambient levels (ppb)	Reaction	Rate constant (cm ³ molecule ⁻¹ sec ⁻¹)
Vinylidene chloride	5-10, ^a <100 ^b	OH	8.1 × 10 ⁻¹²
		O ₃	3.7 × 10 ⁻²¹
		Cl	<6 × 10 ^{-11 c}
Trichloroethylene	400-1700, ^a 500-1000 ^b	OH	2.4 × 10 ⁻¹²
		O ₃	<3 × 10 ⁻²⁰
		Cl	≤2 × 10 ^{-11 c}
Tetrachloroethylene	1,500-2,000, ^a 1,400-2,800 ^b	OH	1.7 × 10 ⁻¹³
		O ₃	<2 × 10 ⁻²³
		Cl	≤7 × 10 ^{-12 c}
Methylene chloride	3,700-12,000, ^a 600-2,500 ^b	OH	1.4 × 10 ⁻¹³
		Cl	5.2 × 10 ⁻¹³
Chloroform	80-220, ^a 10-150 ^b	OH	1.0 × 10 ⁻¹³
		Cl	1.23 × 10 ⁻¹³
Chloroacetyl chlorides	no data	Photolysis	slow? ^d
Chloroacetaldehydes	no data	Photolysis	fast (same as acetaldehyde)
		OH	1.0 × 10 ^{-11 e}

^a Singh et al.³^b Shikiya et al.¹⁰^c Estimated, ≤10 times faster than the OH reaction.^d Dimitriadis et al.¹⁶ report a photolysis rate of 1 × 10⁻³ min⁻¹ (6 percent per hour) for trichloroacetyl chloride.^e Estimated, same as OH + acetaldehyde.

tions.¹ Ambient concentrations are for the Los Angeles area for all precursors for which data exist.^{8,10} Examination of the data in Table IV indicates that concentrations of known precursors in Los Angeles air are more than sufficient to account for the measured ambient phosgene levels of 20-50 ppt, and that the OH-chloroethene reaction and the OH-chloromethane reactions are the major pathways for in-situ formation of phosgene in the atmosphere. Reactions with ozone are essentially negligible. Reactions with chlorine atoms are fast but concentrations of chlorine in

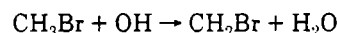
urban air are presumably too low (e.g., ≤10³ molecules cm⁻³ according to reference 6) for this reaction to be important. The importance of chloroacetyl chlorides and chloroacetaldehydes, for which no kinetic and ambient level data are available, cannot be assessed at the present time.

Finally, we attempted to rank the possible precursors of phosgene by using the product of their ambient (Los Angeles) concentrations and the corresponding OH reaction rate constants. This information is summarized in Table V, where all products of concentra-

tions and rate constants are listed relative to that of vinylidene chloride. Table V indicates that the five major precursors of phosgene in Los Angeles air are, in order of decreasing importance, trichloroethylene, 1,1-dichloroethane, 1,1,1-trichloroethane, methylene chloride, and tetrachloroethylene.

In-Situ Removal

Methyl bromide is one of the least reactive toxic air contaminants, with a correspondingly long persistence in the atmosphere. Reactions with O₃ and NO₃ are negligibly slow. Photolysis is a negligible removal process for CH₃Br in the lower troposphere.²¹ Methyl bromide reacts only slowly with the hydroxyl radical:



with a reaction rate constant of 3.5 × 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹.²² This corresponds to a half-life of 5 to 11 months.¹ Upward diffusion and deposition are thus the dominant loss processes for CH₃Br in the troposphere.]*

There have been no kinetic or product studies relevant to the atmospheric removal of epichlorhydrin. Photolysis, reaction with O₃, and reaction with NO₃ are negligible. Slow removal by reaction of epichlorhydrin with OH is expected. The rate constant for the OH-epichlorhydrin reaction, estimated from structure-reactivity relationships,¹ is 3.6 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹. Another recent estimate based on experimental results is ≥0.55 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹.²³ These estimates compare well to the OH reaction rate constants measured for structural analogues including other epoxides (i.e., *k* = 0.5-1.3 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹ for propylene oxide

Table V. Ranking of phosgene precursors.

Precursor	A = 10 ⁻¹² × OH reaction rate constant (cm ³ molecule ⁻¹ sec ⁻¹)	B = ambient concentration (ppt)	Product A × B	Ranking
Chloroethenes				
Vinylidene chloride	8.1	5-10	40-80	4
Trichloroethylene	2.4	500-1,000	1,200-2,400	1
Tetrachloroethylene	0.17	1,400-2,800	240-480	3
Hexachloro 1,3-butadiene	<0.17 (estimated)	5	<0.8	—
Halocarbons				
Methylene chloride	0.14	600-5,000	80-700	2
Chloroform	0.10	50-200	5-20	6
Carbon tetrachloride	<1 × 10 ⁻³	100-120	<0.12	—
1,1-dichloroethane	0.26	60-70	17	5
1,1,1-trichloroethane	0.01	1,000	10	7
1,1,2-trichloroethane	0.33	10	3	8
1,1,1,2-tetrachloroethane	<1 × 10 ⁻²	5	<0.05	—
1,1,2,2-tetrachloroethane	<1 × 10 ⁻²	10	<0.1	—
Hexachloroethane	<1 × 10 ⁻³	no data	small	—
Bromodichloromethane	0.1	10	1	9
Fluorotrichloromethane	<1 × 10 ⁻³	500	<0.5	—
CF ₃ CCl ₃	<1 × 10 ⁻³	300	<0.3	—

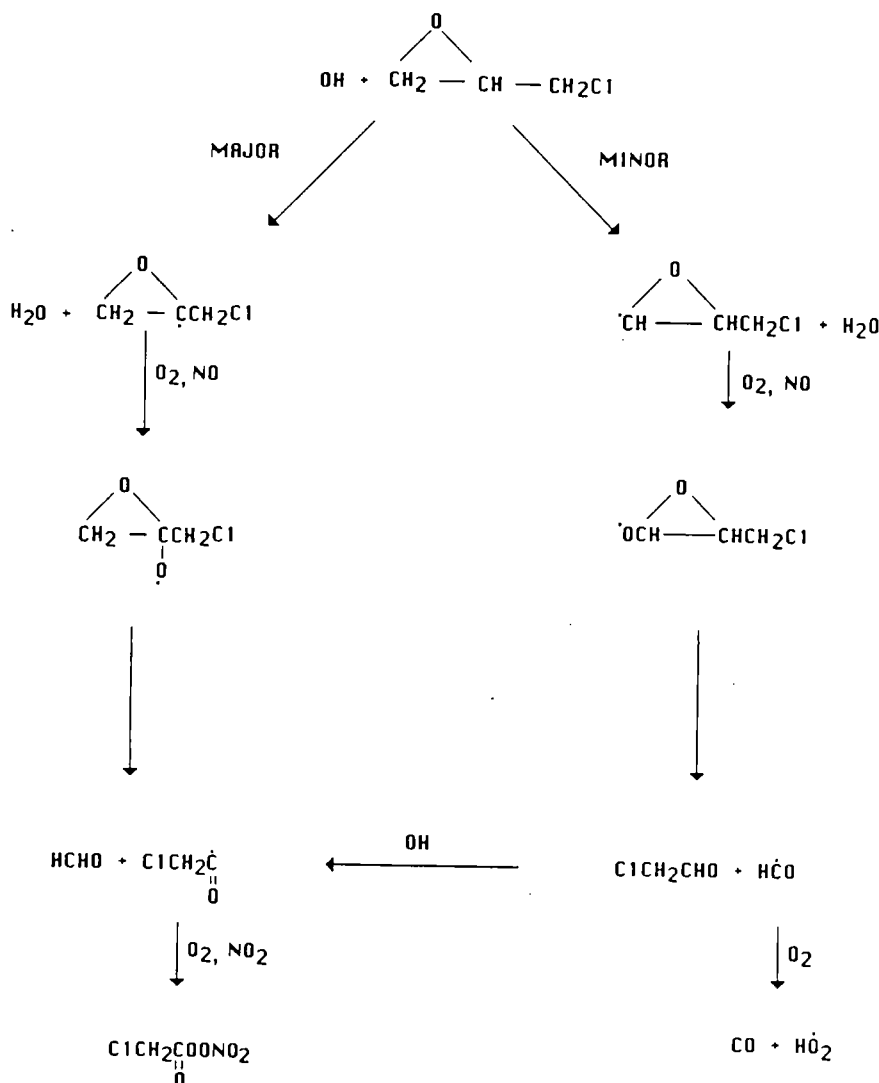


Figure 2. Tentative mechanism for the OH-epichlorhydrin reaction.

and $k = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for 1,2-epoxybutane.²²⁻²⁴⁾

A tentative scheme for the slow removal of epichlorhydrin by OH-initiated photooxidation in the atmosphere is outlined in Figure 2. This mechanism is identical to that proposed earlier² for the reaction of OH with propylene oxide. H-atom abstraction is expected to involve the tertiary C₂ hydrogen atom and, to a lesser extent, the secondary C₁ hydrogen atoms. Both pathways are included in Figure 2. For both alkoxy radicals, unimolecular decomposition may involve C—C as well as C—O bond scission, leading to formaldehyde, chloroacetaldehyde, the chloroacetyl radical (ClCH₂CO), and the formyl radical (HCO). The major product expected to form from both chloroacetaldehyde (by reaction with OH) and the chloroacetyl radical is ClCH₂C(O)-OONO₂, peroxychloroacetyl nitrate. This compound has been identified in

laboratory experiments involving the appropriate precursors (e.g., chloroacetaldehyde or chlorinated olefins). It has not been identified in ambient air. Once formed, phosgene is removed only slowly from the atmosphere. Its reactions with OH, O₃, NO₃, and Cl are of negligible importance. Photolysis and hydrolysis are also deemed negligible on the basis of laboratory studies in which phosgene was stable for ≥ 15 hours in air containing 10,000 ppm of water vapor under irradiation conditions approximating those of sunlight (Singh, 1976). Phosgene is, therefore, removed from the troposphere only by deposition and upward diffusion.

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Yanez prepared the draft and final versions of the manuscript.

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Dear Katie,

The attached may be of some interest to you. It is the chapter on ODPs of the forthcoming UNEP/WMO Scientific Assessment of Ozone Depletion report. I was one of the major authors on this chapter.

You may find the general discussion of what an ODP means of interest. You will also find section 6-4 and Figure 6-4 of particular use if you want to pursue the question of the time dependence of the ODP for methyl bromide (CH₃Br).

Best wishes,

Susan S.

Chapter 6. Evaluation of Ozone Depletion and Chlorine Loading Potentials (ODPs and CLPs)

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SCIENTIFIC SUMMARY

The recognition of the roles of chlorine and bromine compounds in ozone depletion has led to the regulation of their source gases. Some source gases are expected to be more damaging to the ozone layer than others, so that scientific guidance regarding their relative impacts is needed for regulatory purposes. Parameters used for this purpose include the steady-state and time-dependent Chlorine Loading Potential (CLP) and the Ozone Depletion Potential (ODP). Chlorine loading potentials depend upon the estimated value and accuracy of atmospheric lifetimes and are subject to significant (order 20-50%) uncertainties for many gases. Ozone depletion potentials depend upon the same factors, as well as the evaluation of the release of reactive chlorine and bromine from each source gas and corresponding ozone destruction within the stratosphere.

ODPs have generally been calculated with two-dimensional numerical models, which have limitations in the treatments of atmospheric transport and chemistry required for evaluation of ozone losses. In particular, such models do not fully represent the transport processes of the lower stratosphere (so that the calculated release of reactive chlorine from the source gases there is subject to uncertainties) nor do they reproduce in detail the large observed ozone losses in the lower stratosphere, especially in polar regions. The sensitivity of modeled ODPs to these problems is reduced by virtue of the fact that the ODP is a relative parameter, but is not completely eliminated, so that the more conservative assessment parameter represented by the CLP has also been considered. In this assessment, ODPs are estimated both from models and with a new semi-empirical approach which uses measurements and/or deduced correlations between source gases (to evaluate reactive chlorine release) together with observations of ozone losses. A critical assumption in the semi-empirical approach is that observed lower stratospheric ozone losses are due to halogen chemistry. This assumption is well-justified in polar regions and likely to be largely true at mid-latitudes. Therefore, the semi-empirical ODPs are expected to be more realistic than those derived from current models, at least in polar regions.

Modelled steady-state ODPs and CLPs have been evaluated using improved kinetic schemes. Further, some preliminary model results include a treatment of known heterogeneous chemistry on mid-latitude sulfate aerosols. The numerical values of these modeled ODPs are close to those of previous assessments.

Semi-empirical steady-state ODPs are given for the polar lower stratosphere and, in a few cases, for the global average. The semi-empirical ODPs are generally larger than the modeled values for chlorocarbons whose stratospheric loss rates are slower than that of CFC-11 and smaller for those whose loss rates are faster than that of CFC-11. For example, the semi-empirical ODP for HCFC-22 is between about 20 and 80% greater than the range of the model values. For some Halons, the semi-empirical ODPs for polar regions exceed some model estimates by as much as a factor of two. For all of the HCFCs considered here, the inferred ODP values are well below the CLPs and show that the upper limit to ozone loss represented by the CLP is not realized in the stratosphere for these species. This narrows significantly the uncertainties in the ODPs for HCFCs.

During the next decade, stratospheric chlorine abundances are expected to rise substantially. This increase in chlorine will likely lead to further global ozone loss including larger reductions in the Arctic and perhaps in northern mid-latitudes. In this near-term period, the HCFCs and many Halons will have an impact that is considerably larger than their steady state ODPs, in some cases and over some time horizons by as much as a factor of two to five.

Short term
O₃ impact
Steady state
ODP.

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6.1 INTRODUCTION

Understanding of the depletion of stratospheric ozone by anthropogenic halocarbons has led to the need for simple measures for comparing the impact of one halocarbon source gas against others as a scientific guide to public policy. The simplest of these is the chlorine loading potential, or CLP. This index represents the amount of total chlorine delivered from the troposphere to the stratosphere due to emission of a given halocarbon, relative to that from a reference molecule, generally CFC-11 [see, e.g., *Prather and Watson*, 1990]. CLPs can be considered upper limits to the steady-state relative effect on ozone depletion for most gases, and are defined by:

$$\text{CLP} = \frac{\text{Cl (trop) for compound } x}{\text{Cl (trop) for CFC-11}} = \frac{\tau_x}{\tau_{\text{CFC-11}}} \frac{M_{\text{CFC-11}}}{M_x} \frac{n_x}{3} \quad (6-1)$$

where Cl (trop) is the chlorine transported across the tropopause to the stratosphere per unit mass of halocarbon emitted; τ_x , $\tau_{\text{CFC-11}}$, $M_{\text{CFC-11}}$ and M_x denote the lifetime and molecular weights of CFC-11 and the compound in question, respectively; n_x is the number of chlorine atoms per molecule of compound x . Similarly, the steady-state bromine loading potential (BLP) represents the total bromine delivered to the stratosphere relative to the chlorine due to CFC-11, and can be defined as:

$$\text{BLP} = \frac{\text{Br (trop) for compound } x}{\text{Cl (trop) for CFC-11}} = \frac{\tau_x}{\tau_{\text{CFC-11}}} \frac{M_{\text{CFC-11}}}{M_x} \frac{k_x}{3} \quad (6-2)$$

The chlorine loading for many HCFCs is determined largely by their decomposition within the troposphere through reaction with the reactive OH radical. Effective tropospheric OH concentrations can be estimated from observations of the trend in methyl chloroform together with information on its releases [e.g., *Prinn et al.*, 1991]. The lifetimes of other species similarly destroyed by reaction with tropospheric OH can then be inferred using laboratory measurements of their respective rate coefficients [e.g., *Prather and Spivakovsky*, 1990]. Estimates of the uncertainties in lifetimes and hence in CLPs will be discussed in Section 6.2.2.

Ozone depletion due to halocarbons depends not only upon the amount of chlorine or bromine delivered to the stratosphere from the troposphere (the CLP), but also on the following stratospheric processes: (i) the breakdown of the halocarbon within the stratosphere, which is responsible for liberating reactive halogen gases and (ii) the subsequent chemistry of the reactive halogens that controls the magnitude of the ozone depletion. Source gases with long stratospheric lifetimes will break down to release their chlorine or bromine less effectively than CFC-11, making their net impact on ozone smaller than their CLPs. It is important to distinguish between the tropospheric and stratospheric lifetimes, particularly for the HCFCs, which have relatively short tropospheric lifetimes but long stratospheric lifetimes (see Table 6-2 below). The need to consider stratospheric ozone loss processes in the assessment of relative impacts on halocarbons on the ozone layer has led to the use of numerical models for evaluation of the Ozone Depletion Potential (ODP) as first suggested by *Wuebbles* [1983]. The ODP represents the amount of ozone destroyed by emission of a gas over its entire atmospheric lifetime (i.e., at steady-state) relative to that due to emission of the same mass of CFC-11, and is defined in modelling calculations as follows:

$$\text{ODP} = \frac{\text{Globally Averaged Ozone Depletion due to } x}{\text{Globally Averaged Ozone Depletion due to CFC-11}} \quad (6-3)$$

Because the ODP is a relative measure, it is likely that it can be calculated by present stratospheric models with greater reliability than the absolute ozone depletion, but it is important to quantify that

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reliability. The accuracy and reliability of ODP estimates will be addressed in this chapter by considering both statistical ranges of likely uncertainties and by examining observations.

The ODP/CLP ratio represents the efficiency of particular compounds for ozone destruction once in the stratosphere and allows for separation of the effects of stratospheric processes on the ozone depletion potential from those related to tropospheric removal and uncertainties in lifetimes. This will be discussed in more detail in Sections 6.2 and 6.3.

Two-dimensional models have become one of the principal tools for assessing the impact of anthropogenic emissions on the ozone layer. Such models generally include rather detailed representations of gas-phase photochemical processes and parameterized descriptions of stratospheric transport. These models have achieved significant successes in representing the chemical composition of the stratosphere, particularly at mid-latitudes above perhaps 25 km. However, recent research has demonstrated that current ozone depletion takes place largely below 25 km and is not well simulated by gas-phase models [WMO, 1990; and Chapters 2 and 8 of this report]. This occurs in part because current models do not contain satisfactory descriptions of the complicated microphysical processes governing the development of polar stratospheric clouds, the heterogeneous reactions which occur on them, and the important processes of dehydration and denitrification, nor do they simulate in detail the transport processes that link polar and mid-latitude regions.

The breakdown of halocarbons within the stratosphere depends heavily upon both the modelled atmospheric transport and chemistry. It has been shown [e.g., *Podolske et al.*, 1989] that current models fail to predict the very low concentrations of source gases and the correspondingly high concentrations of inorganic chlorine observed in the polar lower stratosphere in late winter. Without a realistic representation of the distributions of source gases and thus their chlorine (or bromine) release, the ODP cannot be calculated reliably even if the heterogeneous chemical processes leading to ozone depletion are considered in complete detail. The fact that the ODP is a relative measure alleviates, but does not eliminate, the role of shortcomings in model transport and ozone loss processes for modelling studies of ODPs, suggesting the need to examine observations to better constrain ODP estimates.

ODPs from gas-phase model calculations were presented in WMO [1990] and *Fisher et al.* [1990]. Calculations by a variety of modelling groups were included. The general behavior, e.g. significantly higher ODPs for CFCs compared to HCFCs, was reproduced by all the models. However, there were also systematic differences between the models. For example, the AER two-dimensional model calculated somewhat smaller ODPs for the CFCs than the Oslo two-dimensional model, presumably a reflection of differences in stratospheric processes, whereas, for the HCFCs, the AER model calculated higher ODPs than the Oslo model, presumably a reflection of differences in tropospheric processes in the two models. These differences suggest that, for any particular model, the relative variation among ODPs of similar compounds (e.g., HCFCs) may be more accurately calculated than that for different types of compounds (e.g., a CFC versus an HCFC). Section 6.2 describes new calculations of ODPs and CLPs including some from models that consider heterogeneous chemistry.

An alternative new approach to modelling studies of ODPs is to use observations of source gases to evaluate the chlorine or bromine release; such information coupled with observations of ozone loss can be used to deduce semi-empirical ODPs as described in Section 6.3. While subject to important uncertainties and assumptions, this semi-empirical method avoids the demanding requirements of accurate numerical simulation of source gas distributions and ozone destruction, and is therefore expected to be more realistic than present models, at least in the polar lower stratosphere where a significant fraction of contemporary ozone loss is found.

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The time scale for the atmosphere to attain steady state with respect to injections of halocarbons ranges from a few years to many centuries, depending upon the lifetime of the species in question. Steady-state ODPs represent the best current understanding of the long-term impacts of such releases, but they do not describe short term (decades or less) responses [WMO, 1990; SORG, 1990]. When specific short term time horizons are considered, time-dependent ODPs provide a more appropriate measure of impacts. Section 6.4 presents estimates of time-dependent ODPs for several halocarbons of interest over a range of time horizons.

6.2 MODEL CALCULATIONS OF CLPs AND ODPs

6.2.1 Compounds and Chemistry Considered

The list of compounds considered in this assessment (Table 6-1) is similar to that in WMO [1990], comprising most of the chlorofluorocarbons (CFCs) and other chlorinated halocarbons of interest, including several already being used or considered as replacements for CFCs, such as HCFC-22, HCFC-225ca, and HCFC-225cb. The list of brominated halocarbons (Halons) considered here is much more extensive than the previous report, reflecting the increased interest in the environmental effects of these compounds. Since WMO [1990], the uncertainties in photolysis cross-sections and reaction rate constants for many compounds have been narrowed considerably by improved laboratory studies. Table 6-1 shows the adopted kinetic parameters for the compounds evaluated in the Lawrence Livermore National Laboratory (LLNL) atmospheric models. It was not possible to ensure that all models presented here used the same kinetic parameters, but most of these differences are expected to be minor.

Detailed information is now available regarding the full temperature dependence of the ultraviolet and visible cross-sections for many of the compounds examined, whereas models used in the WMO [1990] assessment were restricted to a single set of temperature-independent absorption coefficients for nearly all compounds. Inclusion of the temperature dependence can affect the altitude of Cl and Br release in the stratosphere. The temperature dependence of the absorption cross sections also affects the atmospheric lifetimes for several species, including H-1202, H-1211, and H-2402. Many of the bromoalkanes exhibit smooth continuum UV absorption cross-sections in the region of 280-400 nm (near-ultraviolet and visible). As pointed out by Burkholder *et al.* [1991], this region contributes significantly to atmospheric photoprocesses (because of the greatly increased transmitted flux there relative to shorter wavelengths) but the absolute absorption coefficients there are often small and difficult to measure. As an example, lifetimes ranging from 10 to greater than 50 years were calculated for H-1211 with the LLNL 1-D model, depending on the inclusion or exclusion of the temperature dependence of the cross-sections and the extension of the long wavelength tail, emphasizing the need for accurate measurements in this region.

Improved laboratory studies have changed the understanding of reaction rates with OH and hence the lifetimes and CLPs for several of the HCFCs. For example, reaction rates of OH with HCFC-141b [Talukdar *et al.*, 1991] and HCFC-142b [Gierczak *et al.*, 1991] are about 30% and 15% smaller, respectively, than in the previous assessment.

All of the past calculations of ODPs were based on models including only gas-phase chemistry and did not consider heterogeneous chemistry on sulfate aerosols or polar stratospheric cloud particles. In order to provide a historical perspective and because of limited time for preparing this report, most of the model results presented here are still based on gas phase chemistry. Some preliminary calculations are presented that attempt to consider heterogeneous processes (see Chapter 8).

Two-dimensional model calculations of atmospheric lifetimes, chlorine loading potentials, and ozone depletion potentials are included from five modeling groups: Lawrence Livermore National

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Laboratory (LLNL), Atmospheric and Environmental Research, Inc. (AER), University of Oslo/Norsk Institutt for Luftforskning, Norway (Oslo/NILU), and E.I. Du Pont de Nemours and Company (Du Pont). Most of the compounds have been evaluated with both the LLNL and AER models; the other groups evaluated a limited number of compounds.

6.2.2 Atmospheric Lifetimes and Chlorine Loading Potentials

Calculated lifetimes are shown in Table 6-2. The estimated lifetimes of the HCFCs are generally shorter than in the previous assessment, largely as a result of increases in calculated tropospheric hydroxyl concentrations due to new, more accurate measurements of the rate of the reaction of OH with CH_4 [Vaghiani and Ravishankara, 1991]. Differences of 20-30% are obtained for the calculated lifetimes for the HCFCs between the models used, reflecting the extreme difficulty and uncertainty associated with evaluation of tropospheric OH chemistry (see Chapter 5). Due to these problems, the lifetimes of compounds that react predominantly with OH are generally constrained by scaling to an assumed CH_3CCl_3 lifetime deduced from observations. In this chapter, lifetimes for all species in each model will be scaled to match the best estimates given in Chapter 8 and shown in Table 6-2. While such scaling imposes uniform CLPs, it fails to standardize other processes important to determining ODP values. For example, if different models calculate different tropospheric OH densities, then they are also likely to exhibit different stratospheric OH abundances. Stratospheric OH distributions have a minor impact on the lifetimes of the HCFCs, but control their stratospheric breakdown, subsequent chlorine release, and hence the ODP/CLP ratio. Similarly, many of the differences in calculated lifetimes for species destroyed by stratospheric photolysis (e.g., CFC-113) likely reflect differences in model transport and/or radiative transfer treatments that influence stratospheric chlorine release and ODP/CLP ratios, at least to some degree. These important model differences are not improved by standardizing the model lifetimes. In the following, ODP/CLP ratios will be taken directly from the individual model results, but the CLPs used to calculate ODPs will be based upon the standardized lifetimes.

A recent study using observations of CH_3CCl_3 together with estimates of its emissions suggests that the lifetime of CH_3CCl_3 may be shorter than previously thought due to changes in measurement calibrations [Prinn *et al.*, 1991], while others have noted the possible importance of oceanic hydrolysis as a sink for this compound [Wine and Chameides, 1990; Butler *et al.*, 1991]. In contrast, many of the HCFCs are expected to undergo less oceanic hydrolysis, so that the fraction of their total lifetime attributable to loss with OH may differ from that of methyl chloroform. These considerations imply that the use of methyl chloroform to deduce an effective average tropospheric OH concentration is less certain than previously thought, with attendant uncertainties for estimates of CLPs and ODPs for compounds destroyed by reaction with OH. The lifetimes of compounds destroyed by stratospheric photolysis (including the reference molecule for ODP calculations, CFC-11) also have significant uncertainties. These are due in part to uncertainties in the dynamical processes responsible for transporting these compounds to the altitudes where their chemical destruction is rapid. The range of model values shown in Table 6-2 is likely to be representative of these uncertainties.

The range of total uncertainty in chlorine loading potentials for some species is illustrated explicitly in Figure 6-1, wherein estimated accuracies were used to deduce cumulative probability distribution functions [e.g., Lindgren, 1968]. The uncertainties considered are indicated on the figure. This approach assumes that these errors are randomly distributed and is intended only to illustrate the current best estimate of the range of statistically probable error. The figure illustrates the fact that uncertainties in steady-state CLPs can be large for some compounds, and that the CLPs for HCFC-123, HCFC-22, and HCFC-141b are likely (>90% probability) to lie below 0.035, 0.26, and 0.29, respectively.

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Additional uncertainties exist, but most of these are related to fundamental understanding rather than numerical accuracy and are not included in Figure 6-1. In deriving the CLPs shown in Figure 6-1 and Table 6-2, it has been assumed that the products of all decomposition reactions in the troposphere are too short-lived to reach the stratosphere. However, some HCFCs (e.g., HCFC-141b and 142b) likely produce halogen-containing acyl peroxy nitrates as products of their oxidation with tropospheric OH (see Chapter 5). If these peroxy nitrates are sufficiently long-lived to be transported to the stratosphere to some degree, then an effective increase in CLPs will result. Further, it is possible that OH and/or HO₂ radicals may be removed on aerosol surfaces in the troposphere and/or stratosphere, affecting the lifetimes of compounds removed by tropospheric OH and perhaps their stratospheric chlorine release. Although observations of CH₃CCl₃ place some constraints on the magnitude of tropospheric OH in an averaged sense and thus upon such reactions, they cannot be ruled out. Further, CLPs represent best estimates for the contemporary atmosphere but neglect possible changes that may occur over the lifetimes of the compounds in question. For example, future changes in tropospheric water vapor and hence OH concentrations (due, for example, to atmospheric climatic change) would affect the CLPs of many compounds but are not considered here.

6.2.3 Calculated ODPs

Table 6-3 presents ODPs for CFCs, HCFCs, Halons and other halocarbons calculated with the two-dimensional models considered. The model-calculated ODPs for CH₃CCl₃ and the HCFCs are generally less than 0.15, while those for the CFCs and Halons are much larger. Chlorinated compounds with stratospheric lifetimes comparable to or shorter than that of CFC-11 display ODP/CLP ratios close to 1, reflecting the fact that they release their chlorine in a manner similar to the reference gas and hence have similar impacts on ozone once in the stratosphere. As mentioned in Section 6.1, chlorinated compounds with stratospheric lifetimes longer than that of CFC-11 release their chlorine more slowly and display ODP/CLP ratios that are less than 1. Many of the HCFCs have relatively small ODP/CLP values due to their slow stratospheric breakdown by reaction with OH (see Table 6-2). Clearly, the least damaging chlorinated substances are those that are destroyed rapidly within the troposphere (thus limiting their CLPs) but slowly in the stratosphere (reducing the ODP/CLP ratio).

For the Halons, the ODP/BLP ratios depend on the efficiency of bromine as compared to chlorine in destroying ozone as well as on the stratospheric lifetime (hence the bromine release). The efficiency of bromine relative to chlorine in depleting ozone is hereafter referred to as α , and is expected to be close to the ODP/BLP ratio for all of the Halons considered here. It is important to note that α is dependent on the absolute amount of reactive chlorine, due to chemical coupling between chlorine and bromine that controls the impact of bromine on ozone. The α values given here pertain to conditions of total reactive chlorine loading close to contemporary levels. The scenarios presented in Chapter 8 suggest that the future chlorine loading is likely to change by less than 20% for at least the next several decades. The calculated globally averaged α values suggested by the ODP/BLP ratios in Table 6-2 range from about 10 to 80. These illustrate the extreme effectiveness of bromine in catalyzing ozone destruction [first noted by Yung *et al.*, 1980].

The model calculated α values for the Halons depend critically on the portion of bromine species found in the active form (BrO) which in turn depends on the formation and removal rates of the reservoir species, HBr and BrONO₂. Some measurements of HBr appear difficult to reconcile with present theory [Park *et al.*, 1989]. However, measurements of BrO by Brune *et al.* [1988] are in general agreement with model predictions, lending some support to the calculated α values and current photochemical schemes for bromine. The precise values of α for mid-latitudes also depend on calculated concentrations of atomic oxygen, OH, and HO₂ in the lower stratosphere, which are subject to considerable uncertainties. The values reported in the table should therefore be considered as preliminary. Note, however, that the value of α in the polar lower stratosphere is much better understood as discussed later (see Section 6.3).

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Most of the calculations include gas-phase chemistry only, but some calculations have also been carried out with the AER, LLNL, and Du Pont models including a parameterization of known heterogeneous chemistry on sulfate aerosols, and with a treatment of PSC chemistry for the OSLO model (see Chapter 8). The ODP/CLP and ODP/BLP ratios calculated with heterogeneous chemistry in Table 6-2 are very similar to those from the gas phase models presented here for nearly all species. However, as discussed in more detail below and in Chapter 8, the models including heterogeneous chemistry still do not fully describe the chlorine release nor the ozone loss observed in the lower stratosphere at middle and high latitudes, so that their calculated ODPs remain subject to uncertainties.

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from future differences in models.

6.3 COMPARISON OF MODELED ODPs AND INFERENCES FROM OBSERVATIONS

In this section, semi-empirical information useful for estimating the ratio between ODP and CLP will be briefly described, the results presented, and compared to the models used here. Briefly, the approach used [Solomon *et al.*, 1991] consists of using direct measurements of halocarbons to evaluate chlorine release and hence local ODP/CLP ratios, particularly in the polar lower stratosphere. When direct measurements are limited, correlations are used to infer abundances for some halocarbons from those of other tracers and hence their ODP/CLP ratios. Globally averaged ODP/CLP ratios are estimated for some compounds using local ODP/CLP values together with an observationally-derived ozone loss distribution assuming that the ozone loss is due only to halogen chemistry.

The fraction of halocarbon dissociated within the stratosphere (F) can be defined as:

$$F = \frac{\mu_{\text{entry}} - \mu_{\theta,z}}{\mu_{\text{entry}}} \quad (6-4)$$

where μ_{entry} denotes the mixing ratio of halocarbon entering the stratosphere and $\mu_{\theta,z}$ indicates the mixing ratio at any latitude and altitude. Measurements of the distributions of halocarbons within the stratosphere can be used to define $\mu_{\theta,z}$. Since the tropical troposphere is rather well-mixed for species with lifetimes longer than a few months, μ_{entry} is likely to be nearly equal to the surface mixing ratio. Time lags for transport between the troposphere and stratosphere influence the value of μ_{entry} for any molecule whose abundance is changing with time (e.g., HCFC-22, CFC-11). Such lags are believed to be short (2 years or less) over much of the atmosphere, but measurements of CO_2 suggest time lags of about 3 years in the polar lower stratosphere [Heidt *et al.*, 1991; Schmidt and Khedim, 1991].

As noted in WMO [1990], the local ozone depletion in regions of rapid chlorine-catalyzed destruction of ozone is proportional to the relative stratospheric chlorine release (Cl_{rel}) per unit of surface emission of substance, which can be defined as the ratio of fractional dissociation of a particular molecule to that of CFC-11, multiplied by the chlorine loading potential. This implies that the local ozone depletion potential ($\text{ODP}(\theta,z)$) at any point can be defined as follows [see Solomon *et al.*, 1991]:

$$\text{ODP}(\theta,z) = \text{Cl}_{\text{rel}} = \left(\frac{\mu_{\text{entry}} - \mu_{\theta,z}}{\mu_{\text{entry}}} \text{ for } x \right) / \left(\frac{\mu_{\text{entry}} - \mu_{\theta,z}}{\mu_{\text{entry}}} \text{ for CFC-11} \right) \cdot \text{CLP} \quad (6-5)$$

Equation (6-5) allows estimation of the local ODP/CLP ratio from available measurements of CFC-11 together with other halocarbons. This approach has been taken for a number of halocarbons of interest, particularly HCFC-22, CCl_4 , CFC-113, and CH_3CCl_3 in polar regions [Solomon *et al.*, 1991]. Simultaneous airborne measurements of these species together with CFC-11 were obtained by Heidt and coworkers [see, Heidt *et al.*, 1989] during the Airborne Arctic

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Stratosphere Experiment (AASE) in January-February, 1989. The polar measurements of CH_4 , N_2O , and CFC-11 used here have been stringently intercompared with other calibration standards and are believed to be accurate to within a few percent. Because of the large ozone losses in the Arctic and Antarctic as described in Chapter 2, the local ozone depletion potentials of the polar lower stratospheres are of considerable importance in determining the globally averaged ODP as well as in understanding requirements for reducing or eliminating ozone losses such as the Antarctic ozone hole. Table 6-4 presents Arctic lower stratospheric local ozone depletion potentials from these direct measurements, averaged over the region from 15-21 km; similar numbers have been obtained from Antarctic lower stratospheric measurements obtained in September, 1987. Growth rates for these source gases have been taken from WMO [1990] and results are shown for several cases assuming no time lag between the troposphere and stratosphere and assuming a three year lag as discussed earlier.

Direct observations of HCFCs and Halons are, however, extremely limited for many species. In the absence of direct information, correlations among long-lived tracers provide a useful means to infer the distribution of one compound from observations of another, thus extending the possible range in space and in compounds evaluated [see Fahey *et al.*, 1990; Solomon *et al.*, 1991; Plumb and Ko, 1991]. Plumb and Ko [1991] have shown that the correlations between long-lived tracers are likely to be robust parameters that depend largely on the ratio of stratospheric loss rates and not upon the details of transport processes. The correlations between species can therefore be calculated in models with far greater confidence than the absolute tracer abundances or ODPs. In the following, abundances of several HCFCs and their corresponding local ODPs are inferred from observations of CH_4 or N_2O using correlations from model calculations [see Solomon *et al.*, 1991 for details]. Table 6-4 shows that the polar ODP inferred for HCFC-22 using an assumed correlation with CH_4 gave results close to that obtained with direct measurements of HCFC-22 when a three year lag time was assumed. The calibration standard used here for HCFC-22 has not yet been intercompared in detail with others. This comparison nonetheless strengthens confidence in the correlation approach. Further, it is important to note that the semi-empirical ODP deduced from direct measurements of HCFC-22 is sensitive to the assumed age of the air due to the rapid (order 7-10% per year) rate of increase of this compound in the contemporary atmosphere, while the values derived from CH_4 display little dependence on the assumed age since the CH_4 growth rate is only about 0.7% per year.

Figure 6-2 presents the local chlorine release profile inferred for mid-latitude winter for HCFC-22 [based upon measurements of CFC-11 and CH_4 together with an adopted correlation between CH_4 and HCFC-22 that is in good agreement with available direct measurements as described in Solomon *et al.*, 1991]. Values taken from several models used in this assessment are shown for comparison. Because of the possibility of sharp latitude gradients, detailed comparisons between models and measurements should be carried out as a function of latitude as well as altitude, so that Figure 6-2 provides only general guides to the comparisons between models, and between models and quantities inferred from measurements. Figure 6-2 reveals overall consistency between the shapes of the vertical profiles of the modeled and inferred relative chlorine release but many differences in detail. The discrepancies in the lower stratosphere where much of present day ozone loss occurs (see Chapter 2) are of the greatest importance to estimates of ODPs.

Comparison of Tables 6-3 and 6-4 shows that the observationally-based polar lower stratospheric ODP/CLP ratios are generally larger than the globally averaged values obtained in gas phase models for chlorocarbons whose stratospheric lifetimes are longer than that of CFC-11 (e.g., HCFC-22 and HCFC-142b), while the observationally-based values tend to be slightly smaller than the model calculations for chlorocarbons that exhibit stratospheric loss time scales that are shorter than that of CFC-11 (e.g., CCl_4). This primarily reflects differences in the time-dependent breakup of these molecules within the stratosphere relative to CFC-11, coupled with the fact that the air within the polar lower stratosphere is likely to be relatively 'old' compared to other regions where much of the modelled ozone depletion takes place.

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The extrapolation of the local approach to the global scale requires empirically-based specifications of the global distributions of both long-lived tracers and ozone loss. A global semi-empirical ozone depletion potential may be defined as [Solomon *et al.*, 1991]:

$$\text{ODP} = \sum_z \sum_\theta \sum_t \Delta O_3(z, \theta, t) \cdot \cos \theta \cdot \text{Cl}_{\text{rel}}(z, \theta, t) / \left\{ \sum_z \sum_\theta \sum_t \Delta O_3(z, \theta, t) \cdot \cos \theta \right\} \quad (6-6)$$

where $\Delta O_3(z, \theta, t)$ is the estimated decrease in ozone concentration observed in today's atmosphere at each altitude, latitude and time of year [see Solomon *et al.*, 1991 for details of the ozone loss distribution imposed]. This equation involves the important assumptions that all of the observed ozone depletion in the contemporary atmosphere is due to halogen chemistry and that the depletion is proportional to the local relative chlorine and/or bromine release [see also, Solomon *et al.*, 1991]. These assumptions are well-justified in polar regions and likely at mid-latitudes. *from these figures?*

Table 6-4 presents semi-empirical global ODPs for the following compounds: HCFC-22, HCFC-142b, and CCl_4 . A range of values is presented, showing the effects obtained if it is assumed (as extreme cases) that the polar vortex acts as a processor (i.e., assuming that mid-latitude lower stratospheric ozone losses have their origin entirely in polar region) and assuming that the polar vortex is completely isolated (see the discussion in Chapter 4 of this assessment). The global ODP/CLP ratios inferred are dominated by ozone losses in the lower stratosphere, and are similar to those obtained from the direct Arctic measurements. Thus the polar ODPs are likely to be close approximations to the global values.

Observations can also be used to place constraints on local ozone depletion potentials for Halons in the polar regions. The lifetimes of most Halons are rather short within the stratosphere (due to rapid photolysis) (see Table 6-2), and grab-sampling measurements of, for example, Halon-1211 during AASE suggest that it is nearly completely dissociated in the Arctic over the height range from about 15 to 21 km [W. Pollock and L. Heidt, personal communication, 1991]. Assuming that the Halons will be dissociated by at least as large a fraction compared to their input values to the stratosphere as CFC-11 in the polar lower stratosphere, the ozone depletion potentials for Halons (or BODP) in the contemporary stratosphere can be defined as:

$$\text{BODP} \approx \text{BLP} \cdot \alpha \quad (6-7)$$

Direct measurements of BrO , ClO , and OCIO in the polar stratosphere confirm the role of bromine in polar ozone loss and constrain the value of α there considerably better than the global estimates from models discussed earlier. These show that it is at least 40 in this region [see Chapter 8 and references in Solomon *et al.*, 1991]. A value of 40 is thus adopted here.

Table 6-5 presents the semi-empirical ODPs inferred from equation 6-7 for the Halons, compares the semi-empirical and modelled ODPs for all compounds, and presents the recommended ODPs for this assessment, based mainly on the semi-empirical approach with guidance from the models. Semi-empirical ODPs for HCFC-123, HCFC-124, HCFC-225ca and HCFC-225cb were obtained using the correlation between these molecules and CH_4 from the LLNL model, using the approach of Solomon *et al.* [1991]. The ODPs for the Halons derived both semi-empirically and from some models shown in Table 6-3 are considerably larger than the estimates of the previous assessment. The semi-empirical ODP/CLP values for HCFC-22 are larger than the range of the models shown here by about 20 to 80%, while for HCFC-142b, the inferred values are as much as a factor of two greater than some model values. For all of the HCFCs considered here, the inferred ODP/CLP values are, however, far below one, showing that the upper limit represented by the CLPs is not realized.

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The uncertainty in the semi-empirical polar ODP/CLP ratios for most species considered is mainly dependent on the relative calibration of the tracer measurements and is estimated to be on the order of $\pm 10\%$ for compounds inferred from CH_4 measurements. Combining this uncertainty with that of the CLPs discussed earlier allows estimation of the statistically probable error range for ODP values. Figure 6-3 presents the cumulative probability distribution functions for the ODPs of several molecules of interest based upon the known uncertainties considered. The figure shows that current uncertainties suggest that the ODP is highly likely ($>90\%$) to lie below 0.04 for HCFC-123, below 0.11 for HCFC-22, and below 0.23 for HCFC-141b. However, it should be emphasized that these ranges are likely to be underestimates since they are based purely on statistical errors in present understanding and do not include chemical and physical processes whose influences could be large but cannot currently be quantified (see Section 6.2.2).

6.4 TIME DEPENDENT EFFECTS

The ODP of compound x, defined in Section 6.1, refers to conditions when the two compounds, x and CFC-11, have reached their steady state concentrations. Consider the example of compound x, an HCFC with a relatively short tropospheric lifetime. The steady state ODP compares the calculated steady-state ozone loss due to x, which will be realized within perhaps a decade or so, with the ozone loss due to CFC-11, realized on the time scale of centuries. On the other hand, the ratio of the ozone loss due to compound x compared to that from CFC-11, if calculated after about a decade, will be much larger than the steady state ODP of compound x. All of x's ozone depletion has already occurred while the CFC-11 depletion is still increasing. Thus, while the ODPs for some short-lived compounds, including the HCFCs, may suggest only a modest impact on the chronic response by ozone, the acute response over the next several years will be more substantial.

As in estimations of greenhouse warming potentials (see Chapter 7), relative impacts can be assessed not just for steady-state, but also for specific time horizons. The time dependent semi-empirical ODP can be defined as follows [see *Solomon and Albritton, 1992*]:

$$\text{ODP}(t) = \left\{ \frac{\mu_{\text{entry}} - \mu}{\mu_{\text{entry}}} \text{ for } x \right\} / \left\{ \frac{\mu_{\text{entry}} - \mu}{\mu_{\text{entry}}} \text{ for CFC-11} \right\} \cdot \frac{M_{\text{CFC-11}}}{M_x} \cdot \frac{n_x}{3} \cdot \frac{\int_0^t e^{-t/\tau_x} dt}{\int_0^t e^{-t/\tau_{\text{CFC-11}}} dt} \quad (6-8)$$

where t is the time horizon and the other symbols have all been defined previously. The terms in brackets represent the fractional dissociation of x and CFC-11, respectively (equation 6-4) in the region considered. As in the previous section, these will be evaluated below using polar semi-empirical estimates based on observations. In principle, time lags for transport to the stratosphere could be considered in evaluating ODPs over specific time horizons but these are not expected to change the results greatly and were neglected for simplicity in the calculations presented here.

Figure 6-4 shows polar lower stratospheric ODPs for several HCFCs and Halons as a function of time horizon using the CLPs of Table 6-2. The large ODPs for bromine-containing compounds reflect the large value of α . Compounds with relatively short lifetimes display reduced impacts over long time scales but large ODPs over short time horizons. Note that although CH_3Br displays a relatively small ODP over long time horizons, it has a very large ODP for short time scales by virtue of its short lifetime and the large value of α . The large ODPs for CH_3CCl_3 obtained over short time horizons reflect the very short lifetimes of this gas, allowing for large and rapid impacts on ozone. The HCFCs have relatively short lifetimes, and generally display small ODPs over long time horizons, but exhibit ODPs over short time scales that can be as much as three to ten times greater than their steady-state ODPs. The opposite is true for compounds with lifetimes comparable to or longer than that of CFC-11 (e.g., CFC-113), which display smaller ODPs over short time horizons than they do over time scales of centuries.

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The calculations presented here illustrate the roles of various compounds in depleting ozone both over the long and short-term. Likely future changes in atmospheric chlorine and bromine are described in Chapter 8, where various emission scenarios are considered. Current restrictions on emissions of halocarbons suggest that the chlorine content of the stratosphere will continue to increase for at least the next decade, implying that further ozone reductions are likely in the near future. During this period, ODPs for the specific time horizon in question are expected to best represent the anticipated relative ozone response to releases of various compounds.

*Need to
pull on some
growth hits.*

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Table 6-1. Spectroscopic and chemical rate data used in the ODP calculations at LLNL.

Species	Chemical Formula	UV	OH Reaction Rate Constant			
		Absorption Cross-section Reference	A (cm ³	molecules ⁻¹ s ⁻¹)	E/R (K)	Reference
<u>CFCs</u>						
CFC-11	CFCl ₃	a				
CFC-12	CF ₂ Cl ₂	a				
CFC-113	CFCl ₂ CF ₂ Cl	b				
CFC-114	CF ₂ ClCF ₂ Cl	b				
CFC-115	CF ₂ ClCF ₃	b				
<u>HCFCs, etc.</u>						
HCFC-22	CF ₂ HCl	b	1.2 (-12)	1.65 (3)		a
HCFC-123	CF ₃ CHCl ₂	m	6.4 (-13)	8.50 (2)		a
HCFC-124	CF ₃ CHFCl	d	6.6 (-13)	1.25 (3)		a
HCFC-141b	CH ₃ CFCl ₂	m	9.4 (-13)	1.50 (3)		h
HCFC-142b	CH ₃ CF ₂ Cl	m	1.4 (-12)	1.80 (3)		i
HCFC-225ca	CF ₃ CF ₂ CHCl ₂	n	2.0 (-12)	1.30 (3)		j
HCFC-225cb	CF ₂ ClCF ₂ CHFCl	n	6.7 (-13)	1.30 (3)		d
Carbon Tetrachloride	CCl ₄	a				
Methyl Chloroform	CH ₃ CCl ₃	b,c	5.0 (-12)	1.80 (3)		a
<u>Brominated Compounds</u>						
H-1301	CF ₃ Br	b				
H-1211	CF ₂ ClBr	e				
H-1202	CF ₂ Br ₂	e				
H-2402	CF ₂ BrCF ₂ Br	e				
H-1201	CF ₂ HBr	f	7.4 (-13)	1.30 (3)		f
H-2401	CF ₃ CH ₂ Br	g	7.4 (-13)	1.08 (3)		k
H-2311	CF ₃ CHClBr	b	7.0 (-13)	7.30 (2)		l
Methyl bromide	CH ₃ Br	b	6.8 (-13)	8.50 (2)		a

a JPL 90-1

b Gillotay and Simon (1990)

c Vanlathem - Meures et al. (1979)

d Orlando et al. (1991) as quoted in Gillotay and Simon (1990); see also Gierczak et al. (1991)

e Burkholder et al. (1991)

f Talukdar et al. (1991)

g Brown et al. (1990)

h Recommended for this report (See Chapter 8); ~30% smaller than WMO (1989) value @ 277K

i Recommended for this report (See Chapter 8); ~15% smaller than WMO (1989) value @ 277K

j Recommended for this report (See Chapter 8)

k Orkin et al. (1990)

l Based on value at 300K in Brown et al. (1989)

m Gillotay and Simon (1991)

n Braun et al. (1991)

~ if this is relatively high compared to the troposphere, it is not delivered to stratosphere.

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Table 6-2. Lifetimes and Chlorine Loading Potentials. The range of atmospheric lifetimes calculated in the 2-D models used for the ODP analyses are shown, along with the corresponding standardized lifetimes and stratospheric lifetimes used in this report (see Chapter 8), and the Chlorine Loading Potentials (CLPs) derived with the standardized lifetimes.

Species	Model Total Lifetimes (yrs)	Best Estimate Total Lifetimes (yrs)	Approximate Stratospheric Lifetime (yrs)	Adopted CLPs
<u>CFCs</u>				
CFC-11	48.6 - 66	55	55	1.0
CFC-12	104 - 113	116	116	1.597
CFC-113	85 - 109	110	110	1.466
CFC-114	182 - 200	220	220	2.143
CFC-115	414 - 522	550	550	2.964
<u>HCFCs, etc.</u>				
HCFC-22	13.5 - 17.7	15.8	240	0.152
HCFC-123	1.3 - 1.6	1.7	47	0.0185
HCFC-124	5.7 - 7.1	6.9	129	0.0421
HCFC-141b	9.0 - 10.9	10.8	76	0.154
HCFC-142b	19.3 - 23.4	22.4	215	0.185
HCFC-225ca	2.2 - 2.7	2.8	60	0.0230
HCFC-225cb	6.7 - 8.1	8.0	120	0.0656
CCl ₄	40 - 58	47	47	1.018
CH ₃ CCl ₃	5.0 - 6.0	6.1	47	0.114
<u>Brominated Compounds</u>				
H-1301	65.5 - 68.6		67	
H-1211	18.5 - 20.1		40	
H-1202	3.9 (1 model)		33	
H-2402	22.1 - 30.4		38	
H-1201	5.6 (1 model)		58	
H-2401	2.0 (1 model)		46	
H-2311	0.8 (1 model)		29	
CH ₃ Br	1.2-1.8		35	

? = low
much
reside
atmosphere

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Table 6-3. Derived ODPs scaled to UNEP standardized lifetimes and the model-derived ODP/CLP ratio from the two-dimensional models for each of the compounds examined. Based on gas-phase chemistry only results unless indicated otherwise. Brackets indicate derived values with heterogeneous chemistry in the model. For all halons, model-derived ODPs are presented without reference to the standardized lifetime.

Species	LLNL		AER		OSLO		Du Pont	
	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP	ODP	ODP/CLP
CFCs								
CFC-11	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CFC-12	0.88	0.551	0.93	0.586	0.95 [0.93]	0.595 [0.582]	1.06 [1.01]	0.665 [0.635]
CFC-113	0.92	0.631	1.01	0.690	0.99 [0.98]	0.675 [0.668]		
CFC-114	0.57	0.266	0.82	0.382				
CFC-115	0.29	0.099	0.48	0.161				
HCFCs, etc.								
HCFC-22	0.034	0.221 [0.231]	0.045 [0.039]	0.276 [0.255]	0.032 [0.082]	0.221	0.048 [0.043]	0.314 [0.286]
HCFC-123	0.019 [0.016]	0.944 [0.878]	0.020	1.05			[0.013]	[0.709]
HCFC-124	0.016	0.358	0.020	0.449			[0.034]	[0.793]
HCFC-141b	0.12 [0.11]	0.720 [0.731]	0.12	0.767			[0.105]	[0.650]
HCFC-142b	0.035 [0.037]	0.186 [0.200]	0.057	0.305			[0.054]	[0.289]
HCFC-225ca	0.020	0.856	0.021	0.920			[0.016]	[0.714]
HCFC-225cb	0.023	0.348	0.031	0.474			[0.024]	[0.370]
CCl ₄	1.03	1.014	1.15 [1.13]	1.13 [1.11]				
CH ₃ CCl ₃	0.11 [0.13]	0.968 [1.12]	0.13	1.13			0.12 [0.12]	1.032 [1.08]
Halons, etc.								
H-1301	12.7	32.2	10.03	23.9				
H-1211	5.0	49.6	1.8	16.3				
H-1202	1.7	52.9						
H-2402	6.4	42.1	10.2	47.8				
H-1203	1.4	35.1						
H-2401	0.44	66.4						
H-2311	0.28	79.9						
CH ₃ Br	0.74	67.7	0.62 [0.53]	35.8 [30.6]				

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Table 6-4. Semi-Empirical Ozone Depletion Potentials for Chlorine Compounds [adapted from Solomon *et al.*, 1991].

Polar Lower Stratosphere

Molecule	Input data	Test Case	ODP/CLP	ODP
HCFC-22	HCFC-22, CFC-11	Arctic (Jan) 15-21 km, no lag	0.55	0.084
	Direct obs 15-21 km	Arctic (Jan) 15-21 km, 3 yr lag	0.38	0.058
CH ₃ CCl ₃	CH ₃ CCl ₃ , CFC-11	Arctic (Jan) 15-21 km, no lag	1.07	0.122
	Direct obs 15-21 km	Arctic (Jan) 15-21 km, 3 yr lag	1.09	0.124
CCl ₄	CCl ₄ , CFC-11	Arctic (Jan) 15-21 km, 3 yr lag	1.05	1.069
	Direct obs 15-21 km			
CFC-113	CFC-113, CFC-11	Arctic (Jan) 15-21 km, 3 yr lag	0.75	1.100
HCFC-22	CH ₄ , CFC-11	Arctic (Jan) 15-21 km, no lag	0.34	0.052
	model correlation to CH ₄	Arctic (Jan) 15-21 km, 3 yr lag	0.34	0.052
HCFC-142b	CH ₄ , CFC-11	Arctic (Jan) 15-21 km, 3 yr lag	0.36	0.067
	model correlation to CH ₄			
CH ₃ Cl	CH ₄ , CFC-11	Arctic (Jan) 15-21 km, no lag	0.86	0.022
	model correlation to CH ₄	Arctic (Jan) 15-21 km, 3 yr lag	0.89	0.023
HCFC-141b	N ₂ O, CFC-11	Arctic (Jan) 15-21 km, no lag	0.70	0.108
	model correlation to N ₂ O	Arctic (Jan) 15-21 km, 3 yr lag	0.72	0.111

Global

Molecule	Input data	Test Case	ODP/CLP	ODP
HCFC-22	Global CFC-11, CH ₄ data observed Δozone model correlation w/CH ₄ 3 year lag in vortex	global with polar loss, processor	0.372-0.389	0.056-0.059†
		global with polar loss, no processor	0.333-0.344	0.051-0.052†
HCFC-142b	Global CFC-11, CH ₄ data observed Δozone model correlation w/CH ₄ 3 year lag in vortex	global with polar loss, processor	0.377-0.394	0.070-0.073†
		global with polar loss, no processor	0.336-0.345	0.062-0.064†
CCl ₄	Global CFC-11 data observed Δozone model correlation w/CFC-11 3 year lag in vortex	global with polar loss, processor	1.03-1.05	1.049-1.069†
		global with polar loss, no processor	1.05-1.09	1.069-1.110†

† Range shows the effect of different assumptions regarding the magnitude of upper stratospheric ozone losses [see Solomon *et al.*, 1991].

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Table 6-5. Range of Modelled and Semi-Empirical Steady-State ODPs and Recommended Best Estimates

Species	Model Range		Semi-Empirical Range		Best Estimate ODP
	ODP	ODP/CLP or ODP/BLP	ODP	ODP/CLP or ODP/BLP	
<u>CFCs</u>					
CFC-11	1.0	1.0	1.0	1.0	1.0
CFC-12	0.88 - 1.06	0.551 - 0.665			≈1.0
CFC-113	0.92 - 1.01	0.631 - 0.690	1.07	0.75	1.07
CFC-114	0.57 - 0.82	0.266 - 0.382			≈0.8
CFC-115	0.29 - 0.48	0.099 - 0.161			≈0.5
<u>HCFCs, etc.</u>					
HCFC-22	0.032 - 0.048	0.221 - 0.314	0.05-0.08	0.33-0.55	0.055
HCFC-123	0.013 - 0.020	0.709 - 1.050	0.02	1.112	0.02
HCFC-124	0.016 - 0.034	0.358 - 0.793	0.022	0.523	0.022
HCFC-141b	0.10 - 0.12	0.650 - 0.767	0.11	0.70-0.72	0.11
HCFC-142b	0.035 - 0.057	0.186 - 0.305	0.06-0.07	0.33-0.39	0.065
HCFC-225ca	0.016 - 0.020	0.714 - 0.920	0.025	1.093	0.025
HCFC-225cb	0.023 - 0.031	0.348 - 0.474	0.033	0.50	0.033
CCl ₄	1.03 - 1.15	1.014 - 1.130	1.05-1.11	1.03-1.09	1.08
CH ₃ CCl ₃	0.11 - 0.13	0.968 - 1.130	0.122-0.124	1.07-1.09	0.12
<u>Brominated Compounds</u>					
H-1301	10.0 - 12.7	23.9-32.2	15.2-17.2	40	≈16
H-1211	1.8 - 5.0	16.3-49.6	3.9-4.4	40	≈4
H-1202	1.7	52.9	1.25	40	≈1.25
H-2402	6.4 - 10.2	42.1-47.8	5.9-8.5	40	≈7
H-1201	1.4	35.1	1.4	40	≈1.4
H-2401	0.4	66.4	0.25	40	≈0.25
H-2311	0.3	79.9	0.14	40	≈0.14
CH ₃ Br	0.5-0.7	30.6-67.7	0.44-0.69	40	≈0.6

↓
 $\propto$
 efficiency
 relative to
 chlorine.

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Chapter 6: ODPs and CLPs

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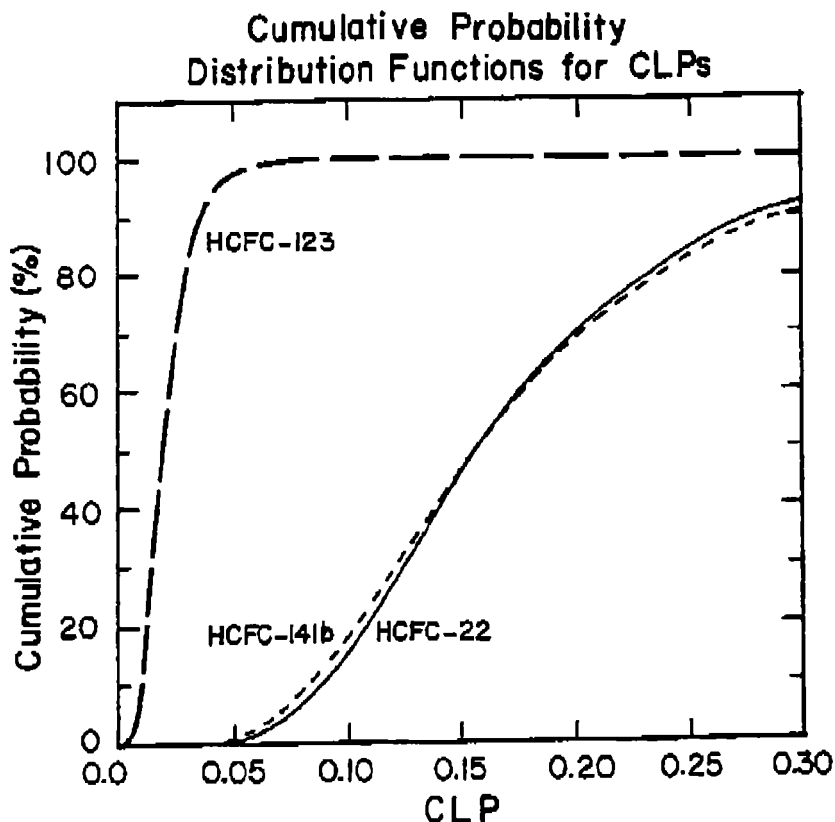


Figure 6-1. Cumulative probability distribution functions estimated for the CLPs of HCFCs 22, 123, and 141b. Uncertainties considered were as follows: the CH_3CCl_3 oceanic hydrolysis time scale was assumed to be 72 years, with an uncertainty of $\pm 50\%$. The rates of reaction of HCFCs 22, 123, and 141b with tropospheric OH were assumed to be uncertain by $\pm 44\%$, $\pm 50\%$, and $\pm 51\%$, respectively (includes an estimated $\pm 13\%$ uncertainty in the tropospheric OH deduced from CH_3CCl_3 measurements). The stratospheric lifetimes of CH_3CCl_3 , HCFC-22, HCFC-124 and HCFC-141b were assumed to be uncertain by about $\pm 30\%$.

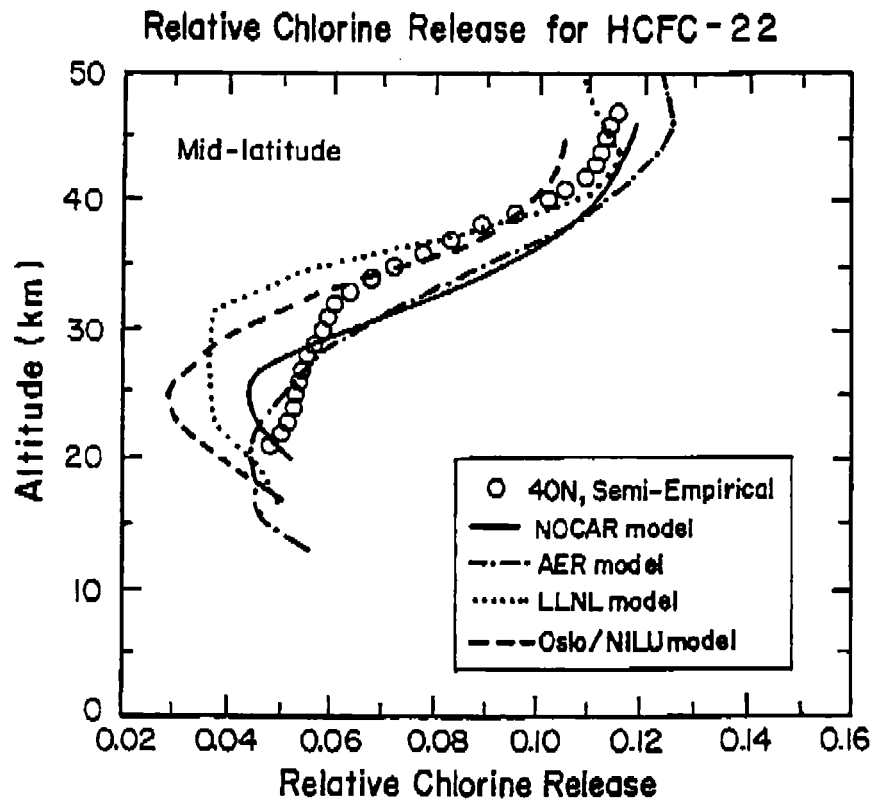


Figure 6-2. Model calculations of the local chlorine release in mid-latitudes for HCFC-22 in winter along with those inferred from an analysis of measured CFC-11 and CH_4 distributions and the correlation between CH_4 and HCFC-22 [see *Solomon et al.*, 1991].

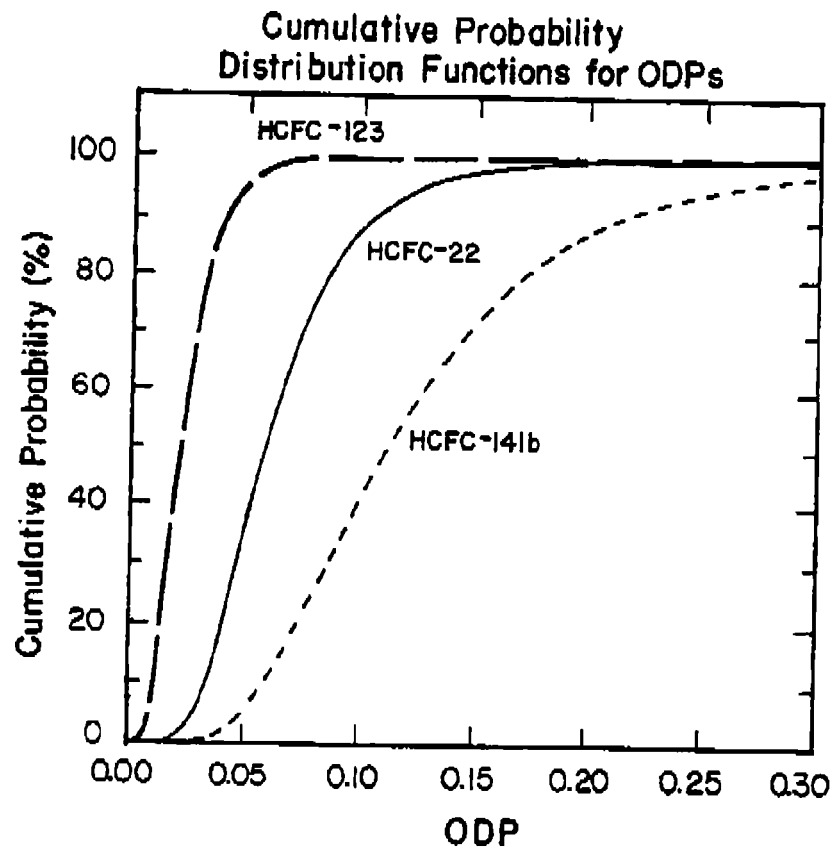


Figure 6-3. Cumulative probability distribution functions estimated for the ODPs of HCFCs-22, 123, and 141b, based on adopted accuracies in CLPs from Figure 6-1 and an estimated $\pm 10\%$ accuracy for the ODP/CLP ratios of these species.

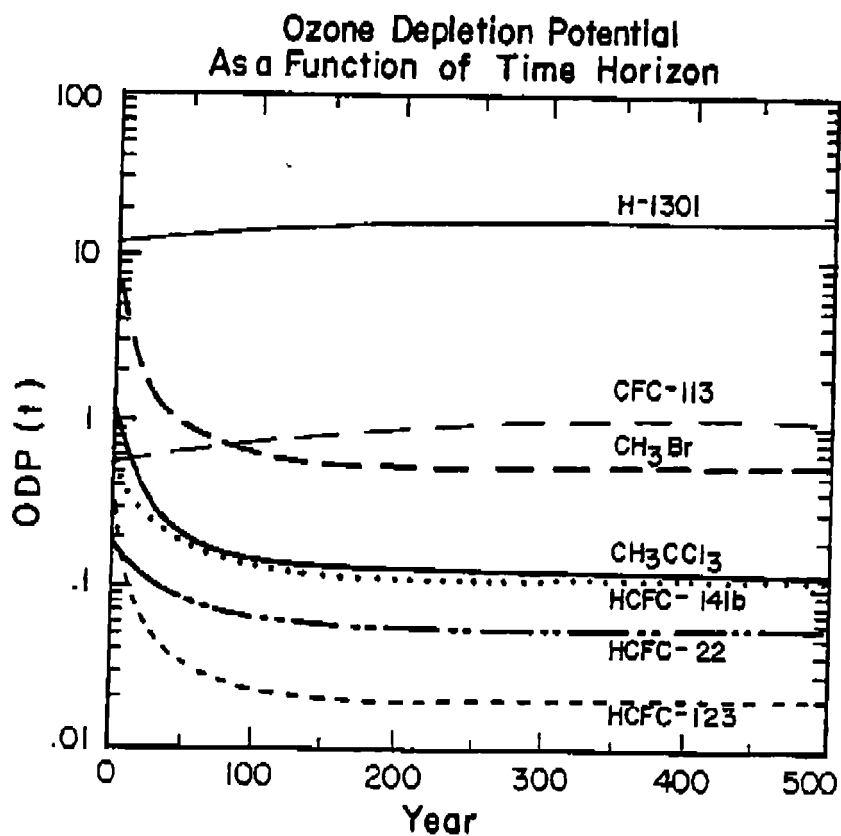


Figure 6-4. ODPs for several representative compounds as a function of time horizon based upon best estimate CLPs of this assessment and the semi-empirical ODP/CLPs.

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IN SITU MEASUREMENTS OF BrO IN THE ARCTIC STRATOSPHERE

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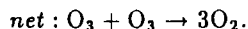
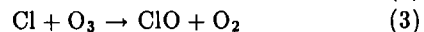
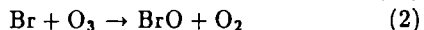
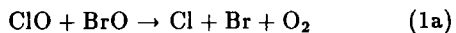
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Abstract. Mixing ratios of BrO have been measured in the arctic lower stratosphere with an instrument mounted on the NASA ER-2 aircraft. Observations from fourteen flights above the Arctic Circle in January and February of 1989 defined mixing ratios within the vortex of 4 ± 2 parts per trillion by volume (pptv) at a potential temperature of 400 K, rising to 8 ± 2 pptv at 470 K. These values are twice as large as values found at equivalent potential temperatures at lower latitudes, and are comparable to the mixing ratios found inside the antarctic polar vortex. Within the statistical uncertainty of the measurements, no BrO was observed in darkness at any time either inside or outside of the vortex, indicating that active bromine was sequestered in long-lived reservoirs, probably BrONO₂ and BrCl. These measurements, in conjunction with measurements of ClO, demonstrate that the interaction of bromine and chlorine could represent a major sink for ozone in the presence of sunlight.

Introduction

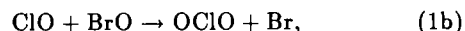
The suggestion that bromine compounds released at the earth's surface could destroy ozone in the stratosphere was first made in 1975 [Wofsy et al., 1975]. During the following decade, while research efforts focussed on quantifying the effects on ozone of chlorine atoms released by photolysis of chlorofluorocarbons in the stratosphere, bromine largely remained ignored. Only recently, after massive seasonal losses of ozone over Antarctica were reported, has this disparity been reduced. A renewed interest in bromine chemistry was initiated in part by the suggestion [McElroy et al., 1986] that bromine oxide (BrO) in the presence of enhanced concentrations of chlorine oxide (ClO) within the antarctic polar vortex could lead to substantial losses of ozone through the catalytic cycle



In contrast with the knowledge of chlorine chemistry obtained from fifteen years of in-situ and laboratory studies [WMO Report 16, 1986], analogous processes involving bromine remain poorly understood. Although the reactivities of related bromine and chlorine species are often similar, there are some important differences. Consequently, BrO represents a large fraction of the total

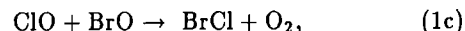
inorganic bromine budget [Yung et al., 1980], which is estimated to be less than 15 pptv [Brune and Anderson, 1986]. Yet these concentrations of BrO are small and pose a serious challenge to both ground-based and in-situ instruments.

The presence of BrO in the antarctic vortex was inferred from ground-based spectroscopic observations of OCIO from McMurdo Station in 1986 [Solomon et al., 1987]. OCIO, formed in the atmosphere primarily by the reaction



was observed during twilight and in total darkness. The observed slant-column depths were consistent with enhanced abundances of ClO and the upper limit of 15 pptv of BrO established by midlatitude balloon measurements.

The first successful in-situ measurements of BrO in the stratosphere were made in the southern hemisphere during the AAOE campaign of 1987 [Brune et al., 1989a]. These observations showed that BrO mixing ratios within the southern polar vortex, ranging from 5 to 7 pptv, were somewhat enhanced compared to values found outside the vortex. Complementary ground-based studies of BrO and OCIO during the same season [Solomon et al., 1989] provided additional strong evidence for occurrence of reaction (1) as well as information regarding the importance of a long-lived reservoir of BrO at night. From the slant-column measurements and a photochemical model, a mixing ratio of ≈ 7 pptv was derived for BrO, and it was concluded that photolysis of BrONO₂ in the morning twilight was more consistent with the observations than was photolysis of BrCl, a species formed by yet another channel of reaction (1),



which represents about 10% of the overall reaction in laboratory studies [Toohey and Anderson, 1988; Friedl and Sander, 1989]. The ER-2-based observations, which were carried out in daylight, were unable to address this photochemical issue. However, they did demonstrate that a significant fraction ($\approx 20\%$) of the ozone depletion observed over Antarctica in 1987 was due to the catalytic cycle rate limited by the reaction of ClO with BrO [Anderson et al., 1989].

Several experiments were carried out in early 1988 to examine bromine and chlorine within the arctic vortex. Ground-based observations of OCIO provided strong evidence again for the presence of BrO and enhanced concentrations of ClO inside the vortex [Solomon et al., 1988], while an in-situ study with the ER-2-based ClO-BrO instrument detected evidence of perturbed halogen chemistry outside the vortex [Brune et al., 1988].

We report here the results of recent measurements of BrO obtained during the AASE mission to the arctic stratosphere in January and February of 1989. As in the

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companion paper that reports ClO observations [Brune et al., this issue, a], we will focus on three of the fourteen flights from Stavanger, Norway, across the Arctic Circle that occurred over the period from January 3 to February 10, 1989. In addition, we will draw upon measurements obtained on December 29, 1988, during a transit flight which passed over the continental United States. These results will be compared to previous measurements of BrO obtained over Antarctica and Canada in 1987 and 1988.

Experiment

The ClO-BrO instrument, which was mounted in a pod on the left wing of the NASA ER-2 aircraft, has been described in detail elsewhere [Brune et al., 1989b]. Detection of BrO is accomplished through addition of nitric oxide to a flow of air which is decelerated to $\approx 20 \text{ m s}^{-1}$ with a double-ducted flow system. The reaction of BrO with NO is greater than 95% complete within 10 to 15 ms at the NO concentrations added ($\approx 10^{13} \text{ molecules cm}^{-3}$); the bromine detection system is positioned approximately 25 ms downstream of the NO injector. Bromine atoms formed by this reaction are then detected by resonance fluorescence with a density-dependent sensitivity ranging from $\approx 10^{-6} \text{ cts s}^{-1}/(\text{Br atom cm}^{-3})$ at the highest flight altitudes achieved, to $\approx 3 \times 10^{-7} \text{ cts s}^{-1}/(\text{Br atom cm}^{-3})$ at the minimum altitude the aircraft could sustain to allow for sufficient signal averaging. For background signals (which were also density dependent) of 5000 cts s^{-1} , a detection limit of $\approx (2-3) \text{ cts s}^{-1}$ was obtained for signal averaging of one hour at most altitudes. Thus, BrO mixing ratios of 6 pptv could be detected with typical signal-to-noise ratios of 3 to 5.

The bromine lamp employed for the first half of the campaign was the same lamp as that used during the AAOE flights, the February flight series based at Moffett Field [Brune et al., 1988], and all test flights. This system has been calibrated at four separate instances. Both the absolute calibration (when scaled to the total background signal at an air density of $2.6 \times 10^{18} \text{ molecules cm}^{-3}$) and the pressure dependence have varied less than 10% over more than 200 hours of operation in the stratosphere and in the laboratory. Calibrations used the rapid reaction of a measured amount of chlorine atoms with molecular bromine, and is described elsewhere [Brune et al., 1989a].

After the flight of January 30, 1989, this lamp was removed. The replacement lamp was calibrated after the flight series, and concentrations of bromine measured with this lamp over the last seven flights of the campaign were in good agreement with values observed during the first half of the flight series. Therefore, although the laboratory calibrations for the two lamps were different, there appears to be no significant systematic difference between bromine concentrations determined with the two systems.

Upon addition of nitric oxide to convert BrO to Br there is a small absorption of the background nonresonant scatter. By reproducing flight conditions in the laboratory, this correction to the bromine signal has been measured to be smaller than $10^{-17} \text{ cm}^2 (\text{molecule NO})^{-1}$ for the lamps employed in these flights. In practice, accounting for this absorption leads to a positive offset of less than 1.5 pptv. Overall, it is estimated that the uncertainty in the BrO calibration is $\pm 35\%$ at the 2σ confidence level.

Observations

A typical ER-2 flight track consisted of a rapid ascent to maximum altitude, a hold at some potential temperature between 440 and 470 K while flying up the Norwe-

gian coast and then toward Spitzbergen, a turn-around at approximately local noon with a dive for a vertical scan, and finally a return leg at a different potential temperature back to Stavanger. These flight tracks were similar to those employed out of Punta Arenas, Chile, during the AAOE mission [Tuck et al., 1989]. We have selected three flights that illustrate key features of the bromine observations that were evident on most of the fourteen flights. Taken together, the flights of January 6, January 16, and February 10, sampled both inner- and outer-vortex air, and sampled inner-vortex air that was both illuminated and in total darkness. In addition, these flights, which span the entire series, serve to define the temporal evolution of BrO during the mission.

The BrO measurements for three flights appear in Figures 1 through 3, overlaid by the measurements of ClO. While these latter measurements are described in detail elsewhere [Brune et al., this issue, a], there are some important points that deserve review here. First, throughout the mission, every flight into the polar vortex revealed highly perturbed concentrations of ClO. Clearly, a significant fraction of the vortex air had been processed by polar stratospheric clouds (PSCs), at least at altitudes accessible to the ER-2. Both ClO and BrO are sensitive to concentrations of NO_2 , which were significantly depleted within the vortex [Fahey et al., this issue]. The observations of high concentrations of ClO in air that has been in total darkness for at least 20 hours leads to the conclusion that a considerable fraction of ClO was bound up in a form other than ClONO_2 . It is likely that the less stable species ClOOCl represents the major nighttime reservoir of ClO. Finally, as the mission progressed, the mixing ratios of ClO rose from several hundred pptv to over 1100 pptv by February 10. This increase was most likely due to increasing solar illumination with continued processing of air by PSCs.

The results for the first flight to encounter highly perturbed ClO, on January 6, appear in Figure 1. The potential temperature and solar zenith angles (SZA) for the entire flight track are shown by Brune et al. [this issue, a]. Interestingly, BrO was highest where ClO was low, and there was no BrO where ClO was highly perturbed. However, upon consideration of the SZA, we note that regions in which no BrO was observed were at very high angles, in this flight greater than 92° . Inversely, portions of the January 6 flight where BrO mixing ratios were high occurred where the ClO was low. The mixing

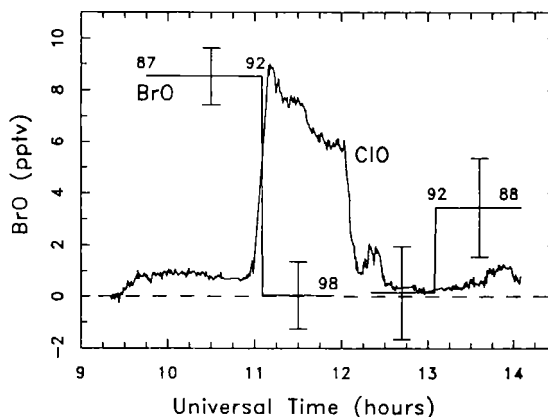


Fig. 1. Overlay of BrO and ClO mixing ratios for the flight of January 6, 1989. Horizontal bars represent time over which signal was averaged to obtain the 1σ statistical uncertainties represented as vertical bars. Numbers indicate solar zenith angles corresponding to various positions along the flight track. ClO axis units are unspecified.

ratio of BrO was 8.5 ± 1.2 pptv along the outbound leg, which was flown at a potential temperature of 475 K, and 3.5 ± 2 pptv along the inbound leg flown at 413 K. Even at this early stage in the flight series these BrO values were greater than values observed at comparable altitudes at midlatitudes and were similar to values observed within the antarctic vortex [Brune et al., 1989a]. Although ClO mixing ratios were relatively low at the start and the end of the flight, these outer-vortex values (25 pptv) were still considerably larger than values measured at midlatitudes at comparable altitudes and SZA [Brune et al., this issue, b], and thus represent a perturbation from typical midlatitude values.

The results obtained on January 16 were similar to those of January 6, and are shown in Figure 2. The mixing ratios of ClO were highly perturbed throughout the entire flight, while the behavior of BrO was identical to that for the flight of January 6. Once again, no BrO was observed at SZA greater than 92° and BrO values in sunlight were moderately high, even at a potential temperature of 400 K on the inbound leg. Within the statistical uncertainties of the measurements (typically ± 1.5 pptv), at no time during any flight was BrO observed at solar zenith angles greater than 94° . At SZA greater than 90° , photolysis rates of BrONO_2 and BrCl decrease rapidly as the sun approaches the horizon (which is near 94° SZA at maximum ER-2 flight altitudes) [Solomon et al., 1989]. Thus, in darkness, BrO was likely sequestered in BrONO_2 or BrCl , or both. These observations also indicate that destruction of ozone by the catalytic cycle rate limited by the $\text{BrO} + \text{ClO}$ reaction was terminated in darkness, even though ClO remained at moderate concentrations. In addition, the observations of zero BrO are important because they add confidence that the small offset due to absorption by NO is valid.

Results of the last arctic flight of the AASE campaign, on February 10, are summarized in Figure 3. The ER-2 flew over Iceland and Greenland staying in sunlight for the entire flight. Here, both the BrO and the ClO profiles strongly resemble those obtained over Antarctica [Brune et al., 1989a]. Within the arctic vortex the BrO mixing ratio was 8 ± 2 pptv at 470 K. However, values outside the vortex were low (1–4 pptv), similar to those observed at midlatitudes. The mixing ratios of ClO early in the outbound leg and late in the return leg were the lowest values measured in sunlight during the latter half of the campaign. Indeed, meteorological analysis indicated that this outer-vortex air was drawn from significantly lower latitudes than earlier in the mission (D. S. McKenna, personal communication, 1989).

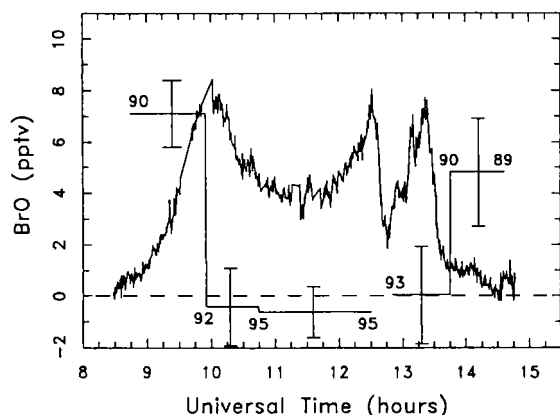


Fig. 2. Overlay of BrO and ClO mixing ratios for the flight of January 16, 1989. Data are represented as described in Figure 1 caption.

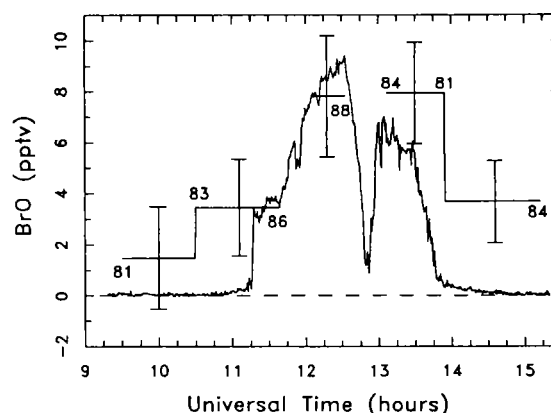


Fig. 3. Overlay of BrO and ClO mixing ratios for the flight of February 10, 1989. Data are represented as described in Figure 1 caption.

Near the end of the campaign, a number of measurements within sunlit portions of the vortex yielded values of 6 to 8 pptv (independent of SZA when SZA was less than 90°), while measurements obtained when ClO mixing ratios were observed to be low yielded values of 2 to 4 pptv. To highlight these differences, and also to compare to the measurements of BrO from over Antarctica, we plot the measurements as a function of potential temperature in Figure 4. Data obtained in air that had ClO mixing ratios typical of those found at midlatitudes are plotted as open symbols. Also included are data from the transit flight of December 29, 1988, which passed over the continental United States. There was indeed BrO enhancement within the two vortices, but much less than corresponding enhancements of ClO. BrO mixing ratios within the vortex were about twice as large as values at midlatitudes. This is consistent with the notion that BrO represents a major inorganic bromine species and reaches a maximum value with only a small reduction in NO_2 concentration.

Although there was a slight increase in mixing ratios of BrO over the course of the flight series, more likely

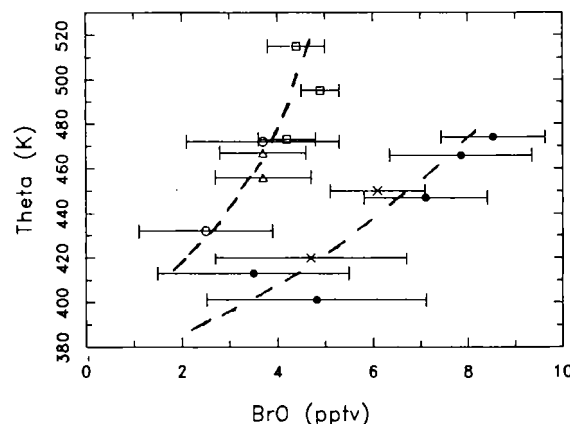


Fig. 4. Observed BrO mixing ratios for a number of flights as a function of potential temperature. Circles are from AASE flights, inner-vortex values represented by closed circles. $\times$ represent values from antarctic observations of Brune et al. [1989a], squares are from February 13, 1988, a flight over Canada [Brune et al., 1988], and triangles are from the transit flight of December 29, 1988, which passed over the continental US at midday. Dashed lines are for emphasis only.

this was due to the ability of the aircraft to reach higher potential temperatures as the vortex warmed than to any real temporal trend in the total burden of inorganic bromine or in its partitioning. While ClO concentrations rose markedly (as solar zenith angles decreased), BrO mixing ratios at a fixed potential temperature in sunlight remained fairly constant over the six-week period. This is consistent with observations from over Antarctica [Brune et al., 1989a]. If the partitioning of bromine was perturbed, as suggested by the significant perturbation in ClO, the burden of inorganic bromine in the stratosphere likely does not exceed 10 to 15 pptv, in contrast to a recent far-infrared emission measurements at midlatitudes which found 25 pptv of HBr [Park et al., 1989]. However, a strong conclusion cannot be drawn until we know the details of heterogeneous reactions of HBr and BrONO₂ on PSC particles.

We can use the simultaneous measurements of BrO and ClO to estimate the rate of ozone loss due to reaction (1). Using a value of 1 part per billion of ClO in sunlight, consistent with the observations late in the mission, a rate of roughly $6 \times 10^5 \text{ s}^{-1}$ is derived for ozone loss, or equivalently, 0.5% each 12 hours of solar illumination. This loss rate is comparable to that observed within the Antarctic Ozone Hole. Therefore, should the arctic vortex remain stable into springtime, the interaction of bromine and chlorine could represent a significant sink for ozone in the arctic stratosphere.

Summary

Mixing ratios of BrO observed within the arctic lower stratosphere during daylight in January and February of 1989 were found to be enhanced by a factor of 2 over values normally found at midlatitudes. These observations are similar to those made over Antarctica in September, 1987. Values as large as 8 ± 2 pptv were observed late into the mission when more than a part per billion of ClO was measured. Within the statistical significance of the measurement, no BrO was observed at any time in complete darkness, indicating that BrO was tied up at night in long-lived reservoirs, most likely BrONO₂ and BrCl. These observations demonstrate the potential for significant loss of ozone, especially if vortex air masses were to experience significant solar illumination.

Acknowledgments. We gratefully acknowledge the expert assistance of Nate Hazen, Norton Allen, and Maria Mueller, all of whom participated with this project in Norway. Joe Demusz, Elliot Weinstock, Ed Thompson, Bob Heroux, and Joyce Makrides provided vital support back at Harvard University. The overall success of the mission depended on the hard work and dedication of the ER-2 pilots, the ground crews, and the personnel from the High Altitude Missions Branch at NASA Ames Research Center. Estelle Condon and Steve Wegener represented an important interface between the scientists and operations personnel while NOAA Aeronomy Laboratory and the Norwegian Air Force provided excellent facilities. This work was supported under NASA contract NASW 3960.

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FIRST
OBS OF
ELEVATED ClO
IN NORTHERN
HemisPHERE

In Situ Northern Mid-Latitude Observations of ClO , O_3 , and BrO in the Wintertime Lower Stratosphere

W. H. BRUNE,* D. W. TOOHEY, J. G. ANDERSON, W. L. STARR, J. F. VEDDER, AND E. F. DANIELSEN

CH_3Br is
major strus.
Source of
Br.

In Situ Observations of BrO Over Antarctica: ER-2 Aircraft Results From 54°S to 72°S Latitude

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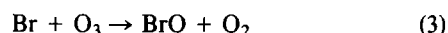
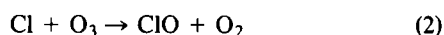
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Bromine monoxide was observed in situ during nine flights of the NASA ER-2 aircraft from Punta Arenas, Chile (54°S latitude), to 72°S latitude over the Palmer Peninsula, Antarctica. The first flight for the BrO detection system was on August 28. The distribution of BrO inside the chemically perturbed region defined by greatly elevated ClO abundances was different from that found just outside. Inside, the BrO mixing ratio was 6.1 ± 1.1 pptv above the 440 K potential temperature surface, 4.7 ± 2.0 pptv between the 400 and 440 K surfaces, and less than 4 pptv below the 400 K surface. At high latitudes outside the chemically perturbed region, the BrO mixing ratio was 5.4 ± 1.4 pptv near the 450 K surface, but decreased to 2.9 ± 1.2 pptv at the 420 K surface. The abundance of BrO showed no discernible temporal trend during the course of the nine flights. Away from the south polar region, at latitudes between 47°S and 37°N and potential temperatures between 435 and 500 K (18.5- to 20.7-km altitude), the BrO mixing ratio was 0.5–3.0 pptv.

INTRODUCTION

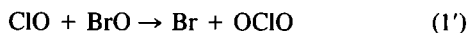
The reaction between ClO and BrO can destroy ozone through the catalytic cycle [McElroy *et al.*, 1986]:



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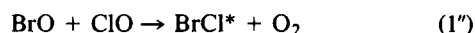
Evidence that large amounts of ClO and perhaps BrO were reacting over Antarctica came from total column absorption observations of elevated OClO taken from McMurdo Station, Antarctica, in October 1986 [Solomon *et al.*, 1987]. The only known source of OClO is the reaction between ClO and BrO:



If this reaction is indeed the only source, then both chlorine and bromine must have participated in the observed large reduction of ozone. Other catalytic mechanisms involving chlorine have also been identified. The primary mechanism apparently involves the self-reaction of ClO to form a dimer, Cl₂O₂, which is then either photolytically [Molina and Molina, 1987] or thermally [Molina *et al.*, 1987] dissociated into chlorine atoms. A second path involves the reaction of ClO with HO₂ to form photolytically labile HOCl [Solomon

et al., 1986]. Clearly the abundances and photochemistry of ClO, HO₂, and BrO all affect the present and future losses of ozone over Antarctica in the austral spring.

Reaction (1), which limits the rate of catalytic ozone destruction for reaction cycle (1)–(3), has recently received considerable scrutiny, since the efficiency of reaction (1) for destroying ozone depends on both its reaction rate and on its products. In addition to (1) and (1'), a third product channel appears to exist [Toohey and Anderson, 1988]:



The fate of BrCl* is dissociation into Br and Cl atoms, or stabilization into BrCl ground state, which then easily photolyzes into the atoms. Sander and Friedl [1988] have determined the temperature dependent rates into the channels (1), (1'), and (1'') to be $(2.9 \pm 1.0) \times 10^{-12} \exp [(217 \pm 50)/T]$, $(1.6 \pm 0.4) \times 10^{-12} \exp [(426 \pm 50)/T]$, and $(5.8 \pm 2.0) \times 10^{-13} \exp [(168 \pm 50)/T]$, respectively, in one torr of helium, all in units of cm³ molecule⁻¹ s⁻¹. For BrO in the sunlit stratosphere, reaction channels (1) and (1'') both result in Br and Cl atoms; however, in the dark, the stabilization of BrCl* into BrCl limits the growth of OClO in a manner consistent with observations [Salawich *et al.*, 1988]. The fraction of reaction in the product channels is 0.52 in (1') and 0.48 into (1) and (1'') at room temperature, and is 0.60 into (1') and 0.40 into (1) and (1'') at 200 K.

The homogeneous photochemistry of stratospheric bromine appears similar to the more familiar chlorine photochemistry, as illustrated in Figure 1, but is actually quite different. This difference is seen most clearly in the partitioning of the halogen families into component species in the lower stratosphere. Near 20-km altitude at midday and mid-latitudes, the fraction of inorganic chlorine in ClO, ClONO₂, and HCl is approximately 0.01, 0.2, and 0.8, respectively. For inorganic bromine, the fraction in BrO, BrONO₂, and HBr is approximately 0.4, 0.4, and 0.15, respectively [World Meteorological Organization, 1986].

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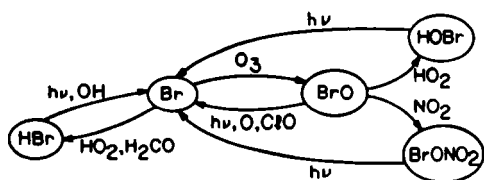


Fig. 1. Schematic of bromine photochemistry in the lower stratosphere.

While HCl and ClONO₂, two relatively inert species, dominate the inorganic chlorine content, reactive BrO and BrONO₂ dominate inorganic bromine. HBr is such a small fraction because its production is limited to reactions of Br with HO₂ and H₂CO, since reactions between Br atoms and the major hydrocarbons are endothermic, and the loss of HBr by reaction with OH is fast, about 25 times faster than the reaction between HCl and OH [DeMore *et al.*, 1987].

The partitioning of inorganic bromine between the two main bromine species, BrO and BrONO₂, under midday steady state conditions, is given by

$$\frac{[\text{BrO}]}{[\text{BrONO}_2]} = \frac{J_{\text{BrONO}_2}^{\text{Br}}}{k_{\text{NO}_2}^{\text{BrO}}[\text{NO}_2][M]} \quad (5)$$

where $J_{\text{BrONO}_2}^{\text{Br}}$ is the photolysis rate in s⁻¹ for BrONO₂ conversion to Br atoms, which react rapidly with O₃ to form BrO, and $k_{\text{NO}_2}^{\text{BrO}}$ is the termolecular rate constant for the reaction



While reaction (6) is approximately equal to its chlorine counterpart, the photolysis rate of BrONO₂ is ~30 times larger than that of ClONO₂. BrO, as a result, is as abundant as BrONO₂, while the abundance of ClO is 20 times less than that of ClONO₂. In the lower stratosphere, BrO and ClO have comparable concentrations and reaction rates for the catalytic destruction of ozone despite the factor of 100 difference in the inorganic mixing ratios [Prather *et al.*, 1984].

Clearly, how much of the inorganic bromine is BrO depends strongly on the NO₂ abundance in the same air parcel. Since the lifetime of BrONO₂ against photolysis is less than a hour, rapid variation in either time or space of the NO₂ content would cause the same variation in BrO. Inside the Antarctic polar vortex, where NO₂ abundances were measured to be 5 times lower than at mid-latitudes [Mount *et al.*, 1987], BrO should be essentially the only inorganic bromine species during the day. A measurement of BrO, however, may not be an accurate measure of the total inorganic bromine because the heterogeneous chemistry, which is virtually unknown, may act to reduce or redistribute bromine. A key question, then, is how BrO is distributed in and around the region of cold temperatures and polar stratospheric cloud formation associated with the polar vortex.

The atmospheric composition of bromine species is largely unknown, although much progress has been made since the original suggestion by Wofsy *et al.* [1975] that bromine might have a role in atmospheric photochemistry. The measurements of atmospheric bromine species have recently been reviewed by Salawitch *et al.* [1988]. They conclude that the

total organic bromine source is between 6 and 20 pptv, with 3 pptv being the man-made perhalogenated bromine gases, CF₃Br and CF₂BrCl, and the rest being methyl bromide, CH₃Br. Because 80% of organic bromine should be converted to inorganic forms at 20-km altitude, and methyl bromide has a 1-year lifetime in the troposphere, the total inorganic reservoir in the lower stratosphere should also be 6–20 pptv.

Brune and Anderson [1986] attempted balloon-borne in situ BrO measurements at northern mid-latitudes in May 1986 and saw no signal attributable to BrO. They placed upper limits on BrO mixing ratio of 7 pptv at 34 km, 10 pptv at 30 km, and 12 pptv at 25 km. If the current understanding of bromine photochemistry is correct, then these upper limits restrict stratospheric inorganic bromine to less than 15 pptv at mid-latitudes. However, most observations of BrO have been made over Antarctica. An assessment of BrO mixing ratios over Antarctica was made by Salawitch *et al.* [1988], who modeled the observed column of OCIO taken in October 1986 from McMurdo Station, Antarctica [Solomon *et al.*, 1987]. BrO mixing ratios of 7–12 pptv gave equally good fits to the data. Finally, the total column abundance of BrO was measured from McMurdo Station in October 1987 by Carroll *et al.* [this issue]. They found that the average vertical column abundance was $2.5 \times 10^{13} \text{ cm}^{-2}$, consistent with BrO mixing ratios of 5–15 pptv located between 12- and 24-km altitude. All of these observations imply BrO abundances of 5–15 pptv in the lower stratosphere. Results from other measurements of the total column absorption of BrO, taken over Antarctica with a spectrometer on board the NASA DC-8 aircraft during September 1987, are forthcoming (G. H. Mount, private communication, 1988).

We discuss in this paper our measurements of BrO taken over Antarctica using an instrument mounted on the NASA ER-2 high-altitude aircraft. BrO and ClO were measured together on nine flights from Punta Arenas, Chile (53°S–72°S over the Palmer Peninsula), and on three ferry flights from 54°S to 37°N. These three flights are reported here, since BrO has not been measured away from the polar regions before. We begin with a discussion of the bromine detection system. Then in the observation section, we present the BrO measurements in context of the chemically perturbed region defined by elevated ClO mixing ratios. A calculation of the contribution of the catalytic cycle involving bromine is presented elsewhere [Anderson *et al.*, 1989].

EXPERIMENT

Bromine monoxide is detected in situ in the same manner as chlorine monoxide: reagent NO added to the laminar airstream reacts with BrO to form Br atoms, which can then be detected with resonance fluorescence. Thus a single instrument mounted in the left wing of the ER-2 aircraft can be used to measure ClO and BrO simultaneously. Its architecture and operation are discussed by Brune *et al.* [this issue], and only a summary will be presented here. Those aspects specific to BrO will be discussed at length following the summary.

The instrument, shown in Figure 2, accepts the free airstream and decelerates it from 200 m s⁻¹ to ~20 m s⁻¹ while maintaining laminar conditions. The reagent nitric oxide is then added into this flow through injectors in a square duct, 5 cm on a side, at flow rates of 3.0, 1.2, and 0.5

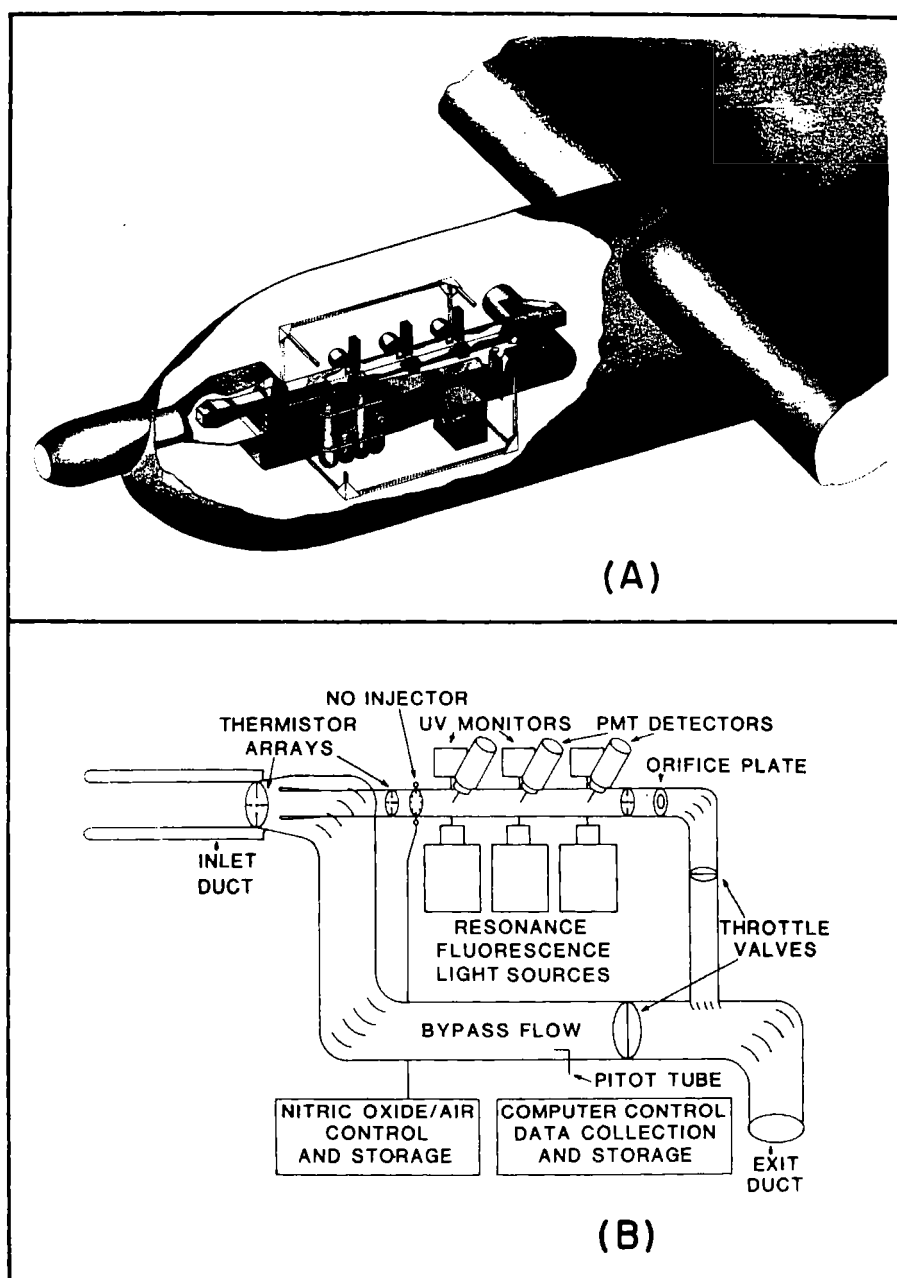


Fig. 2. (a) A perspective of the instrument showing the primary duct (20 cm o.d. and 10 cm i.d.) protruding from the ER-2 wing pod. A secondary duct extracts a laminar core from the primary duct, passing that flow through three optical axes, each of which is capable of detecting either Cl or Br atoms. Nitric oxide (NO) is added to the flow in the secondary duct upstream of the optical axes to convert ClO to Cl and BrO to Br. (b) Schematic of the major instrument subsystems including lamp modules, detectors, gas addition systems, primary/secondary ducting, throttle valves, and thermistor arrays.

STD $\text{cm}^{-3} \text{min}^{-1}$ in a 32-s cycle during which NO is added for 14 s, the injector is purged for 5 s, and the background is measured for 13 s. Bromine and chlorine atoms produced in this chemical conversion are then detected with resonance fluorescence, and the photomultiplier detector signal is stored, along with diagnostic data, by the computer-controlled flight operation and data management system. The observed BrO concentrations are retrieved from the data by taking the difference between the signal when NO is added and the signal when it is not and multiplying the difference signal by the appropriate calibration and correction factors determined in the laboratory and during flight.

The two aspects of this detection process which are specific to either BrO or ClO are the conversion chemistry

and the optical detection of atoms. The chemistry induced by the reagent NO consists predominately of two reactions. The step which converts BrO to Br atoms,



has a rate constant of $3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 210 K [DeMore *et al.*, 1987], slightly faster than the chlorine conversion reaction. The interfering termolecular atom removal reaction,



has a rate constant 6 times slower than its chlorine counterpart, $k^{\text{III}} = 1.5 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ [Tröe, 1977].

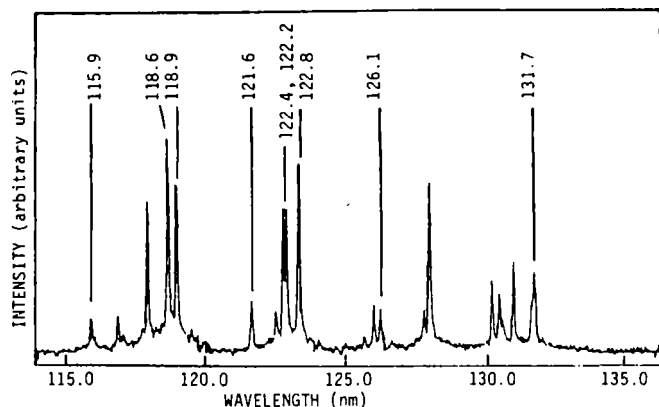


Fig. 3. Vacuum ultraviolet spectrum of the Br resonance lamp filtered by 0.2 atm cm of molecular oxygen (equivalent to flight operation at 18.5 km). Emissions labeled with wavelengths correspond to the $^2P_{3/2}$ ground state; unlabeled emissions correspond to the $^2P_{1/2}$ state lying 0.46 eV above the ground state.

The removal of Br atoms by reaction (8) is less than 5% for all flight conditions. With this slow removal reaction, it was possible to locate the bromine detection system on the third detection axis, 45 cm downstream of the NO injectors, without affecting the conversion efficiency.

The bromine detection axis, mechanically identical to the ClO axis shown in Figure 3 of Brune *et al.* [this issue], consisted of a resonant light source set at a right angle to an EMR photomultiplier with a potassium bromide photocathode. The light beam from the lamp and the detector field of view crossed the flow tube, intersecting in the center to define the detection volume. Razor blade light traps were placed opposite the lamp and detector, and a photodiode behind the lamp light trap monitored the ultraviolet flux from the lamp. The resonant lamp was a low-pressure helium discharge containing trace bromine and excited by 25 W of 180-MHz radio frequency power. The ultraviolet flux from the lamp was stabilized to better than 1% by optical feedback to a heater controlling the amount of bromine released into the helium plasma from a palladium bromide source arm attached to the lamp body. The spectral bandpass was limited by molecular oxygen flowing through cells in front of both the light source and detector at a pressure slightly above ambient.

The detector signal, when NO is added to the flow, is the sum of four contributions:

$$S_{\text{total}} = S_{\text{Br}} + S_{\text{ray}} + S_{\text{ch}} + S_{\text{dark}} \quad (9)$$

where S_{Br} is the resonance fluorescence signal scattered from bromine atoms, S_{ray} is the Rayleigh scattered signal from air, S_{ch} is the lamp light scattered off of flow tube surfaces, and S_{dark} is the signal observed when the lamp is off. The last three signals comprise the background signal, S_{backgr} . S_{dark} is always less than 10 counts s^{-1} and is negligible compared with all the other contributing signals. Several emissions from the bromine lamp contribute to the resonance, Rayleigh, and chamber scattered signals. In Figure 3 the spectrum of the lamp, taken at air densities appropriate for the Antarctic lower stratosphere, contains emissions which terminate at the $^2P_{3/2}$ bromine ground state, labeled with wavelengths, and emissions which terminate at the $^2P_{1/2}$ state which lies 0.46 eV above the ground state

[Tech, 1963]. These latter emissions do not contribute to the resonance fluorescence signal, but do contribute to the background signal composed primarily of the Rayleigh and chamber scattered signals. All of the emissions shown in Figure 3 lie in "windows" in the molecular oxygen absorption spectrum [Ogawa and Ogawa, 1975], but with different absorption cross sections for each line, the relative strengths of the emissions vary with the total amount of O_2 in the optical path, and thus with altitude.

The sensitivity for detecting bromine atoms with resonance fluorescence can be written as [Anderson *et al.*, 1980]

$$S_{\text{Br}} = \sum_i \left(\int F^i(\nu) \sigma^i(\nu) d\nu \right) \cdot \exp(-\sigma_{\text{O}_2}^i[\text{O}_2]l)(\epsilon\tau\eta)V[\text{Br}] \quad (10)$$

where the overlap between the flux of emission line i , $F^i(\nu)$, and the atomic absorption cross section of the same emission i , $\sigma^i(\nu)$, are integrated over the line shapes. The exponential term is the molecular oxygen absorption at each line, where $\sigma_{\text{O}_2}^i$ is the absorption cross section, which does not vary over the line width, and l is the total optical path, ~ 7.2 cm. The terms ϵ , τ , η , and V are the collection efficiency, optical transmission, photomultiplier quantum efficiency, and detection volume, respectively. Since the bromine lamp used in this experiment is optically thin, the emission profiles can be described by Doppler line shapes, and (10) can be written as [Schwab and Anderson, 1982]

$$S_{\text{Br}} = \sum_i (F^i \sigma_0^i \exp(-\sigma_{\text{O}_2}^i[\text{O}_2]l)) \cdot \left(\frac{T_A}{T_L + T_A} \right)^{1/2} (\epsilon\tau\eta)V[\text{Br}] \quad (11)$$

where σ_0^i is the atomic absorption cross section at line center, T_A is the stratospheric bromine temperature, and T_L is the emitting bromine atom temperature inside the lamp. T_L for the bromine lamp is similar to that for the chlorine lamp: $T_L = (800 \pm 300)$ K. While each term on the right-hand side of (11) could be measured independently, in practice, the detection system is calibrated by adding a known amount of bromine to an airstream which mimics the stratospheric densities. The expression for the absolute sensitivity for bromine detection can then be reduced to

$$S_{\text{Br}} = C([M, T_L, T_A])[Br] \quad (12)$$

where C is the proportionality constant, in units of (counts $\text{s}^{-1})/(\text{Br atoms cm}^{-3})$, and is dependent on the ambient air density and temperatures.

The background signal contains nonresonant scattering of the emission lines in Figure 3 that have either the $^2P_{3/2}$ or $^2P_{1/2}$ lower state. The scattering from nitrogen and oxygen molecules, Rayleigh scatter, can be described by

$$S_{\text{ray}} = \sum_j (F^j \sigma_{\text{ray}}^j \exp(-\sigma_{\text{O}_2}^j[\text{O}_2]l))(\epsilon\tau\eta)V[M] \quad (13)$$

where σ_{ray} is the Rayleigh scattering cross section for emission line j , $[M]$ is the air density, and all other factors are identical to those in (10). The chamber scatter can be written as

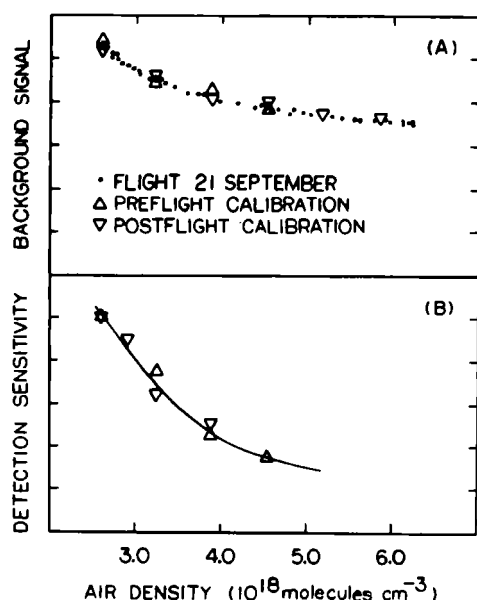
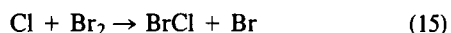


Fig. 4. Variation of background signal and detection sensitivity over the range of air densities encountered in flight. (a) Background signals from the flight on September 21 (solid circles); preflight (triangles) and postflight (inverted triangles) laboratory calibrations are scaled to show the similarity in curvature. (b) Preflight (triangles) and postflight (inverted triangles) calibrations for detection sensitivity are scaled to the curve determined by the average of all bromine calibrations.

$$S_{\text{ch}} = \sum_j [F^j p_{\text{ch}}^j \exp(-\sigma_{\text{O}_2}^j [\text{O}_2] l)] \quad (14)$$

where p_{ch}^j is the probability that flux from emission j , F^j , will be scattered into the detector. Both terms have the same dependence on the O_2 density in the optical path, but since in the absence of O_2 absorption, Rayleigh scattering is linearly dependent on air density, the resulting variation of the total background must be measured directly. An example of the variation of the bromine background signal with altitude is given in Figure 4a. These data were taken during a rapid descent at 72°S on September 21, 1987, over Antarctica and clearly show that the effect of O_2 absorption is stronger than the effect of increased Rayleigh scatter.

Both before and after the flight series, the bromine axis was calibrated in the laboratory over the range of air densities encountered in the Antarctic lower stratosphere: $2.0\text{--}4.5 \times 10^{18}$ molecules cm^{-3} . In the flow, a trace amount of chlorine was dissociated on a hot filament, producing chlorine atoms which were detected with chlorine resonance fluorescence and absorption 17.5 cm either upstream or downstream of the bromine axis. For most calibrations, a stable Cl resonance fluorescence system was first calibrated against resonance absorption, using either the 118.9 or 134.7-nm emission, and then this calibrated chlorine system was used for the more sensitive resonance fluorescence detection. The concentration of chlorine was established, with 2×10^9 atoms $\text{cm}^{-3} < [\text{Cl}] < 3 \times 10^{10}$ atoms cm^{-3} , and then molecular bromine was added to the air upstream of the Cl injection point, resulting in the quantitative conversion of Cl to Br by the fast reaction



The Br_2 concentration was adjusted to minimize the chlorine signal and maximize the bromine signal, and a large range in $[\text{Br}_2]$ produced the same results. The conversion of Cl to Br was also insensitive to the Cl and Br_2 addition positions, the initial chlorine concentrations over the range given, and whether the Cl detection axis was upstream or downstream of the Br detection axis. Loss of Br and Cl on flow tube wall surfaces was also found to be negligible.

The variation of the Br detection sensitivity with air density is presented in Figure 4b. Detection sensitivity varies about a factor of 3 over the range of altitudes encountered over Antarctica. From the preflight and postflight laboratory calibrations, the bromine detection sensitivity decreased to 0.75 ± 0.13 of the initial value, while the background signal decreased to 0.68 ± 0.10 of its initial value over the course of 12 flights. Furthermore, the variations of both the sensitivity and background with air density were the same before and after the flights, and the variation of the background with air density observed during the flights was the same as that observed in the laboratory. The constancy of the background and its relationship with the detection sensitivity means that the background signal can be used as an indicator of the sensitivity for bromine detection. These relationships imply that the relative contributions of Rayleigh and chamber scatter were constant. It is clear from the trend in the background signals over the flight series that the degradation during each ~ 7 -hour flight was $\sim 2.5\%$. The absolute sensitivity for bromine detection is $(1.2 \pm 0.4) \times 10^{-6}$ (counts $\text{s}^{-1})/(\text{Br atom cm}^{-3})$ at an air density of 2.6×10^{18} molecules cm^{-3} , and the background scatter is 6860 counts s^{-1} . For this air density, 5 pptv of bromine could be detected with a signal to noise ratio of 4 in 40 min.

Bromine monoxide is detected by taking the difference between the signal when reagent nitric oxide is added to the flow and when it is not and multiplying this difference by the calibration factor appropriate for the air density and detector background signal. This approach assumes that the background signal does not change when the NO is added to the airstream. In reality, the reagent nitric oxide absorbs some of the ultraviolet light, causing a small negative offset to the observed signal. From laboratory simulations and portions of flights where no BrO was expected, we have determined that the fraction of signal absorbed is $(6 \pm 3) \times 10^{-4}$ for the NO concentrations and air densities normally encountered in flight. This fraction of absorbed signal translates into a mixing ratio offset of $\sim (1.5 \pm 1.0)$ pptv. The BrO mixing ratio is calculated from the data using the equation

$$[\text{BrO}]/[M] = \frac{[\Delta S + (6 \times 10^{-4}) S_{\text{backgr}}]/C([M, T_L, T_A])}{9.66 \times 10^{18} (P_{\text{duct}}/T_{\text{duct}})} \quad (16)$$

where ΔS is the difference signal and P_{duct} and T_{duct} are the pressure and temperature in the measurement flow duct. The absolute error at the 2σ confidence level is $\pm 35\%$.

OBSERVATIONS

The bromine resonance fluorescence system was installed in the third detection axis at 47.5 cm downstream from the NO injector just prior to the flight on August 28, 1987. It remained in place for the next nine flights from Punta Arenas to 72°S latitude over Antarctica and for the ferry flights from Punta Arenas, Chile, north to Moffett Field, California. The

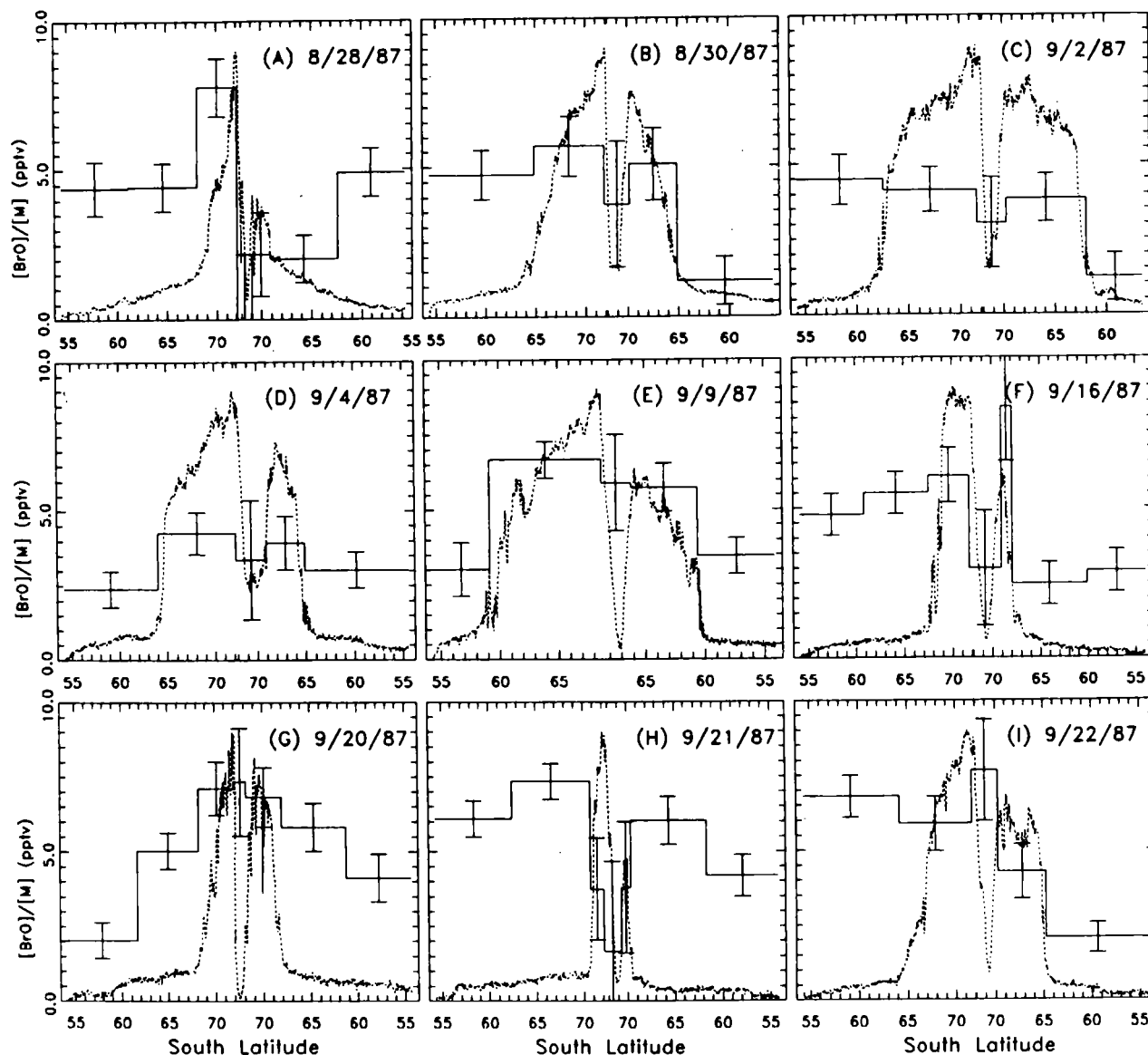


Fig. 5. BrO mixing ratio versus latitude for the nine flights from Punta Arenas to 72°S latitude and back. Horizontal bars represent the distance over which the signal was averaged; vertical bars represent the $\pm 1\sigma$ statistical uncertainty of the average. Superimposed are the observed ClO mixing ratios which define the chemically perturbed region inside the polar vortex.

three legs of the ferry flights (from Punta Arenas to Puerto Montt, Chile, on September 29, from Puerto Montt to Panama on October 1, and from Panama to Moffett Field on October 3) provide a measure of the BrO content of the atmosphere away from the vortex and will be discussed later. The nine flights into the polar vortex occurred on August 28 and 30 and on September 2, 4, 9, 16, 20, 21, and 22. The typical profile for these flights included a rapid ascent from takeoff to the altitude of a predetermined isentropic surface, flight along that surface south to 72°S latitude, an ascent to maximum altitude just before a turn to the north and rapid descent to 14-km altitude, an ascent to the altitude of another isentropic surface, flight along that surface to a point just north of Punta Arenas, and then a rapid descent for landing. The details of each flight, including the adherence to potential temperature surfaces and the

depth of penetration into the Antarctic polar vortex, are presented elsewhere [Brune *et al.*, this issue].

The observed BrO mixing ratios for the nine flights are plotted against latitude in Figures 5a–5i. The ClO mixing ratios, described elsewhere [Brune *et al.*, this issue], are also plotted to indicate the position of the chemically perturbed region where the chlorine chemistry was clearly the strongest. To maximize the statistical significance of the BrO data and yet answer some key questions about bromine photochemistry, the individual measurements of BrO mixing ratio attained in a 32-s cycle have been treated as follows. First the data were separated into five regions defined by the ClO mixing ratios: outside the chemically perturbed region, aircraft heading south; inside the chemically perturbed region, at altitude; the turnaround, dive, and ascent of the aircraft; inside the vessel at altitude, aircraft heading north; and

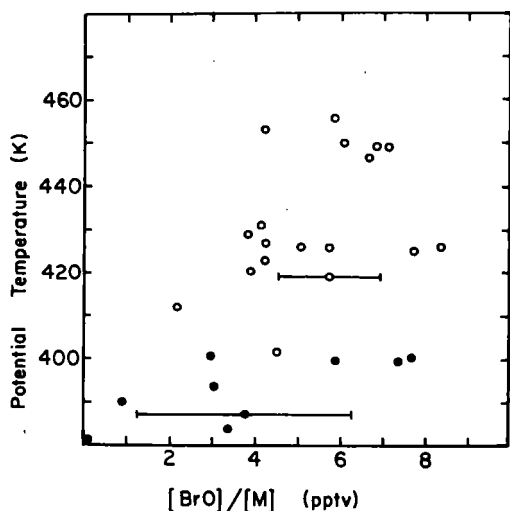


Fig. 6. Variation of the BrO mixing ratio inside the chemically perturbed region with potential temperature. Open circles represent data taken during flight on constant potential temperature surfaces; solid circles represent data taken during the dive at 72°S latitude.

outside, heading north. The length of the horizontal bar in the figures gives the distance over which the BrO signal was averaged (the signal is typically averaged for about an hour). The vertical error bars represent $\pm 1\sigma$ statistical uncertainty. The uncertainty in the absolute calibration of $\pm 35\%$ is not included. Where counting statistics permit, individual regions have been subdivided to give an indication of structure. The statistical uncertainty in the data at the 1σ confidence level results in an uncertainty in the BrO mixing ratio of less than 1 pptv with two exceptions. The first was on September 21 inside the chemically perturbed region when signal integration times were less than 20 min. The second was the dive region of all flights where the integration times were less than 40 min and the background signal was only slightly diminished, while the detection sensitivity was 2–3 times less than at higher altitudes (see Figure 4).

Some basic features of lower stratospheric BrO near the Antarctic pole can be discerned from these data. The most obvious feature is that, for the time intervals required to produce statistical significance, the BrO volume mixing ratio never exceeded 8.5 pptv and was sometimes as low as 2 pptv. Also, BrO was higher inside the chemically perturbed region than it was outside, except during the southbound leg of flights on September 21 and 22. Since the aircraft generally was flown along an isentropic surface on both the southbound and northbound legs, the BrO mixing ratios outside the chemically perturbed region can be compared with those inside the region for the same leg of the same flight. The average enhancement of BrO inside was a factor of 1.7 ± 1.0 for the nine flights with two flight legs each.

This enhancement in the BrO mixing ratio was substantial only at the lower potential temperature surfaces, below 430 K. For each flight, the BrO mixing ratio was usually higher at the higher potential temperature both inside and outside the chemically perturbed region. The variation of the BrO mixing ratio with potential temperature inside the chemically perturbed region is presented in Figure 6, where the open circles represent averages taken at altitude and the solid circles represent averages taken during the dive portion of

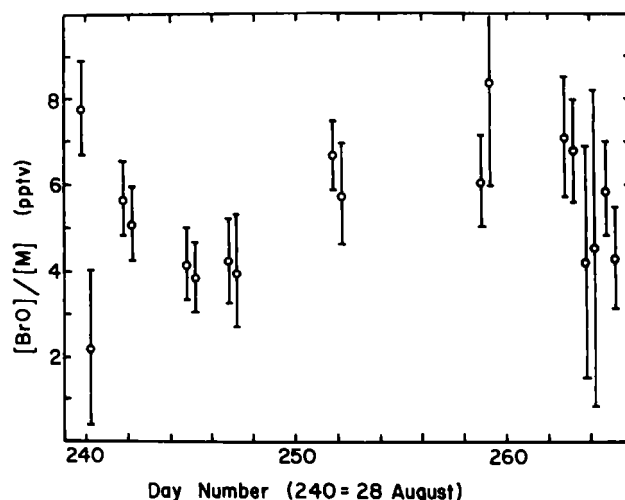


Fig. 7. BrO mixing ratios inside the chemically perturbed region versus day of the year. Mixing ratios are from the two flight legs at potential temperature surfaces between 400 and 460 K for the nine flights.

the flight. The potential temperatures are averages over the same time intervals as the corresponding BrO mixing ratios. Inside the chemically perturbed region, the BrO mixing ratio was 6.1 ± 1.0 pptv near the 450 K surface, and dropped only slightly at lower potential temperature surfaces, becoming 4.7 ± 2.0 pptv between the 400 and 440 K potential temperature surfaces. If this slight variation is neglected, the average BrO mixing ratio inside the chemically perturbed region between the 400 K and 460 K potential temperature surfaces was 5.4 ± 1.6 pptv. Outside, the BrO mixing ratio was 5.4 ± 1.4 pptv near the 450 K potential temperature surface and fell to 2.9 ± 1.2 pptv near the 420 K surface, a change of almost a factor of 2. The variation of BrO with potential temperature was distinctly different inside and outside of the chemically perturbed region.

During the dive portion of the flight at the southernmost point in the chemically perturbed region, the BrO mixing ratio was less than 4 pptv when the average potential temperature was less than 400 K. Since these averages contain the BrO mixing ratios over the extended altitude of the dive and are less than or equal to those obtained during flight at altitude, they are an upper limit to the true BrO mixing ratios below the 400 K potential temperature surface. The relatively high statistical uncertainty of the data does not permit us to derive better altitude information from this portion of the flight, as can be done for ClO.

The abundance of BrO inside the chemically perturbed region showed no discernible trend during the course of the nine flights, as illustrated in Figure 7. The apparent slight increase in the BrO mixing ratio during the month of September results from flying the aircraft at higher potential temperature surfaces more frequently for the later flights. The small increase of the BrO mixing ratio with increasing potential temperature (see Figure 6) thus gives the appearance of a small increase with time. The BrO abundances observed outside the chemically perturbed region near the 420 K potential temperature surface likewise show no trend during the flight series.

Now that the general morphology of bromine monoxide at high latitudes has been presented, we consider BrO at lower

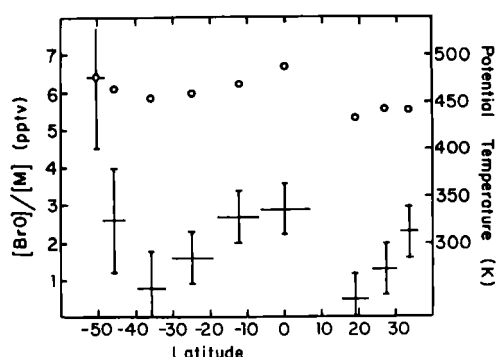


Fig. 8. BrO mixing ratios versus latitude for the ferry flights north. Horizontal bars with $\pm 1\sigma$ vertical error bars indicate BrO mixing ratios as in Figure 5; open circles give the average potential temperature corresponding to each BrO mixing ratio.

latitudes. The latitude range from 53°S to 37°N was covered during the three legs of the ferry flights. The aircraft was flown from Punta Arenas to Puerto Montt, Chile, on September 29, from Puerto Montt to Panama on October 1, and from Panama to Moffett Field, California, on October 3. The BrO mixing ratios for the three flights are shown together, plotted against latitude in Figure 8, along with potential temperature of the flight track. As in Figure 5, the length of the horizontal bar for BrO mixing ratio indicates the distance of the averaging, and the vertical error bars indicate $\pm 1\sigma$ statistical uncertainty in the data. While the BrO mixing ratio is 4.5 pptv from 52° to 45°S latitude, it is less than 3 pptv for the remainder of the transit north. The flight profiles for the various legs are sufficiently different that little information can be obtained about the altitude and latitude variation of BrO away from the southern high latitudes. However, BrO is clearly present in small abundances and is less than a factor of 5 different from the abundances detected over Antarctica at similar potential temperature surfaces.

CONCLUSIONS

The magnitude and morphology of BrO observed at high southern latitudes (54°S–72°S) in the austral spring can be explained by 5–15 pptv of total inorganic bromine and gas phase photochemistry alone. Basically, where NO_2 was high, inorganic bromine was partitioned into both BrO and BrONO_2 ; where NO_2 was low (inside the chemically perturbed region), inorganic bromine was primarily BrO. Thus inside the chemically perturbed region the BrO mixing ratio was almost constant at 5.4 pptv between the 410 and 460 K potential temperature surfaces because NO_2 was low there [Mount *et al.*, 1987]. Outside the chemically perturbed region, where the NO_2 abundance was greater, inorganic bromine would be partitioned between BrO and BrONO_2 , with the BrONO_2 fraction increasing at lower potential temperatures. These conclusions are, however, held hostage by our poor understanding of heterogeneous bromine chemistry, and so must remain tentative.

The BrO mixing ratio observed inside the chemically perturbed region (5.4 ± 1.7 pptv) agrees moderately well with the ground-based total column measurements taken at McMurdo Station, Antarctica (77°S latitude) in September 1987 [Carroll *et al.*, this issue; Solomon *et al.*, 1989]. These observed column densities are consistent with 5–15 pptv of

BrO distributed between 150 and 20 mbar. At the present level of analysis, the BrO mixing ratios observed in situ tend to be smaller and distributed at slightly higher altitudes than those derived from the total column measurements.

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PESTICIDES STUDIED IN MAN

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tion seems to be available. For reasons that remain obscure, a slight chemical difference may determine a large difference in toxicity. For example, Klaassen and Plaa (1966, 1967) found 1,1,1-trichloroethane to be the least toxic and 1,1,2-trichloroethane to be the most toxic of seven compounds they studied in mice and dogs.

Some of the halogenated hydrocarbon fumigants commonly are employed as mixtures, either to take advantage of the combined insect toxicity of two or more compounds or, more generally, to take advantage of the high toxicity of one compound while rendering it nonflammable by mixing it with a less toxic but fire-suppressant compound. So far, none of the mixtures used has shown mammalian toxicity substantially different either quantitatively or qualitatively from what would be predicted from the toxicities of the constituents. The possibility that interaction between constituents might occur was specifically investigated in connection with three of the most widely used mixtures; although statistically significantly potentiating effects were found, the differences were so small as to be of no practical importance from an industrial hygiene viewpoint (McCollister *et al.*, 1956).

The compounds discussed in the following sections are shown in Figure 5.5. They are arranged with the smaller molecules first and the larger ones last.

5.4.1 Methyl Bromide

5.4.1.1 Identity, Properties, and Uses. Chemical Name. Bromomethane.

Structure. See Figure 5.5.

Synonyms. Other names for methyl bromide are MBX and

monobromoethane. Trade names include Dowfume MC-2®, Dowfume MC-2® Soil Fumigant, Dowfume MC-33®, and Embafume®. The CAS registry no. is 74-83-9.

Physical and Chemical Properties. Methyl bromide has the empirical formula CH_3Br and a molecular weight of 94.95. It is a colorless gas with a burning taste and a sweet, chloroform-like odor at high concentrations. It is nonflammable in air but does burn in oxygen. Methyl bromide has a melting point of -93.6°C and a boiling point of 3.56°C . The vapor pressure at 20°C is 1420 mm Hg. The solubility in water at 20°C is 1.75 g/100 g. Methyl bromide is freely soluble in alcohol, chloroform, ether, carbon disulfide, carbon tetrachloride, and benzene. It is stable and noncorrosive.

History and Use. Methyl bromide was introduced as an insecticide in 1932. It is used widely as a fumigant for all types of dry foodstuffs, especially produce contained in bags or packages. It is used in mills, warehouses, ships, and freight cars. It is a soil fumigant used in greenhouses and fields for the control of nematodes, fungi, and weeds. Methyl bromide is mixed with ethylene dibromide and carbon tetrachloride when it is applied to large, unencased bulk produce, but this use is limited.

5.4.1.2 Toxicity to Animals. Basic Findings. All rabbits given an oral dosage of 63.9 mg/kg died, and one died after 56.3 mg/kg; those receiving 56.1 mg/kg or less survived (Dudley *et al.*, 1940).

Sayers *et al.* (1929) exposed guinea pigs to methyl bromide and reported a series of straight line relationships when logconcentration was plotted against logtime for immediately fatal, delayed fatal, and tolerated exposures. Animals that died during exposure to high concentrations fell on their sides, struggled to breath, and died quickly. Guinea pigs exposed four hours to low

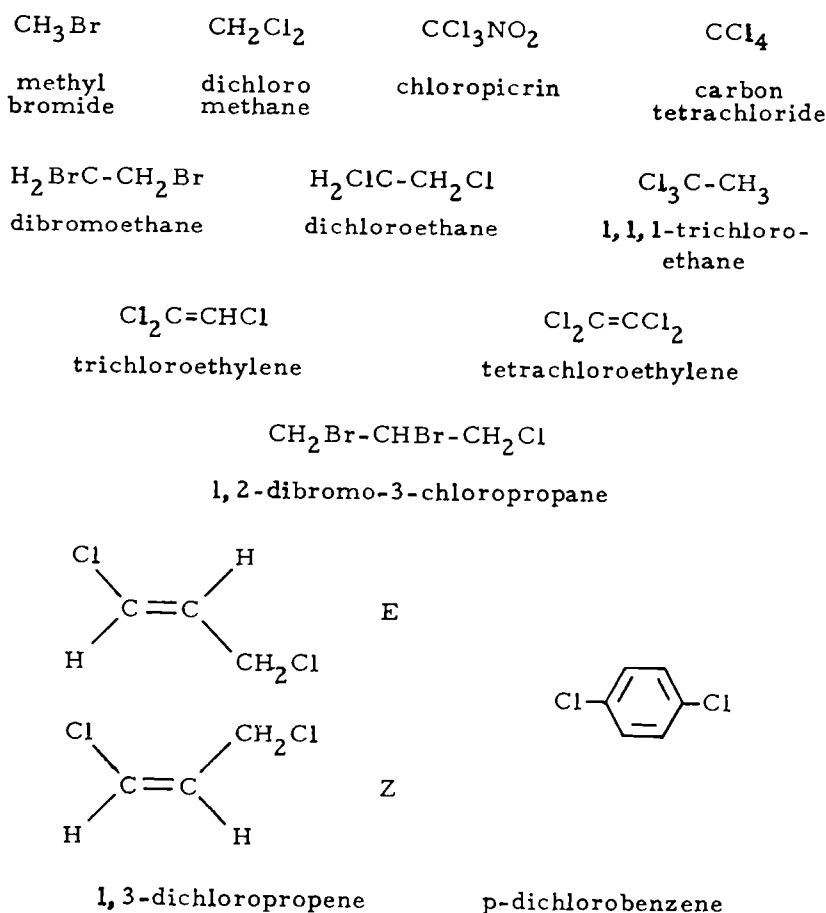


Figure 5.5 Some halogenated hydrocarbon fumigants and nematocides.

concentrations showed delayed weakness, rapid pulse, roughened fur, and signs of lung irritation and pneumonia; they died sometimes several days after exposure. Straight line logconcentration-logtime curves were found for rats and rabbits also. The duration of exposure at high concentrations necessary to produce death differed somewhat for the two species, but both were killed by a concentration of 1,000 mg/m³ for 20 hours (Irish *et al.*, 1940).

When animals were exposed to methyl bromide 7.5 to 8 hours/day, 5 days/week for 6 months, they tolerated a daily exposure not far below the maximal concentration tolerated for a single exposure of 8 hours. Specifically, rats and rabbits tolerated a concentration approximately one-fourth as great as the maximal tolerated single 8-hour exposure. Rats and guinea pigs tolerated 250 mg/m³, monkeys tolerated 130 mg/m³, and rabbits tolerated 65 mg/m³, all for 6 months and with normal growth, no symptoms, and no histopathological change. Higher concentrations eventually produced wild activity subsiding into muscular tremors in rats and into paralysis of the extremities in rabbits and monkeys. These functional disorders disappeared if the animals were removed from exposure. At tolerated levels, methyl bromide was eliminated rapidly (Irish *et al.*, 1940).

Absorption, Distribution, Metabolism, and Excretion. Methyl bromide is metabolized in part to inorganic bromide. The blood of control rabbits contained about 10 ppm of non-volatile bromide and those showing paralysis from methyl bromide contained about 110 ppm. However, when rabbits were fed sodium bromide repeatedly so that their blood levels were about 620 ppm, no paralysis occurred. Similar experiments with methanol showed that possible metabolism of methyl bromide to methanol could not account for the functional changes observed after methyl bromide. These and other studies led to the conclusion that the functional changes caused by methyl bromide are associated with the intact molecule (Irish *et al.*, 1940). In a similar way, not enough hydrogen bromide and/or methyl alcohol could be formed from a concentration of methyl bromide capable of killing anthrax spores to explain the disinfection (Kolb *et al.*, 1952).

It was argued by Miller and Haggard (1943) that the difference might lie in the release of some bromide intracellularly after exposure to methyl bromide and its restriction to the extracellular fluid after ingestion of inorganic bromides. Although evidence was given that this is true, the argument does little or nothing to exclude the direct toxic effect of methyl bromide or a free radical derived from it. Such direct action is consistent with the fact that the illness produced by methyl bromide is closely similar to that produced by methyl chloride and quite distinct from the conditions produced by inorganic bromides or methyl alcohol.

Biochemical Effects. Methyl bromide reacts *in vitro* with a number of SH enzymes and causes progressive and irreversible inhibition (Lewis, 1948). Winteringham *et al.* (1958) concluded that, at least in houseflies, the biochemical picture was not consistent with SH enzyme inhibition as an explanation of death. It is interesting that they found that initial immobilization of flies was apparently due to a reversible breakdown of ATP, and that temporary recovery was associated with a return toward normal levels of ATP. The later collapse and death of the flies was not accompanied by renewed breakdown of ATP and remained unexplained.

Whereas the relation of the inhibition of SH enzymes to the toxicity of methyl bromide remains obscure, there can be no doubt that its action is chemical, as distinct from physical. In view of the vapor pressure of the compound, the concentration necessary to kill 50% of a population of the grain weevil *Calandra granaria* indicated that the thermodynamic activity was only 0.0004 (Ferguson and Pirie, 1948).

Treatment of Poisoning in Animals. In a study of rats, mice, and rabbits that had been exposed to LD 50 doses of methyl

bromide, cysteine had not only prophylactic effect but also therapeutic effect when administered subcutaneously within 30 minutes after poisoning (Mizyukova and Bakhishev, 1971). In both mice and rabbits, glutathione was slightly more effective than BAL when both were given before an otherwise fatal respiratory exposure to methyl bromide; at a dosage of 750 mg/kg glutathione prevented death in all mice tested (Ueda and Kaai, 1971; Kawai and Ueda, 1972). However, Edson as quoted by Winteringham and Barnes (1955) reported that BAL was useless when administered to rats already poisoned by methyl bromide.

5.4.1.3 Toxicity to Man. Accidental and Intentional Poisoning. Von Oettingen (1955) tabulated 47 fatal and 206 non-fatal cases of poisoning by methyl bromide arising mainly from its manufacture or from its use as a fumigant or as a fire extinguishing fluid. Use as a fumigant led to 11 of the fatal and 44 of the nonfatal cases. More recent cases associated with fumigation have been reported by Rathus and Landy (1961), Drawneek *et al.* (1964), Collins (1965), Brodniewicz (1967), Hine (1969), Araki *et al.* (1971), Takahashi *et al.* (1973), Nakakita (1973), Garcia Rico *et al.* (1974), Toyonaga and Tokuda (1976), Ushio and Osotsuka (1977a, 1977b), Shield *et al.* (1977), and Takayama and Numajiri (1979).

High concentrations of methyl bromide can produce rapid unconsciousness during exposure leading to a prompt, "anesthetic" death (Garcia Rico *et al.*, 1974). However, anesthesia plays no part in the great majority of cases, which are characterized by delayed onset, a great variety of symptoms, and delayed recovery, if death does not occur. The delay in onset usually is several hours, but a delay of only a few minutes has been observed (Araki *et al.*, 1971) and a delay of 48 hours has been observed. In fatal cases with delayed onset, death generally occurs within 4 to 6 hours but sometimes after 24 to 48 hours. In rare instances, death may be delayed as much as 18 days (Davay, 1972). The cause of death in these cases usually is circulatory failure.

The most common initial symptoms in fatal or nonfatal cases with delayed onset are malaise, headache, visual disturbances, nausea, and vomiting. Later, a great variety of central nervous system manifestations appear, including numbness, ataxia, tremor, myoclonus, exaggerated (or absent) deep reflexes, positive Romberg's sign, paroxysmal abnormalities of the EEG, great agitation, change of personality, coma, and clonic, tonic (often Jacksonian) convulsions. Whereas convulsions generally occur in fatal cases (and many nonfatal ones too), death usually is the result of pulmonary edema leading to respiratory failure or cardiovascular collapse.

When death does not intervene, recovery may occur in a few days or hospitalization may be required for many weeks and the patient may be left with gross, permanent disability (Rathus and Landy, 1961; Ohsawa *et al.*, 1978).

There is no reason to doubt that dermal exposure can produce systemic illness, and severe illness occurred in a case involving gross contamination of the skin (Longley and Jones, 1965). However, the occurrence of severe systemic illness without significant respiratory involvement is no proof of a lack of respiratory exposure; such cases have occurred when exposure was exclusively respiratory (Shield *et al.*, 1977).

Use Experience. What has been said about accidents emphasizes the very real hazard of using methyl bromide as a fumigant.

The early literature contains accounts of similar cases associated with manufacturing. One form of injury, that is, the formation of large blisters by direct toxic action of methyl bromide on the skin, has occurred from industrial exposure (Watrous, 1942). This effect generally occurs only when evaporation is retarded and is especially likely following prolonged exposure to contaminated clothing and shoes, including rubber articles. Blistering apparently has not resulted from fumigation.

A number of deaths and other serious poisonings caused by methyl bromide used as a fumigant involved leakage of the gas from the space being treated into an occupied work or other area where no warning had been posted (California, 1958; Hine, 1969).

Dosage Response. Partly because most cases of poisoning by methyl bromide have involved respiratory exposure, there apparently is no information on the dosages involved. The threshold limit value (60 mg/m^3) would permit an occupational exposure of about 8.6 mg/kg/day .

Laboratory Findings. Hine (1969) reported blood bromide levels of 400 and 250 ppm in two fatal cases. Patients who presented with severe, moderate, and mild symptoms had blood levels of 220, 180, and 120 ppm, respectively. Blood bromide on hospital admission may be as low as 24 ppm or as high as 400 in nonfatal cases (Rathus and Landy, 1961). In an extremely severe but nonfatal case, the serum level was 328 ppm and the urinary level 296 ppm (Ushio and Osotsuka, 1977b). Finally, a serum bromide level of 550 ppm was found in a man who suffered repeated epileptic convulsions and, after partial recovery, was left with disabling, unilateral nerve involvement (Longley and Jones, 1965).

An average urinary bromide concentration of 23 ppm was found in people working in an atmosphere containing methyl bromide at a bromide concentration of 4 to 5 ppm. This was not associated with symptoms (Momotani *et al.*, 1976).

According to Drawneek *et al.* (1964), serum bromide levels over 50 ppm may, in the absence of any illness, be accompanied by mild euphoria leading to carelessness in the handling of methyl bromide.

Among workers exposed for a few months to 11 years, subjective symptoms could not be related to blood bromine levels in the range of 4 to 23 ppm. However, slight electroencephalographic changes and a small increase in serum transaminase levels were related to these bromide concentrations (Verberk *et al.*, 1979).

Methyl bromide itself can be measured in expired air, and the gas chromatographic method is sensitive to 6 ppm in air. Unfortunately human data obtained by this method are not available (Steward, 1974). Presumably the same chromatographic method could be applied to blood samples also. However, the only common measurement is for inorganic bromide derived metabolically from the organic compound. This measurement is meaningful insofar as exposure to more than minimal amounts of preformed inorganic bromides can be excluded. Bromides occur naturally in soil and in food. A blood bromide level of 50 ppm may be considered normal. However, any increase above this level due to absorption of methyl bromide is an indication of potentially hazardous exposure from which the person must be withdrawn immediately. Yet, volunteers who took a full dosage (5 doses/day) of a popular bromide headache remedy reached blood bromide levels of approximately 50 ppm after 1 day and, after 7 days of administration, their levels ranged from 270 to 310 ppm. When dosage was stopped, blood levels fell promptly but only gradually; the average was 70 ppm 24 days after the last dose. It was estimated that blood bromide levels of 700 to 800 ppm are not uncommon among those who habitually use bromide headache remedies. When inorganic bromides were prescribed, blood levels greater than 1,000 ppm were achieved regularly, and levels of 1,500 ppm usually did not cause concern (Gay, 1962).

Treatment of Poisoning. Treatment is symptomatic.

In a poisoned man suffering from action myoclonus, the condition was controlled by diazepam (60 mg/day). However, because of severe somnolence, the treatment was changed to clonazepam at 3 to 4 mg/kg. This treatment was effective; the somnolence disappeared, and the myoclonus was decreased conspicuously (Toyonaga and Tokuda, 1976). Clonazepam pro-

duced mild improvement in another case with action myoclonus (Shield *et al.*, 1977). Although BAL has been used for treating methyl bromide poisoning (Rathus and Landy, 1961), there is no evidence that it was beneficial.

5.4.2 Dichloromethane

5.4.2.1 Identity, Properties, and Uses. *Chemical Name.* Dichloromethane.

Structure. See Figure 5.5.

Synonyms. Dichloromethane also is known as methylene chloride, methylene bichloride, and methylene dichloride. The CAS registry no. is 75-09-2.

Physical and Chemical Properties. Dichloromethane has the empirical formula CH_2Cl_2 and a molecular weight of 84.94. It is a colorless liquid with a density of 1.3255 at 20°C . It solidifies at -95°C and boils at 39.75°C . It is about 2% soluble in water and miscible with alcohol, ether, and dimethylformamide. The vapor is nonflammable and nonexplosive.

Use. Fruit ripening agent.

5.4.2.2 Toxicity to Laboratory Animals. *Basic Findings.*

Rats of different ages showed relatively little difference in susceptibility to dichloromethane, as compared to the corresponding differences for some other solvents. The oral LD 50 values for 14-day-old rats, young adults, and older adults were 2,385, 2,120, and 3,047 mg/kg, respectively (Kimura *et al.*, 1971). A rabbit that received dichloromethane subcutaneously at a rate of 2,700 mg/kg died; a few that received smaller doses survived. Dogs that received dichloromethane orally at rates of 3,000 mg/kg or greater died, whereas the few that received rates of 2,750 mg/kg or less survived. Small numbers of dogs were killed by an intravenous dosage of 200 mg/kg but others survived 175 mg/kg or less (Barsoum and Saad, 1934).

The intraperitoneal LD 50 in mice was 1,990 mg/kg (Klaassen and Plaa, 1966).

The LC 50 for a standard 7-hour exposure in mice was $27,800 \text{ mg/m}^3$ (von Oettingen *et al.*, 1949).

Two of four dogs showed slight to moderate fatty degeneration of the liver following six 4-hour exposures at a concentration of $34,000 \text{ mg/m}^3$, which caused slight to moderate narcosis during exposure. Guinea pigs also developed liver injury after repeated exposure. Rats, rabbits, and monkeys did not develop liver injury when exposed to the same concentration 4 hours/day, 5 days/week, for 7.5 weeks. However, some rats and rabbits died of acute pulmonary edema. Guinea pigs grew slowly, but rats, rabbits, and dogs showed no adverse effect when exposed to $17,000 \text{ mg/m}^3$ 7 hours/day, 5 days/week, for 6 months. The possibility of liver damage was studied with particular care in the dogs, but no evidence of such injury was found (Heppel *et al.*, 1944).

Although an air concentration of $8,500 \text{ mg/m}^3$ had no depressant effect on young male rats as judged by ordinary inspection, it greatly diminished their running activity during exposure as measured by a standard revolving drum (Heppel and Neal, 1944).

Repeated application of dichloromethane to the ears of rabbits caused hyperemia followed by scaly exfoliation (Heppel *et al.*, 1944).

Absorption, Distribution, Metabolism, and Excretion. The blood of rabbits just after 1 hour of exposure to $10,000 \text{ ppm}$ of dichloromethane vapor ranged from 87 to 171 ppm (Heppel *et al.*, 1944).

In dogs subjected to anesthesia for 7 hours at a concentration of $15,000 \text{ ppm}$ ($52,110 \text{ mg/m}^3$), the blood level approached a steady state (430 ppm) within 1.5 to 2 hours; the highest level reached temporarily by any dog within the 7-hour exposure period was 566 ppm. Dogs exposed to $40,000 \text{ ppm}$ died soon

HANDBOOK OF TOXIC AND HAZARDOUS CHEMICALS AND CARCINOGENS

Second Edition

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Disposal Method Suggested: Controlled incineration whereby oxides of nitrogen are removed from the effluent gas by scrubber, catalytic or thermal device.

References

- (1) See Reference (A-61).
- (2) See Reference (A-60).

METHYL BROMIDE

- Carcinogen (potential, EPA)(1)
- Hazardous waste (EPA)
- Priority toxic pollutant (EPA)

Description: CH_3Br , methyl bromide, is a colorless liquid or gas with a chloroformlike odor at high concentration. It boils at $3^\circ\text{--}4^\circ\text{C}$.

Code Numbers: CAS 74-83-9 RTECS PA4900000 UN 1062

DOT Designation: Poison gas

Synonyms: Bromomethane, monobromomethane, Embafume®, Iscobrome®, Rotox®.

Potential Exposure: Methyl bromide: The primary use of methyl bromide is as an insect fumigant for soil, grain, warehouses, mills, ships, etc. It is also used as a chemical intermediate and a methylating agent, a refrigerant, a herbicide, a fire extinguishing agent, a low-boiling solvent in aniline dye manufacture, for degreasing wool, for extracting oils from nuts, seeds, and flowers, and in ionization chambers. It is used as an intermediate in the manufacture of many drugs (A-41).

Incompatibilities: Aluminum or strong oxidizers.

Permissible Exposure Limits in Air: The Federal standard for methyl bromide is 20 ppm (80 mg/m^3) as a ceiling value. The ACGIH (1983/84) has adopted a TLV for methyl bromide of 5 ppm (20 mg/m^3) as a TWA with an STEL value of 15 ppm (60 mg/m^3). The notation "skin" is added to indicate the possibility of cutaneous absorption. The IDLH level is 2,000 ppm.

Determination in Air: Charcoal adsorption, workup with CS_2 , analysis by gas chromatography. See NIOSH Methods, Set J. See also reference (A-10).

Permissible Concentration in Water: To protect human health—preferably zero. An additional lifetime cancer risk of 1 in 100,000 is posed by a concentration of $1.9\text{ }\mu\text{g/l}$.

Determination in Water: Inert gas purge followed by gas chromatography with halide specific detection (EPA Method 601) or gas chromatography plus mass spectrometry (EPA Method 624).

Routes of Entry: Inhalation, percutaneous absorption, ingestion, skin and eye contact.

Harmful Effects and Symptoms: *Local* — Methyl bromide is irritating to the eyes, skin, and mucous membranes of the upper respiratory tract. In cases of moderate skin exposure, there may be an itching dermatitis, and in severe cases,

vesicles and second-degree burns. Methyl bromide may be absorbed by leather, resulting in prolonged skin contact.

Systemic – High concentrations of methyl bromide may cause lung irritation which may result in pulmonary edema and death. Acute exposure to methyl bromide may produce delayed effects. Onset of symptoms is usually delayed from 30 minutes to 6 hours; the first to appear are malaise, visual disturbances, headaches, nausea, vomiting, somnolence, vertigo, and tremor in the hands. The tremor may become more severe and widespread, developing into epileptiform-type convulsions followed by coma and death due to pulmonary or circulatory failure or both. A period of delirium and mania may precede convulsions, but convulsions have been reported without any other warning symptoms. Kidney damage may occur; permanent brain damage may result.

In chronic poisoning, the effects of methyl bromide are usually limited to the central nervous system: lethargy, muscular pains; visual, speech, and sensory disturbances; and mental confusion being the most prominent complaints.

Points of Attack: Central nervous system, respiratory system, lungs, skin, eyes.

Medical Surveillance: Evaluate the central nervous system, respiratory tract, and skin in preplacement and periodic examinations.

First Aid: If this chemical gets into the eyes, irrigate immediately. If this chemical contacts the skin, flush with water immediately. If a person breathes in large amounts of this chemical, move the exposed person to fresh air at once and perform artificial respiration. When this chemical has been swallowed, get medical attention. Give large quantities of salt water and induce vomiting. Do not make an unconscious person vomit.

Personal Protective Methods: Wear appropriate clothing to prevent any possibility of skin contact. Wear eye protection to prevent any reasonable probability of eye contact. Employees should wash immediately when skin is wet or contaminated. Remove nonimpervious clothing immediately if wet or contaminated. Provide emergency showers.

Respirator Selection:

- 200 ppm: SA/SCBA
- 1,000 ppm: SAF/SCBAF
- 2,000 ppm: SA:PD, PP, CF
- Escape: GMOV/SCBA

Disposal Method Suggested: The recommended disposal procedure is spray the gas into the fire box of an incinerator equipped with an afterburner and scrubber (alkali).

References

- (1) U.S. Environmental Protection Agency, *Halomethanes: Ambient Water Quality Criteria*, Wash., DC (1980).
- (2) U.S. Environmental Protection Agency, *Bromomethane*, Health and Environmental Effects Profile No. 29, Wash., DC, Office of Solid Waste (April 30, 1980).
- (3) See Reference (A-61).
- (4) See Reference (A-60).
- (5) Parmeggiani, L., Ed., *Encyclopedia of Occupational Health & Safety*, Third Edition, Vol. 1, pp 330-31, Geneva, International Labour Office (1983) (Bromomethane).
- (6) United Nations Environment Programme, *IRPTC Legal File 1983*, Vol. II, pp VII/437-40, Geneva, Switzerland, International Register of Potentially Toxic Chemicals (1984).

MET

Description: $\text{CH}_3\text{CO}(\text{Cl})$ odor, boiling at $127^\circ\text{--}128^\circ\text{C}$.

Code Numbers: CAS 59

DOT Designation: –

Synonyms: 2-hexanone,

Potential Exposure: The annual worker exposure at 2

Incompatibilities: Strong

Permissible Exposure Limit: (mg/m³). NIOSH (1) has recommended a TWA of 5 ppr. IDLH level is 5,000 ppm.

Determination in Air: (gas chromatography. See NIOSH)

Permissible Concentration

Routes of Entry: Inhalation.

Harmful Effects and Symptoms: neuropathy; weakness, paresis

Points of Attack: Central

Medical Surveillance: Periodic respiratory conditions. In the event of exposure, should be given to the central

First Aid: If this chemical contacts the skin, in large amounts of this chemical, move the exposed person to fresh air at once and perform artificial respiration. When this chemical has been swallowed, get medical attention. Give large quantities of salt water and induce vomiting. Do not make an unconscious person vomit.

Personal Protective Methods: Wear appropriate clothing to prevent any possibility of skin contact. Wear eye protection to prevent any reasonable probability of eye contact. Employees should wash immediately when skin is wet or contaminated. Remove nonimpervious clothing immediately if wet or contaminated. Provide emergency showers.

Respirator Selection:

- 1,000 ppm: CCRC
- 5,000 ppm: GMOV
- Escape: GMOV

Disposal Method Suggested:

References

- (1) Nat. Inst. for Occupational Safety and Health, *Occupational Exposure to*
- (2) See Reference (A-60).

March 1986

chemicalWATCH

METHYL BROMIDE

A soon-to-be-published study of soil and structural fumigants differently exposed to methyl bromide (MeBr), sulfur dioxide (Vikane), or a combination of the two, shows that fumigant exposure causes subtle neurological damage. Conducted by the National Institutes of Occupational Safety and Health researchers W.K. Anger et al., the study shows significant impairment of finger sensitivity, increased paresthesias (tingling, loss of feeling) in hands, and decreased memory-related cognitive ability, particularly in the group exposed to both fumigant pesticides. This study provides a prime example of the little-studied problem of "chemical synergism" where chemicals in combination exert effects greater than either alone.

MeBr is an odorless, colorless gas, widely used in California, Florida, and Hawaii both as a soil-sterilant and to control dry-wood termites and powder-post beetles. Recent evidence has shown that MeBr is a direct-acting carcinogen in the rat, where it causes stomach cancer. In humans and animals, death results from pulmonary irritation and edema; non-lethal exposures can produce muscle weakness, abnormal reflexes, and visual disorders, head-ache and malaise.

Vikane is another highly toxic and odorless structural fumigant. Very little is known of the toxic effects of Vikane, and even the poly-ethylene sheeting commonly used to protect articles in the home during applications is permeable to the chemical. Residues have been found on such soft household goods as rubber, feathers, rayon and wool as long as 40 days after fumigation.

When used as a structural fumigant, MeBr and Vikane are mixed with another fumigant chloropicrin, which, in this case, serves solely as a warning agent by irritating the eyes and nose. Under a 1982 data call-in, EPA asked that registrants supplement the extremely deficient data-base with new and more complete residue data. Sub-chronic and chronic animal study requirements were waived and until review of other data is completed, no tolerances exist for residues in food commodities.

The Anger study suggests that

more long-lasting effects of exposure may have been overlooked thus far. The changes noted are so subtle, he says, that workers themselves might not readily recognize they had occurred.

TRICHLOPYR

Following up on court victories in the Northwest which have put a potential end to forest spraying, the California Coalition for Alternatives to Pesticides (CCAP) is suing to prevent routinized renewal of herbicide registrations for forest use until the data-bases on these chemicals are fully reevaluated.

One such herbicide is trichlopyr (Garlon), a Dow Chemical Co. compound widely used for the control of broad-leaved weeds in forest-site preparation and rights-of-way management programs.

Structurally, Garlon (registered in 1973) is a chemical cousin of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and like 2,4,5-T it mimics plant growth hormones called auxins, readily translocating throughout the plant. Unlike 2,4,5-T, however, due to a structural difference, Garlon is not contaminated with dioxins. It is slowly metabolized by soil microbes, having a soil half-life ranging from 79 days at 60 F. to 156 days at lower temperatures. The breakdown products, trichloropyridinol and trichloromethoxy pyridine, are more persistent, with half-lives ranging between 8-279 days and 50-300 days, respectively. However, Garlon

binds poorly to soil-particles, and is therefore expected to leach easily into ground and surface waters. Of the two salt formulations sold, the triethylamine and the butoxyethylester (Garlon 3A and 4), the latter is much more toxic to fish.

Summaries of health and safety data reviewed by independent toxicologist Dr. Ruth Shearer reveal that a statistically significant increase in benign pulmonary tumors was found in a two year mouse feeding study, at an eight-fold lower dose than normally is recommended in a carcinogenicity study.

LINDANE

Eight years after initiating an investigation into the potential toxic effects of the organochlorine insecticide lindane, and two years after EPA killed its own proposal to ban most uses of the chemical, the Agency's recently released registration guidance document indicates that many of the original concerns remain. Meanwhile, high exposure use of the chemical in products such as delousing shampoos continues.

EPA proposes to regulate lindane as a "Class C" carcinogen, one considered to have the lowest weight of evidence, in spite of two studies showing that lindane and its metabolite cause liver cancer in mice. EPA has apparently joined the ranks of those in academic circles who have questioned recently the "significance" of liver cancer induction in male mice. EPA also cites a lack of any

continued on page 6

ChemBRIEFS

Parathion

Monsanto Chemical Co. has announced that its parathion manufacturing process and Alabama production facility would be offered for sale. The only other producer of parathion is Chemi-Nova, of Denmark.

Parathion, a highly toxic organophosphate insecticide, degrades to an even more toxic metabolite, paraoxon. Monsanto says it plans to get out of the insecticide business (its only insecticide is parathion). Instead, it will focus on its herbicides and biotechnology. In 1985, EPA called in data on residues, re-entry, neurotoxicity, and "additional pathology stud-

ies" on rat thyroid adenomas (benign tumors).

Tributyltins

EPA put nine tributyltin compounds into Special Review January 7, 1986, as water monitoring of several major harbors suggests that leaching from vessels treated with tributyltin-containing marine anti-fouling paints poses a "chronic and acute risk of toxicity to non-target organisms". Tributyltins bioaccumulate and can kill or cause developmental malformation of aquatic algae, molluscs, crustacea and fish at part per trillion concentrations.

Great Britain (1986) and France (1982) have already banned the products in most cases.

data supplied?
EPA's data
supplied?
data?

Methyl Apholate

Chemistry

COMPOSITION: 2,2,4,4,5,5-Hexahydro-2,2,4,4,5,5-hexakis (2-methyl-1-aziridinyl)-1,3,5,2,4,6-triazatriphosphorine.

Action/Use

ACTION: Insect chemosterilant.

Methyl Aphoxide — see Metepa.

Methyl Bromide

Identification

COMMON NAME: Methyl bromide.

OTHER NAMES: Brom-O-Gas*, Brom-O-Sol*, Brom-O-Sol* 90, Terr-O-Cide* II, Terr-O-Gas* 98, Celfume*, Kayafume, MeBr*, Terr-O-Gas* 33, Terr-O-Gas* 45, Terr-O-Gas* 50, Terr-O-Gas* 57, Terr-O-Gas* 67, Terr-O-Gas* 70, Terr-O-Gas* 80.

CODE NUMBERS: CAS 74-83-9; SHA 053201; DOT 1062.

DISCONTINUED NAMES: Terr-O-Gas* 100 (Great Lakes Chemical Corp.).

Chemistry

COMPOSITION: Bromomethane.

FAMILY: Alkyl bromide.

PROPERTIES: Colorless, odorless gas at normal temperature and pressures; liquefied gas handled as a liquid (14.4 lb/gal) under moderate pressure. Specific gravity at 0°C and 760 mm Hg = 1.732; vapor density = P3.27; boiling point 3.6°C; vapor pressure at 20°C 1400 mm/Hg, at 40°C 2600 mm/Hg. Viscosity = 0.22 centistokes at 0°C.

Action/Use

ACTION: Fumigant.

inted for Preliminary planning only.
nformation/directions supplied by manufacturer.

1991 Farm Chemicals Handbook

Methyl Bromide (Cont.)

USES: Insect and rodent control in space and commodity fumigations. Preplant soil fumigation (only with chloropicrin) to control nematodes, insects, weed seeds and fungi.

Registration Notes

All applications classified by U.S. EPA as RUP. Only the registrant is authorized to refill cylinders.

Environmental Guidelines

SOLUBILITY: Solubility in water at 20°C = 1.75 g/100g. Methyl bromide is readily soluble in lower alcohols, ethers, esters, ketones, halogenated hydrocarbons, aromatic hydrocarbons and carbon disulfide.

Safety Guidelines

SIGNAL WORD: DANGER.

TOXICITY CLASS: II.

TOXICITY: (Rat): Oral LD₅₀ 214 mg/kg. Inhalation LC₅₀ 3120 ppm (15 min.). (Human): Inhalation LC₅₀ 60,000 ppm (2 hrs.). OSHA PEL: 20 ppm C (skin); ACGIH TLV: 5 ppm (skin); EPA fumigation limit requiring SCBA: 5 ppm. Methyl bromide is a poison and can cause respiratory distress, cardiac arrest and central nervous system effects. Liquid may cause skin and eye burns. Mutagenic in Ames test at levels above the TLV, but not carcinogenic in 90-day oral study in rats.

PROTECTIVE CLOTHING: Avoid tight clothing, jewelry, gloves, and boots when handling methyl bromide. Methyl bromide may be trapped inside and cause skin irritation or injury. If full-face respiratory protection is not required, wear goggles or full-face shield for eye protection when handling liquid. Do not reuse contaminated clothing and shoes until thoroughly cleaned and aerated. Respiratory protection for enclosed spaces: If the concentration of methyl bromide in the worker area, as measured by a pump and appropriate detector tubes (for example, Draeger, Kitagawa, MSA, and Sensidyne), does not exceed 5 ppm (20 mg/m³), no respiratory protection is required. If this concentration is exceeded at any time, all persons in the fumigation area must wear a NIOSH/MSHA approved self-contained breathing apparatus (SCBA) or respiration air-supplied/SCBA respirator.

HANDLING AND STORAGE CAUTIONS: Store in a locked, dry, cool, well-ventilated area. Post as a pesticide storage area. Do not contaminate water, food, or feed by storage. Store cylinders upright, secured to a rack or wall to prevent tipping. Cylinders should not be subjected to rough handling or mechanical shock such as dropping, bumping, dragging, or sliding. Do not use rope slings, hooks, tongs or similar devices to unload cylinders. Transport cylinders using hand truck, fork truck or other device to which the cylinder can be firmly secured. Do not remove valve protection bonnet and safety cap until immediately before use. Replace safety cap and valve protection bonnet when cylinder is not in use. When cylinder is empty, close valve, screw safety cap on to valve, and replace protection bonnet before returning to shipper. Only the registrant is authorized to refill cylinders. Do not use cylinders for any other purpose.

Emergency Guidelines

FIRST AID: Skin, wash thoroughly with soap, water for at least 15 minutes. Remove contaminated clothes, shoes immediately; thoroughly decontaminate before reuse. Destroy contaminated leather goods. **INHALATION:** Move to fresh air. Keep warm. Give artificial respiration if breathing has stopped. Get immediate medical aid.

EMERGENCY TELEPHONE: 501-862-5141 (Great Lakes).

REG: Great Lakes Chemical Corp. (Brom-O-Gas*, Brom-O-Sol*, Meth-O-Gas*, Terr-O-Cide* II, Terr-O-Gas*)

Methyl Chloroform — see Trichloromethane

Casarett and Doull's
TOXICOLOGY

The Basic Science of Poisons

SECOND EDITION

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phosphide, in the presence of moisture, may evolve phosphine, which inhaled in sufficient concentration can cause fatal pulmonary edema.

Thallium sulphate is lethal to most animals in doses of 10 to 20 mg/kg. It apparently acts by reacting with free sulfhydryl groups, but the precise mechanism of poisoning is uncertain. Acute poisoning is accompanied by gastrointestinal irritation, motor paralysis, and death from respiratory failure. Lower, sublethal doses taken over a period of time result in reddening of the skin and loss of hair. Pathologic changes include perivascular cuffing around blood vessels and degenerative changes in brain, liver, and kidney. Neurologic symptoms are prominent in repeated subacute poisoning and include tremors, leg pains, paresthesias of the hands and feet, and polyneuritis especially in the legs. Psychoses, delirium, convulsions, and other kinds of encephalopathy may also be noted. Dimercaprol (BAL) is of little benefit as a chelating agent in removal of absorbed thallium. Diethyldithiocarbamate has been demonstrated to accelerate the rate of excretion of thallium in experimental animals and to aid in the treatment of thallium-poisoned children (Hayes, 1963). Use of 1 percent thallium sulfate to control ground squirrels has resulted in outbreaks of thallotoxicosis in humans. In a 20-year period between 1935 to 1955, 778 persons were reported to have been poisoned by thallium-containing insecticides, rodenticides, and therapeutic chemicals, resulting in 46 fatalities (Grossman, 1955). Because of its high, cumulative toxicity the use of thallium has been restricted to applications by qualified personnel, with a resultant marked decline in its use as a rodenticide (Lisella *et al.*, 1971).

White or yellow elemental phosphorus has caused poisoning because of the practice of spreading pastes containing this element on bread as a rodenticide bait (Lisella *et al.*, 1971). A dose of 15 mg of phosphorus can cause severe poisonings in humans and as little as 50 mg may be fatal. Shortly after ingestion phosphorus produces severe gastrointestinal irritation, and if a sufficient dose is ingested, hemorrhage and cardiovascular failure may prove fatal within 24 hours. The vomitus after phosphorus ingestion is luminescent and has a characteristic garlic odor. If the patient survives the initial gastrointestinal irritation phase, secondary systemic poisoning due to liver necrosis may ensue. Severe acute yellow atrophy of the liver is one delayed sequela that may ultimately prove fatal.

Barium carbonate and arsenic trioxide have also been used as rodenticides, but currently have little application for this purpose. Barium

produces severe colic, diarrhea, and hemorrhage. It has a direct action on smooth muscles of the arterioles and cardiac muscle, which can result in increased blood pressure, cardiac irregularities, and death.

A variety of other compounds have some occasional application in rodent control. Carbon monoxide, methyl bromide, and hydrogen cyanide have been used as fumigants to kill rodents in enclosed spaces. These chemicals are generally toxic to all species. DDT, commonly thought of as an insecticide, is used as a poison for the house mouse and for bats. The principle of this treatment is to treat inaccessible areas where mice travel so that they will pick up a sufficient amount of DDT on their feet and fur, and ultimately, in preening, ingest the DDT and become poisoned. At best this seems an inefficient means of rodent control. Further discussion of action and therapy for poisoning by various rodenticides may be found in Hayes (1963).

FUMIGANTS

Fumigants are used in the control of insects, rodents, and soil nematodes. They have in common the property of being in the gaseous form at the time they exert their pesticidal action and are used because they will penetrate to areas otherwise inaccessible for pesticide application (e.g., grain storage areas, rodent runways). Fumigants may be liquids that readily vaporize, solids that release a gas by chemical reaction (e.g., HCN from $\text{Ca}[\text{CN}]_2 + \text{H}_2\text{O}$), or gases contained in cylinders or ampuls (e.g., methyl bromide). Thus they provide a potential hazard from the standpoint of inhalation exposure as well as, in the case of solids and liquids, accidental ingestion or dermal exposure. Fumigants used in the protection of stored foodstuffs include acrylonitrile, carbon disulfide, carbon tetrachloride, chloropicrin, ethylene dibromide, ethylene oxide, hydrogen cyanide, methyl bromide, and phosphine.

These chemicals have many other applications in industry and their toxicology has been discussed in other sections. In connection with pesticides it is worthy of comment that methyl bromide is said to have been responsible for more deaths in recent years among occupationally exposed persons in California than all of the more publicized organophosphate group of insecticides (Hine, 1969). During the period of 1957 to 1964, 62 systemic poisonings with five deaths were reported. In the usual case the early symptoms are malaise, headache, visual disturbances, and nausea and vomiting. Pulmonary effects included acute pulmonary edema, and neurologic effects in fatal poisonings included clonic and toxic convulsions. Several nonfatal

atrophies
escape

cases resulted in persistent neurologic and psychiatric complaints ranging from muscular soreness and headache through decreased libido, mental depression, phobias, and paranoia. Although the neurologic and psychiatric symptoms resemble chronic poisoning by inorganic bromides, the serum bromide levels achieved in serious cases of methyl bromide poisoning are considerably lower than those required for poisoning by inorganic bromides (Rathus and Handy, 1961; Collins, 1965). It has been suggested that this may be due to greater lipid solubility of methyl bromide and hence greater penetration into the brain. However, since methyl chloride produces many of the same neurologic symptoms, it seems unlikely that the neurotoxicity of methyl bromide is due only to bromide ion. Methyl bromide methylates SH groups of cysteine, glutathione, and several SH-containing enzymes. Methylation of SH groups essential to cellular oxidation can be suggested as a possible mechanism for the neurologic effects of methyl bromide and methyl chloride, and therefore BAL has been considered of possible usefulness in therapy. BAL given before exposure protected against lethal exposures in animals, but had much less effect when given after exposure.

Phosphine (see Rodenticides), released from aluminum phosphide, although more acutely toxic than methyl bromide, is said to be safer for use as a grain fumigant under practical conditions (Hayes, 1971). Use of acrylonitrile as a fumigant is limited by its flammability and high cost. Its toxicity has been attributed to release of CN ion *in vivo*, however, differences in symptoms and CN blood levels associated with poisoning by inorganic cyanides and acrylonitrile have led to some question about that mechanism (Paulet and Desnos, 1961). Chloropicrin (CCl_3NO_2) is a strong irritant, and sensory irritation gives early warning of its presence. It is, therefore, sometimes added in small amounts to other comparatively odorless fumigants to act as a warning agent. Ethylene oxide toxicity is also primarily due to its irritant actions in the lungs.

Ethylene dibromide in high concentrations (> 200 ppm) produces primarily lung inflammation and edema in laboratory animals while repeated exposures to lower concentrations resulted in histopathologic changes in their livers and kidneys as well. No abnormal signs were observed in rats and guinea pigs given 40 to 50 mg/kg/day for four months. A dose of 2 mg/kg/day given to bulls was reported to have resulted in impaired spermatogenesis within two weeks. Ethylene dibromide residues in fumigated cereal grains have been observed for up to two months after fumigation, and laying hens fed

diets containing 10 ppm (daily dose of 1 to 2 mg/kg) had a decrease in egg weights. Investigation of the possible mechanism of this effect led to observation of impaired follicle growth apparently arising from impaired permeability of the follicular membrane to protein transfer (Alumot, 1972). In a case of fatal human poisoning resulting from ingestion of 4.5 ml of ethylene dibromide, massive centrilobular necrosis of the liver and proximal tubular damage in the kidney were observed. Ethylene dibromide and 1,2-dibromo-3-chloropropane (DBCP), another nematocidal fumigant, were both found to rapidly produce highly malignant gastric squamous cell carcinoma in rats and mice (Olson *et al.*, 1973; Powers *et al.*, 1975; IARC, 1977).

DBCP also received considerable notoriety as a result of its being the probable cause of sterility and/or abnormally low sperm counts in workmen engaged in its manufacture. This resulted in a drastic reduction in its production and use (joint news release, OSHA, FDA, EPA, Sept. 8, 1977). Studies in laboratory animals 16 years earlier had suggested the potential for this toxic effect when it was observed that repeated inhalation exposure to as little as 5 ppm of DBCP has an adverse effect on the testes and on reproductive function of male rats (Torkelson *et al.*, 1961). Although the investigators, in that report, warned of the potential hazard, this warning was apparently not strong enough to prompt appropriate warnings to workers and/or improve industrial hygiene practice sufficiently to protect workers. The future use of both ethylene dibromide and DBCP as fumigants will likely be severely curtailed because of their strong carcinogenicity and their adverse action on reproductive function.

SPECIAL PROBLEMS

Interactions

Organophosphate Potentiation. For several years following the observation by Frawley and coworkers (1957) of marked synergism of the acute toxicity of EPN and malathion, the Food and Drug Administration Act required that all safety evaluations on anticholinesterase insecticides for which food residues were established should include tests of the toxicity of combinations. This led to routine tests for toxic interactions among this class of compounds. Most of these were acute toxicity tests using simultaneous administration. In 1961 DuBois reported studies in which the acute toxicity of various combinations of 13 different organophosphorus (OP) insecticides were tested in rats. Twenty-one pairs were additive in toxicity, 18 pairs less than additive, and four pairs synergistic. Since that

Chloro-
phosphine
is very
poisonous
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CHEMICAL USE IN FOOD PROCESSING AND POSTHARVEST HANDLING:

ISSUES AND ALTERNATIVES

Report of a 1987-88 Study Group on
Chemicals in the Human Food Chain:
Sources, Options, and Public Policy

Sponsored by the
University of California
Agricultural Issues Center
1989

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PREFACE

Harold O. Carter and Carole Frank Nuckton

This is the third in a series of reports stemming from the UC Agricultural Issues Center's major study in 1987-88:

Chemicals in the Human Food Chain: Sources, Options, and Public Policy

An interdisciplinary approach was used with the project as over 60 faculty and extension specialists applied their expertise from diverse fields—veterinary medicine, medicine and health sciences, nutrition, environmental toxicology, agricultural economics, food science and technology, agronomy, pomology, entomology, law, and others. Participants came from three UC campuses—Berkeley, Davis, and Riverside—and Stanford University. Many persons from outside the university also participated in the study as consultants, study-paper reviewers, and panelists at the Center's June symposium.

Each of the three main topics—Sources, Options, and Public Policy—was divided into a number of subgroups. Co-leaders of the Sources group were James N. Seiber, professor of environmental toxicology and associate dean for research, College of Agricultural and Environmental Sciences, UC Davis, and Michael W. Stimmann, statewide pesticide coordinator, UC Division of Agriculture and Natural Resources, and extension entomologist, UC Davis. This group examined five major sources of chemicals in the human food chain—animal products, crop plant products, food additives, natural toxicants, and industrial/environmental contaminants.

The overall chair of the Options group was James M. Lyons, professor, Vegetable Crops, UC Davis and acting director, Office of Program Information and Analysis, Division of Agriculture and Natural Resources, University of California. The Options group had three study teams: animal products chaired by Bennie Osburn, professor of pathology and associate dean of the research and graduate programs at the School of Veterinary Medicine, UC Davis; plant products, chaired by William C. Liebhardt, extension specialist, Agronomy and Range Science, UC Davis and director of the UC Sustainable Agriculture Program; and postharvest handling and processing, chaired by Adel A. Kader, professor and chair of the Pomology Department, UC Davis. This report represents the efforts of the postharvest handling/processing study group which selected four case studies: sulfites on grapes, postharvest fungicides on citrus, methyl bromide on dried fruits and nuts, and nitrites in processed meat.

The Public Policy group, chaired by Sandra Archibald, assistant professor, Stanford University, was concerned with society's mechanisms for dealing with chemicals, including criteria for food safety, risk assessment and the regulatory environment. Its approach was to involve panels of experts to solicit differing perspectives on regulatory effectiveness. Participating were consumer groups, food producers-processors-retailers, chemical manufacturers, risk assessors, and regulators.

Key findings of the study groups were presented at a symposium on June 2-3, 1988. (The proceedings may be ordered from the Center.) The complete study group reports are published or are in preparation for publication. Supplementing this report on case studies in postharvest handling/processing are: *Agricultural Chemicals in California Plant Production: Are There Alternatives?* The report on alternatives to chemical use in animal production is in preparation. A reference book on sources of chemicals in the human food chain is being compiled, and a report documenting the varying viewpoints of the participants in the policy process is now available: *Regulating Chemicals: A Public Policy Quandary*. Video tapes from the symposium have been produced for classroom and extension workshop use. Additional outreach is planned, and new areas of research inquiry have been opened that may well continue for a number of years.

The efforts, comments, responses and cooperation of the many experts from within and outside of the university who contributed to this study are greatly appreciated. Their names are acknowledged on the title pages of the individual chapters of this report.

Helene Obradovich, publications assistant for the UC Agricultural Issues Center, designed and prepared the camera-ready copy of this report.

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INTRODUCTION

Adopted from James Lyons, *Options and Alternatives: An Overview*¹

A myriad of chemicals is used within our sophisticated industrialized society and some hazards are associated with their use. This report explores the postharvest and processing level of the food system and analyzes the potential of various options and alternatives to this use of chemicals.

From a historical perspective, as populations increased and cities grew in size, there was a limit to the distance from a city boundary that farmers could deliver commercially acceptable horticultural products to an ever expanding population. It was not until Bordeaux mixture, a mix of copper sulfate and lime which could control the fungus organisms that attacked fruit crops, was developed in the late 1800s that tree fruits could be shipped any distance from the production areas into the industrial centers of large populations. From the 1880s to 1900, the development of cold storage and improved transportation facilities coincided with an effective chemical control of insect and disease problems; this allowed the population centers to begin to enjoy the availability of a wide array of fresh and processed fruit and vegetables over an extended period of the year, for these chemicals preserved quality and prevented development of harmful organisms during shipment. But their use raises the same questions about food safety at the postharvest level as does the use of chemicals for increasing productivity and yields at the production level.

Thus, as we examine the options and alternatives to the use of chemicals, we need to visit the issue of risk and benefit. Does the postharvest use of these chemicals present a health risk to the consumer? What about the safety of this wide array of food items in our supermarkets?

A brief review of the principal elements involved will help to set the stage for a discussion on the potential of options and alternatives. The late 1960s saw a body of literature evolve which evaluated data on the toxic properties of chemical substances from animal studies, from controlled epidemiologic investigations and from clinical studies and case reports of exposed humans. It is important

to make the distinction between the toxicity of a substance and the hazard from that substance. That is, toxicity is the inherent capacity of a substance to produce injury, whereas hazard from that substance is defined as the capacity to produce injury under the normal circumstances from common use. Every substance is toxic at some dose, but not every substance is hazardous at commonly used doses. This distinction leads to the concept of a risk/benefit ratio—a phrase that causes much debate among research scientists, consumers, and those responsible for risk management and the ensuing regulatory policies. That is, scientific analysis quickly enters those areas of risk assessment which revolve around the subjective and emotional perceptions addressing the distinction between “vital” versus “nonvital” risk and “voluntary” versus “involuntary” risk.

While an informed public can generally accept the risk/benefit concept, most people are not willing to accept the concept with regard to applied chemicals in the food system because they *question* whether use of these potentially hazardous chemicals is really *vital* to food production, packing, processing, and marketing. The consuming public insists that the notion of *prevention* of use of these chemicals be exhaustively explored before the risk/benefit equation be applied. That is, are the current patterns of use truly “vital” to our bountiful supply of fresh and processed fruits, vegetables and meat products or are there options and alternatives to their use? This notion of prevention as part of the risk/benefit equation is fundamental to bringing the scientific community and consuming public to a common basis of understanding.

The topic of this report—*Options and Alternatives in Postharvest Handling and Processing*—addresses that notion of prevention: Changes in food handling or processing practices that *avoid, reduce, or eliminate* the use of potentially toxic substances. The study panel approached its analysis using selected case studies considered representative of problems encountered in the postharvest-processing area. The four case studies were: (1) sulfites on grapes, (2) postharvest fungicides on

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METHYL BROMIDE ON DRIED FRUITS AND NUTS: ISSUES AND ALTERNATIVES

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METHYL BROMIDE ON DRIED FRUITS AND NUTS: ISSUES AND ALTERNATIVES

Introduction

Storage is a critical component in the marketing of dried fruit and nuts since it allows coordination of the peaks of agricultural production with the requirements of consumer demand. However, if products deteriorate during storage, economic losses can arise. Insect infestation is one of the main factors adversely affecting the quality of dried fruits and nuts during storage.

Currently, the industry controls stored product insects on dried fruits and nuts through periodic fumigation with methyl bromide (bromomethane) or phosphine (hydrogen phosphide). The need for insect control during storage is not in question, but there is a reason to explore alternatives to these chemical treatments. In the case of methyl bromide, consumer safety is an issue; for phosphine, resistance by targeted insect species is an emerging problem.

This study looks at current treatment practices, possible alternatives to these practices, and the economic impact of changes in costs or conditions within the dried fruit and nut industries.

Current Industry Practices

There are several different species of insects which feed on the products in storage, and the infestation can occur at any step of the harvest-processing-storage chain. Some of the major pests are navel orangeworm (*Ameylois transitella*), Indianmeal moth (*Plodia interpunctella*), driedfruit beetle (including *Carpophilus hemipterus*), sawtooth grain beetle (*Oryzaephilus surinamensis* (L.)), merchant grain beetle (*O. mercator*), raisin moth (*Cadra figulilella*), and fruit fly (*Drosophila melanogaster*). In addition, codling moth (*Cydia pomonella*), which originates in the orchards, must be controlled to meet quarantine requirements of some importing countries. Some of these pests, like the navel orangeworm, infest the crop in the field and are carried into storage; others, like the Indianmeal moth, may infest the product at any time and thrive in storage conditions. The pests cause direct damage by feeding on the fruits or nuts, and they make the food unsaleable for sanitary and aesthetic reasons. Large scale control measures are necessary

to protect product quality and to satisfy the Food and Drug Administration's (FDA) sanitary regulations for processing plants. The measures used must not be harmful to the commodity, workers, or consumers (Mitchell and Kader, 1985).

Current practice is to fumigate after harvest with either methyl bromide or phosphine at least once, and possibly at regular intervals during storage, depending on the nature of the insect problem. In some cases the product may be kept under fumigation until it is processed. Three functions of such fumigation are: to control insect populations, to prevent feeding damage, and to meet sanitary requirements through reduction or elimination of live insects (Rhodes, 1986). These fumigants are widely used because they: (1) quickly kill all targeted insects when applied correctly; (2) are easy to use; (3) are efficient, treating up to 4-5,000 tons at once; and (4) are inexpensive and don't necessitate large capital expenditures.

Under proper conditions, methyl bromide fumigation usually induces mortality within 24 hours. Phosphine's effectiveness is more temperature dependent, and the average time to mortality is about 48-72 hours (Mitchell and Kader, 1985), although when temperatures drop to 15°C (about 60°F) or below, the required fumigation time with phosphine may be as long as 96 hours.

Both fumigation treatments are applied under sealed storage conditions. The dried fruits or nuts may be in bins which are stacked and sealed with paper to make them airtight, or held in sealed concrete storage rooms and silos. Tablets or pellets containing aluminum phosphide and ammonium carbamate are put into the fumigation stack or chamber (at a rate of about 30 tablets/1000 cubic feet of storage space for raisins) where exposure to the atmosphere causes decomposition of the tablets to form phosphine, ammonia, carbon dioxide and aluminum hydroxide. Methyl bromide gas is blown into the fumigation chamber at a concentration of 1.5 pounds per 1000 cubic feet of storage space for raisins. With either fumigant, the storage chamber is aerated after the desired exposure period to remove the remaining fumigant (Gardner et al., 1982).

Methyl Bromide on Dried Fruits and Nuts:

According to a raisin industry survey (Soderstrom et al., 1984), methyl bromide is typically used in concrete storage chambers and phosphine in laminated paper covered stacks of storage bins.

Dried prunes are sometimes treated with nightly fogging with pyrethrin and piperonyl butoxide in lieu of periodic refumigation. This controls flying insects which infiltrate the storage chamber before they can reproduce, without penetrating commodity packs, but doesn't control immature stages already infesting the commodity. The chemicals break down quickly and don't leave residues on the product (Rhodes, 1986).

Methyl bromide, phosphine, and piperonyl butoxide are toxic to humans, and workers need to follow safety precautions during and after fumigation. In fact, methyl bromide is a "restricted use" pesticide which can only be used under limited conditions and by certified applicators (Gardner et al., 1982). In addition to its use as a stored product fumigant, methyl bromide is also extensively used as a soil fumigant.

Problems Associated with Current Practices

Methyl bromide use as an insecticide is currently under scrutiny, based upon recent reports that it may be carcinogenic in laboratory animals (Mitchell and Kader, 1985). Other laboratory studies have demonstrated mutagenicity (Rounds, 1980) and mitotic recombinations (Mortelmans and Shepherd, 1980) from methyl bromide. Unlike phosphine, which does not leave "appreciable" residues, methyl bromide fumigation produces residues of inorganic bromine which build up and remain on the product (Gardner et al., 1982). The current FDA tolerance limits for residues of inorganic bromine on dried fruits and nuts are 200 and 125 ppm (parts per million), respectively. These standards are currently under review and may be lowered. The industry routinely meets tougher standards for the portion of production which is exported. The residue tolerance limits for some countries importing California dried fruits and nuts are more stringent: 100 ppm in most European countries and 50 ppm in West Germany and Japan. Those using methyl bromide frequently employ techniques such as vacuum extraction or other accelerated airflow methods to speed aeration of the storage chambers and lower residues. Elevated temperatures during fumigation also result in lower residues by allowing the use of less methyl bromide to achieve the same degree of effectiveness.

Packing and storage facility workers are particularly at risk from excessive or repeated exposure to methyl bromide, although when using

correct precautions it is theoretically safe to apply. Methyl bromide is odorless at low concentrations and non-irritating, so if safety precautions fail, workers may unknowingly be exposed. Acute effects range from headaches, dizziness and nausea, to lung edema (swelling) which may result in death. Repeated exposure above safe limits can cause "blurred vision, staggering gait, mental imbalance, and psychosis" (Rowe, 1957, p. 1). These symptoms may or may not disappear over time, depending on the degree of overexposure. Direct exposure to the skin can also cause burns.

Phosphine, the most widely used chemical alternative to methyl bromide is not considered to pose any health risks for consumers since it doesn't leave residues on the fruit. It is toxic to workers if exposed during fumigation, so safety precautions are required, and there is evidence to suggest that one insect species has developed resistance to it (Price, 1980). This resistance problem and the possibility that methyl bromide use could be further restricted or prohibited has stimulated the dried fruit and nut industry to search for nonchemical alternatives as a means for protecting product storability and quality (Mitchell and Kader, 1985; Rhodes, 1986).

Importance of Dried Fruits and Nuts to California Agriculture

Nuts and dried fruits together comprise an important segment of California's agricultural economy and contribute to the state's trade balance. Here we present an economic profile of the industry in California.

California is the major producing state for several types of nuts and dried fruit products including almonds, walnuts, pistachios, raisins, prunes, dried apricots, figs, dates, peaches and pears. Dried fruits and nuts together accounted for over \$1 billion farm level sales, on 864 thousand acres, representing 7 percent of California farm marketings in 1986. Comparisons of farm level with export values suggests that initial processing and storage adds approximately another 80 percent to the per pound value at the time of shipment (California Crop and Livestock Reporting Service, CCLRS, 1987, and USDA, FATUS, 1987).

In 1986, there were 634.4 thousand bearing acres of tree nuts in the state, with an output valued at \$767.6 million (farm level). Almonds represent two-thirds of the tree nut acreage and just over two-thirds of the value (68.9 percent), followed by walnuts with 28.6 percent of the acreage and pistachios with 5 percent.

Dried fruits are also an important California agricultural product class, with roughly 229 thousand acres¹ yielding a value of about \$300 million (farm level) in 1986. By far the largest dried fruit category is raisins which accounts for 57 percent of dried fruit acreage and 61 percent of the farm value, followed by prunes, with 31 percent of the acreage. Other dried fruit products include apricots, figs, dates, peaches, and pears. Most fruits which are dried have other possible market outlets (fresh, canning, crush for wine and juice), so the amount of acreage devoted to the dried use fluctuates annually.

One hundred percent of all U.S. exports of each of these dried fruit and nut products is from California, and in total they represented 25.2 percent of the value of California agricultural exports in 1986. Total dried fruit and nut export sales of \$716.7 million in 1986 were led by almonds (\$420.3 million), followed by raisins (\$109.3 million), walnuts (\$94.9 million) and prunes (\$72.9 million). The majority of California almonds (71.5 percent in 1986) and prunes (60.4 percent) are exported. The export market is a less important, though still major, outlet for California walnuts (32.2 percent exported in 1986), pistachios (23.1 percent), raisins (14.8 percent) and other dried fruits. The leading export destinations vary among products, but overall, countries within the European Economic Community, Japan, Scandinavia, and Canada figure prominently.

California dried fruits and nuts also face some import competition in the U.S. market. The U.S. was a net importer of pistachios, dried apricots and dried figs in 1986, with smaller proportions of dates and raisins also imported.

After a lull during the 1970s, U.S. per capita consumption of dried fruits recovered to 1960s levels during the first half of the 1980s. In particular, raisin consumption increased to 2.1 pounds per capita by 1984; meanwhile consumption of dried figs and prunes declined. U.S. per capita consumption of tree nuts also expanded during the 1980s to 2.3 lbs. in 1985. More than half (54.4 percent) of the expansion between 1965-70 and 1980-85 was due to increased consumption of almonds, with another 32.8 percent attributable to higher walnut consumption (Bunch, 1987).

Farmers responded to increased demand by expanding almond acreage by 38 percent over the 1978-1986 period. Pistachio acreage has risen tenfold (1978-1986) as domestic nuts replaced

imports for consumption. Despite consumption increases, walnut acreage has not expanded. It is difficult to determine acreage response to changes in dried fruit demand because of multiple outlets for these products. For example, some of the increase in raisin grape acreage in the early 1980s is due to increased demand for fresh market Thompson seedless.

Organization and Structure of the Industry

All of these fruits and nuts are perennial crops which must be planted some years before they begin producing on a commercial scale. Once they begin bearing fruit, their total output is spread over decades, so orchards and vineyards represent a major capital investment for the farmer. Switching to an alternate crop is very expensive, and such decisions are presumably based on expectations of long run conditions. This aspect makes producers of tree and vine crops vulnerable to short run fluctuations in market conditions. Growers of tree nuts have few market options. They can sell domestically or on the export market. Within these markets, nuts can be sold for processing or for final consumption. Dried fruit producers have some latitude to switch to the fresh or processed (canned, frozen or crush) markets. On the other hand, fruit driers and nut processing firms have no immediate alternatives.

While some product is sold immediately, the majority of each season's dried fruit and nut output is stored for part of the year. This provides a steady flow onto the market, minimizing the seasonality problems faced in the fresh produce markets and allowing for processing throughout the year. Output can also be carried over to the next marketing year, so stocks can be drawn down in years with poor harvests. This is particularly important for almonds and pistachios, whose output tends to fluctuate due to high and low yields in alternate years.

The structure of the dried fruit and nut industry in California has the hourglass shape typical in agriculture: There are thousands of farmers whose product funnels into a few processing/storage facilities, from which it is eventually distributed to many thousands of intermediate and final market destinations. Much of the capacity at the processor/storage level is accounted for by grower cooperatives such as the Blue Diamond Growers (formerly the California Almond Growers Exchange) and Sun-Diamond Growers of California (raisins, prunes, walnuts, figs and specialty fruits).

¹Using CCLRS *Fruit and Nut Acreage* and *Fruit and Nut Statistics*, the proportion of the respective crops that was dried in 1986 was multiplied by the acreage in that crop and the results were totaled.

Despite concentration at the processor level, which in nonagricultural industries would suggest a high degree of market control, demand and supply uncertainties have led to the establishment of formal organizations of industry members under the auspices of federal or state marketing orders for each of the major products. Within this framework, research, advertising, quality control and sometimes supply control can be pursued. This includes cost sharing for research into and development of solutions to industrywide problems such as the one under investigation here—reliance on chemical fumigants.

Alternatives to Chemical Fumigation

There may well be chemical (pesticide) alternatives to methyl bromide or phosphine fumigation for control of insect infestations during the processing and storage of dried fruits and nuts. However, the difficulty and costs of gaining regulatory approval for new pesticides, the increasing scrutiny of chemical additives for their effects on health and the environment, and the risk of increased insect resistance to chemicals argue for nonchemical means of controlling stored product pests. These considerations have directed much of the recent research effort towards nonchemical alternatives to methyl bromide and/or phosphine. The two currently plausible alternative treatments are controlled atmospheres and irradiation.

Use of Controlled Atmospheres for Insect Disinfestation

Controlled atmosphere disinfestation of stored products is simple in concept: It works by asphyxiating stored product pests. It is appealing on environmental and public health grounds since it does not add any foreign substances to a food product, relying instead on altering concentrations of oxygen, carbon dioxide, and nitrogen, which are already significant components of the earth's atmosphere (Bailey and Banks, 1980). The controlled atmospheres used for insect disinfestation usually involve reducing the oxygen concentration to less than 1 percent and/or increasing the carbon dioxide to well above 10 percent.

Biological and other factors which are crucial to the success of low-oxygen atmospheres for insect control include the following:

- The atmosphere must be easily obtained in sufficient volume to displace the existing atmosphere in bulk storage;
- It must be lethal to storage pests within a reasonable amount of time;

- It must not harm the quality (including taste and odor) or storage life of the treated product; and
- The storage structure must have an adequate gas holding capacity and must be sealable (Storey, 1979; Soderstrom and Brandl, 1985).

Temperature and humidity are also important determinants of the effectiveness of low-oxygen atmosphere (and other) insect control treatments. Other considerations include the equipment required and cost.

Several successful approaches have been identified including:

- Introduction of carbon dioxide into storage chambers;
- Purging the storage chamber with nitrogen from vaporized liquid nitrogen or separated from compressed air using molecular sieve or membrane systems; and
- Generation of low oxygen atmospheres by burning oxygen (Gardner et al., 1982).

To qualify for commercial adoption, a method must be shown to be effective against targeted insect populations, be safe to apply, leave no harmful or distasteful residues, have no adverse effect on storage life, and be cost effective. The choice of a particular controlled atmospheric mixture is dependent on many variables including: type of storage facility; commodity to be treated; volume, weight, moisture content and temperature of the product; the pest species to be controlled including the life stages (i.e. egg, larva, pupa, adult) and/or age distribution; the availability of gases or generators; and the time interval required and available to achieve insect control (Davis and Jay, 1977).

Because the processing and storage facilities for nuts and grains in California are not located near sources of inexpensive liquid nitrogen or carbon dioxide, most of the research on controlled atmospheric disinfestation of nuts and dried fruits has focused on the effectiveness and feasibility of on-site low oxygen atmospheric generators.

How on-site low oxygen atmospheric generators work

Portable atmospheric generators burn natural gas or propane in air at specific ratios to produce atmospheres with desired gas composition. Undesirable nitrogen oxide is avoided through water cooling. The low oxygen atmosphere passes

through a heat exchanger and is further cooled through refrigeration, which extracts moisture to achieve the desired relative humidity. Finally it is filtered through activated charcoal to eliminate oil, unburned hydrocarbons and odors before piping into the storage chamber (Soderstrom et al., 1984).

The amount of time required to achieve the desired atmospheric mixture is dependent on the capacity of the chamber or stack and the purge rate, but can generally be accomplished in one to two days. Once the atmosphere is achieved, it must be maintained through continued generation for a specified number of hours, depending on a host of conditions. Since maintenance requires less generated atmosphere than the initial purging, the process can be set up sequentially, with a new stack or chamber beginning the purging process when the previous stack/chamber reaches the maintenance stage. At the end of the maintenance control period, the storage area is either "purged" or is gradually allowed to return to a normal atmospheric mix. Soderstrom et al. (1984, p. 459) found that "within a month's time, 25 stacks [of raisin bins] could be sequentially purged and maintained with a single 283 m³/h generator."

To make efficient use of the heat generated through this energy-intensive process, it is possible to employ co-generation techniques whereby heat or hot water is captured for use elsewhere in the plant using a heat (or steam) recovery system. The Pacific Gas and Electric company estimates steam generation recovery efficiency at more than 80 percent (Soderstrom et al., 1984).

Their Cost

Estimated costs at 1984 prices for six months worth of insect control for raisins varied from 0.44¢/pound with 90 percent heat recovery to 0.48¢/pound without heat recovery. A doubling of natural gas prices made little difference to the per pound cost in the 90 percent heat recovery case, but raised the cost in the no recovery case to 0.54¢/pound (Soderstrom et al., 1984:460-1). The 1980 cost comparisons for three controlled atmosphere systems for raisins and two chemical treatments are (Gardner et al., 1982):

0.38¢/lb.	Methyl bromide
0.49¢/lb.	Phosphine
0.44-0.48¢/lb.	Low oxygen atmospheric generators
0.81¢/lb.	Trucked liquid nitrogen, controlled atmosphere
0.74¢/lb.	On site liquid nitrogen, controlled atmosphere

Recently new technologies for on-site nitrogen production from compressed air using molecular sieve or membrane systems have been developed. These systems are competitive with other controlled atmosphere systems in terms of capital costs, but their operation and maintenance costs are lower.

Effectiveness

Storey (1980) reports that the atmosphere generated by the on-site combustion method is lethal to the insects which commonly infest stored products at all life stages, although the time-temperature-atmospheric composition combinations vary among different insects and at various stages in their life cycles. Soderstrom and Brandl (1985) discovered differences in response to relative humidity and low oxygen levels between a pest which infests commodities in the field (humidity sensitive) and a storage infesting pest (low oxygen sensitive). Soderstrom and Brandl (1984) report times ranging from 48 to 120 hours for 100 percent mortality of different insects at 27° C (80.6° F), and from three days to more than 14 days at 16°C (60.8° F). At 27°, nearly all species tested were killed (100 percent mortality) after 60 hours, whereas at 16°C all but one were killed after five days. The exception is *D. melanogaster*, a type of fruit fly which exhibits significantly longer kill times at both temperatures studied. In general, Storey (1980) showed that even with sublethal exposures to a controlled atmosphere environment, surviving insects often suffer abnormalities in form or structure and other physiological damage which interfere with normal development.

Safety and Product Quality

Controlled atmosphere treatments have several safety advantages over chemical treatments: They leave no potentially toxic residues on the product; they are nonpolluting; and when used correctly they are theoretically safer to apply since they don't involve handling of toxic substances (Gardner et al., 1982). They also have been shown to be effective in maintaining product quality as long as the controlled atmosphere conditions are continued during storage. A study of raisins stored in a low oxygen controlled atmosphere for one year found them to be "equal or superior in flavor quality and acceptability to similar samples stored in normal atmosphere for the same length of time" (Guadagni, Storey and Soderstrom, 1978). Bulk almonds and other dried products may deteriorate more slowly under controlled atmosphere conditions (low oxygen and/or high carbon dioxide) than under conventional conditions (Mitchell and Kader, 1985).

Disadvantages

Under some conditions the longer exposure time required for controlled atmosphere treatments than for chemical fumigation can be disadvantageous (Brandl, Soderstrom, and Schreiber, 1983). For commodities such as early season walnuts and almonds which are intended for shipment without storage, controlled atmosphere treatment increases the time they must be held at the processing facility. In general, longer duration of treatment for insect disinfestation implies a need for increased capacity of suitable treatment and/or storage chambers.

There is also a potential risk of increased tolerance over time to low oxygen and/or high carbon dioxide atmospheres by stored product pests, although the risk is considered to be less significant than for chemical treatments (Bailey and Banks, 1980).

Irradiation Disinfestation of Nuts and Dried Fruits

Irradiation of nuts and dried fruits has been investigated in a comprehensive study sponsored by the U.S. Department of Energy, California dried fruit and nut marketing orders and the USDA Agricultural Research Service (Rhodes, 1986). The FDA approved irradiation levels up to 1 kilogray (100 kilorads) on food in 1986. Some key factors in the potential for commercial use of irradiation to disinfest dried fruits and nuts are:

- (1) Exposure to radiation at allowable levels must be effective against the problem pest species.
- (2) The exposure level needed to kill the insect pests must not harm the fruit or nut product's quality (appearance, flavor, nutritive value) or storage life.
- (3) The procedure must be safe to workers, consumers and the environment.
- (4) Irradiation disinfestation must be cost effective, including any adverse demand effects from consumer concern about the process.

Each of these aspects is considered in turn following a brief description of how the method works.²

How it works

When living organisms such as insects are exposed to ionizing radiation (from gamma rays or electrons), chemical changes are induced at the molecular level. Sufficient exposure impairs metabolic reactions. Insects are less sensitive to radiation

exposure than humans, but more sensitive than fungi, molds, bacteria or viruses.

The key to successful disinfestation is to subject the commodity to a dose sufficiently high to kill insects without causing unwanted changes in its texture, color or flavor (organoleptic changes). For food products, conveyor belts typically move the items to be treated through the irradiator. Depending on the energy levels of the radiation source, the product density and the desired dose, the configuration (including conveyor speed) can be designed to control total absorbed radiation.

Effectiveness

Tests using a cesium-137 irradiator to treat almonds, raisins and walnuts infested with one or more of three common pests (Indianmeal moth, navel orangeworm and dried fruit beetle) at relevant life stages were conducted to determine the doses needed to effect insect control. The researchers found the most "practical" dose for a "sufficient" level of insect control to be 0.30 kilogray (kGy) [30 kilorad (KR)], indicating an applied dose between 0.45 and 0.60 kGy (45 to 60 KR). For some insects (in some developmental stages) this dose caused sterility rather than death; complete mortality of irradiated navel orangeworm and Indianmeal moth larvae can take as long as two months. Nonetheless, it was stated that the insect control of these pests would be "comparable" to conventional methyl bromide fumigation.

Separate tests on codling moth disinfestation of walnuts using a cobalt-60 irradiator suggest that 0.188 kGy (18.8 KR) is sufficient to completely halt infestations (99.9968 percent mortality), with somewhat lower doses preventing emergence of normal adult moths.

Product quality

Unlike fresh produce items which are easily damaged by irradiation treatments, direct product damage (physiological changes) from irradiation of dried fruits and tree nuts (with a moisture content of less than 10 percent) is unlikely to occur. However, "free radical oxidation reactions" due to irradiation may speed rancidity, especially in tree nuts with high levels of unsaturated fatty acids.

Three nut products (almonds, walnuts and pistachios) and two dried fruit products (raisins and prunes) were tested for immediate and delayed eating quality effects following irradiation with 0.15 to 0.90 kGy (15 to 90 KR) from cesium-137. In each

²Unless stated otherwise, all information in this section is from Rhodes (1986).

case, taste tests included untreated control samples. One conclusion was that there were no "immediate significant differences" in quality following irradiation in any of the products. After storage, different effects were observed for the various items: The quality of walnuts did suffer, particularly at the higher dosages, while almond quality scores were unaffected; quality deterioration was observed in some raisin samples for some radiation levels (0.15 kGy and 0.69 kGy = 15 and 69 KR) but not for others (0.30 and 0.90 kGy = 30 and 90 KR); all pistachio samples remained acceptable, although flavor scores dropped for some samples receiving high (0.60 kGy = 60 KR) doses; the flavor of irradiated prunes was unaffected.

The overall recommendation based on these findings is that dried fruits and nuts be irradiated at < 0.60 kGy (60 KR) for insect disinfestation, with 0.30 to 0.45 kGy (30 to 45 KR) the preferred level.

Safety

At the levels suggested for stored product pest disinfestation of dried fruits and tree nuts, it has been established to the satisfaction of the FDA that irradiated foods are safe for the consumer (Mitchell and Kader, 1985). Using approved methods, it is impossible to make the foods radioactive (Rhodes, 1986).

There are a number of different configurations for food irradiators, and all are designed to shield workers from exposure to radiation. The use of conveyor belts means that humans do not enter the irradiator while it is in operation, so worker safety should not be a problem.

Irradiators utilizing radioisotopes (cesium-137 or cobalt-60) do involve movement of radioactive materials, and these materials maintain their radioactivity even when the machines are not in use. Machine generated electron beam or x-ray machines, however, do not involve transportation of radioactive materials, so when properly constructed, should not be considered an environmental hazard, and may not require as much shielding as radioisotope irradiators.

Food irradiators are fundamentally different from nuclear power plants or nuclear weapons and do not pose significant environmental or public safety risks during operation if they are constructed and operated properly. Flaws in design, construction, or operation introduce a risk of exposure to workers, in addition to any transportation/handling problems for the radioactive materials used in some of the irradiators.

Cost effectiveness

Because of several factors including volume of product to be treated and seasonality (which implies unused capacity much of the year), the unit cost of irradiation disinfestation of dried fruits and tree nuts was found to significantly exceed those of alternative treatments (chemical fumigants and controlled atmosphere)—even under the most favorable conditions of operation. For example, researchers found that "... even at half of the ... estimated cost, irradiation disinfestation of newly harvested almonds and walnuts still costs five to 10 times as much as current fumigation practice for even the largest processors" (Rhodes, 1986, p. 213).

Further, the capital investment in an irradiation facility is so high that it may be prohibitive for smaller operators, and would lock in those who made the investment to the particular technology for an extended period of time. With a 20 year amortization, the fixed costs of owning and operating an irradiator were estimated to be in the \$500,000/yr range (Vail et al., 1987).

Surveys have found some consumer resistance in the United States to the idea of irradiated food (Morrison and Roberts, 1985). The process has gained better acceptance in other countries, so negative effects on consumer demand in the domestic market would probably not be matched in export markets. For bulk sales of dried fruits and nuts domestically, consumer labeling indicating the radiation treatment might pose some logistics problems.

General comments

Irradiation disinfestation of California dried fruits and tree nuts has been demonstrated to be a technologically feasible option in terms of its efficacy, safety, and product quality results. Under current conditions it does not meet economic feasibility criteria when compared with available alternatives, although this could change if some of the chemical alternatives were to become unavailable. A final set of disadvantages is that live (though damaged) insects may remain in the products for up to two months—a distinct liability for product marketing; and only limited protection is afforded against reinfestation via the mating of sterile insects with new entrants. Current regulations do not allow repeated irradiation.

Other Possible Methods

Freezing of stored dried fruits and nuts is technically feasible for control of pest infestation, but is not economically feasible on a large scale, although it is practical for home use. Some research

has been conducted on the use of heat to kill insects on raisins. A vapor heat treatment has been developed in Japan which forces vapor through the commodity, heating it to 38-50°C (100-120°F) for up to eight hours. Disadvantages of this method are that it is expensive and may damage the product, especially nuts with high oil contents.

Conclusion

Storage is a necessary component of the dried fruit and nut industry as it is currently organized. Given field infestation by some pests (e.g., the codling moth) and the inevitable infiltration of storage facilities by others, some form of insect control program is essential.

At present the industry is heavily reliant on two chemical insecticides, methyl bromide and phosphine, with some use in the prune industry of pyrethrin fogging. The continued use of both of the major fumigants is in jeopardy: methyl bromide because of the suspected carcinogenicity of residues and other deleterious health effects; and phosphine due to the development of resistance in one pest specie. Pyrethrin fogging is not used for initial disinfestation, but is a preventative treatment against reinfestation of flying insects.

Unless alternatives are adopted, the withdrawal of methyl bromide and increased insect tolerance to phosphine could be devastating to California's dried fruit and nut industry, with consequences for the state's economy as a whole. Dried fruits and nuts are important to California's agricultural economy, and can be very important to local areas.³ Economic losses would not be confined to this industry, and effects in terms of lost output, wages and tax revenues could be expected to percolate throughout the state. Using factors estimated for California (Goldman and O'Regan, 1983), for every 1 percent decline in marketings (farm level), state income will decline by \$13.8 million at 1986 prices.

Fortunately there are two major types of treatments which are technically feasible as substitutes for the currently used pesticides: controlled atmospheres and irradiation disinfestation. Comparative cost studies of these methods, neither of which is currently in commercial use in the industry, indicate that one method of controlled atmosphere

generation, use of on-site low oxygen atmosphere generators, is competitive with chemical disinfestation on a cost basis, with per pound treatment costs falling between those of methyl bromide and phosphine. It may, however, require construction of additional storage capacity given the length of time involved with each treatment. Sealing of existing concrete or metal storage chambers is estimated to cost about \$5 per 100 cubic feet, with an annual maintenance cost of 17.5 cents per 100 cubic feet of storage space; average costs to build new storage chambers are \$1 per cubic foot; covering stacked bins (of dried fruits or nuts) costs about 79 cents per ton per year; and requirements for additional in-plant fumigation space for packing to order or immediate shipment could be as much as six times existing capacity (Rhodes, 1986). The other method, irradiation, was not found to be cost competitive with either the current chemical fumigants or with controlled atmosphere disinfestation.

Demand in the domestic market and in major foreign importing countries for California almonds (Bushnell and King, 1986) and natural Thompson seedless raisins (Nuckton, French, and King, 1988) has been thoroughly studied, with statistical evidence indicating in both cases that demand for these products is not very sensitive to price changes. Less is known about the pass-through of processor cost changes to retail prices for dried fruits and nuts, but according to available cost studies, insect disinfestation (whether with chemical fumigation or, prospectively, with controlled atmospheres) represents only a small fraction of processor's total costs. The coincidence of these two aspects implies that small per pound changes in processor costs due to a shift in disinfestation methods (even if fully passed through to consumer prices) would not appreciably change product demand or industry size.

However, if an industrywide shift to irradiation disinfestation occurred, some changes could be expected: Processor costs would increase some, triggering a small but noticeable reduction in sales if cost increases were passed along in prices; a further drop in demand could occur due to consumer hesitations about irradiation; and since efficiency is related to size, an already concentrated market segment could become even more centralized at the processor/packer level.

³For example, all of the state's Thompson Seedless raisins are grown within 75 miles of Fresno (Nuckton, French, and King, 1988).

Summary Table. Options and alternatives for insect disinfection of dried fruits and nuts.

CHARACTERISTIC	Chemical Fumigation:		Alternatives:	
	Methyl Bromide	Phosphine	Controlled Atmospheres (low O ₂ &/or high CO ₂)	Irradiation
Treatment duration	up to 24 hrs + purging/aeration	2-3 days + purging/aeration	3-7 days at 27°C (80.6°F) +purging/aeration	relatively short exposures
Effectiveness	100% kill rate.	100% kill rate.	Can achieve 100% kill rate.	Some larvae may survive up to 2 mos.
Protection against reinfestation	NONE, unless combined w/ nightly pyrethrin or Vapona fogs; requires refumigation.	Same as Methyl bromide.	NONE. Requires repeated treatments or continuous maintenance of the CA.	Some limited protection due to possible presence of sterilized males. Reirradiation not allowed.
Quality of product	Good	Good	Good—may be better than with chemical fumigation.	Good at recommended levels.
Health effects: Workers	Highly toxic if directly exposed.	Highly toxic if directly exposed.	Presumed safer than chemical fumigation.	Safe if facility properly shielded and operated.
Consumers	Methyl bromide leaves residues which may be carcinogenic.	No known hazards.	No known hazards.	No known hazards.
Environmental effect	May involve release of toxic chemicals into environment.	May involve release of toxic chemicals into environment.	Does not pollute environment; somewhat energy-intensive; good potential for co-generation.	Some versions involve transportation & use of radioactive materials.
Approximate annual cost of treatment (cents/lb):				
Almonds	-	<0.1¢	(low O ₂ generator) 0.1–0.25¢	.36–1.0¢
Walnuts	<0.1 ¢	-	0.25–0.5¢	.42–3.6¢
Raisins	<0.3¢	0.6¢	0.5¢	.43–1.4¢
Prunes	<0.1¢	-	0.5¢	.43–2.1¢
Other considerations	Requires little capital investment; same per lb cost for small and large operators; could be withdrawn from market or require Prop. 65 identification in California	Has some potential insect resistance problems; same per lb cost for any size operator.	Longer kill times could require construction of additional treatment chambers at some locations or alteration of existing storage facilities to make them gas-tight. Elevated temperatures may affect shelf life of nuts.	Requires large capital investment; more economical for large operators; requires labeling of treated product w/ potential for consumer resistance.

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TO: Katie McGinty
FROM: Cornelia Burr
DATE: January 29, 1992
RE: CAB92.020

Here are a few comments to accompany the draft for the phase out language:

(1) The language in the instructions concerning production or consumption was changed to "manufactured, processed, or used" to key to existing definitions under the Emergency Planning and Community Right-to-Know Act of 1986. This meets your intent to cover the full spectrum of handling the chemical. Consumption could be read to imply that the chemical is used up. A broader range of possibilities exists.

(2). The exception in the instructions looks as if you intended a waiver process, whereby the Administrator makes a determination whether or not to allow a use or activity. The instructions were so broadly written as to allow for a loophole you do not intend. Each specific use may not directly destroy the stratospheric ozone layer. The aggregate effect of such uses could have a significant effect. Therefore, this draft is written in terms of whether the use contributes to the destruction of the stratospheric ozone layer, rather than whether the use directly destroys it.

Please do not hesitate to call if you have any questions. I marked this draft as a discussion draft so that you may review it to see if it meets your intent.

102D CONGRESS
2D SESSION

S. _____

IN THE SENATE OF THE UNITED STATES

Mr. GORE introduced the following bill; which was read twice and referred to
the Committee on _____

A BILL

1 *Be it enacted by the Senate and House of Rep-*
2 *resentatives of the United States of America in Congress*
3 *assembled,*

4 **SECTION. 1.**

5 The Congress finds that:

6 (1) Ozone in the stratospheric layer of the at-
7 mosphere (hereafter referred to as "stratospheric
8 ozone") protects all living things from harmful ultra-
9 violet radiation from the sun, and has been signifi-
10 cantly depleted over almost every geographic area of
11 the Earth because of the effect of air pollution con-
12 taining certain halogenated chemicals.

1 (2) Recently the International Ozone Trends
2 Scientific Assessment Panel of the United Nations
3 Environment Program and the World Meteorological
4 Organization reported that the depletion of strato-
5 spheric ozone is occurring at a rate that is twice the
6 rate that had previously been measured or predicted,
7 and that even during summer months stratospheric
8 ozone continues to be significantly depleted.

9 (4) The findings described in paragraphs (1)
10 through (3) necessitate a reappraisal of national and
11 international policies concerning the control of
12 chemicals that contribute to the depletion of the
13 stratospheric ozone.

14 (5) Bromine in the stratospheric layer of the at-
15 mosphere (hereafter referred to as "stratospheric
16 bromine") is estimated to be 30 to 120 times more
17 efficient than chlorine with respect to causing the
18 destruction of stratospheric ozone, and the major
19 source of stratospheric bromine is methyl bromide.

20 (6) Methyl bromide is not currently regulated
21 under the Clean Air Act or the Act entitled "An act
22 to amend the Clear Air Act to provide for the estab-
23 lishment of health protective national ambient air
24 quality standards, and for other purposes" (com-

1 monly known as the Clean Air Act Amendments of
2 1990).

3 (7) Reductions in emissions of methyl bromide
4 would contribute effectively to the restoration of
5 ozone in the stratospheric layer.

6 **SEC. 2. PHASE-OUT OF METHYL BROMIDE.**

7 (a) IN GENERAL.—Title VI of the Clean Air Act (42
8 U.S.C. 7671 et seq.) is amended by adding at the end
9 of the title the following new section:

10 “PHASE-OUT OF METHYL BROMIDE

11 “SEC. 619 (a) IN GENERAL.—Except as provided in
12 subsection (b), it shall be unlawful to manufacture, proc-
13 ess, or use methyl bromide, or import methyl bromide into
14 the United States for processing or use.

15 “(b) WAIVERS.—(1) The Administrator may waive
16 the requirements of subsection (a), if—

17 “(A) a person submits an application (in such
18 form and manner as the Administrator shall pre-
19 scribe by regulation) for a waiver under this sub-
20 section to the Administrator; and

21 “(B) on the basis of the information in the ap-
22 plication, the Administrator determines that the use
23 of the methyl bromide that is the subject of the
24 waiver will not contribute to the destruction of strat-
25 ospheric ozone.

1 “(2) The Administrator may attach such conditions to
2 a waiver under this subsection as the Administrator deter-
3 mines to be appropriate.

4 “(c) MANUFACTURE, PROCESS, DEFINED.—For the
5 purposes of this section—

6 “(1) the term ‘manufacture’ has the meaning
7 given by section 313(b)(1)(C)(i) of the Emergency
8 Planning and Community Right-To-Know Act of
9 1986 (42 U.S.C. 11023(b)(1)(C)(i)); and

10 (2) the term ‘process’ has the meaning given by
11 section 313(b)(1)(C)(ii) of such Act (42. U.S.C.
12 11023(b)(1)(C)(ii)).

13 “(d) EFFECTIVE DATE.—The provisions of this sec-
14 tion shall become effective on January 1, 1996.”.

METHYL BROMIDE

PURPOSE: To provide for the phase-out of production and consumption of methyl bromide.

FINDINGS: The Congress finds the following:

The stratospheric ozone layer which protects all living things from harmful ultraviolet radiation from the sun has been significantly depleted in nearly all areas of the globe due to the action of halogenated chemicals.

Recently, the United Nations/World Meteorological Organization International Ozone Trends Scientific Assessment Panel reported that the depletion is occurring twice as rapidly as had previously been measured or predicted; is persisting into the warmer months of the year, and has reached significant levels even in summer.

These findings necessitate a reappraisal of both domestic and international policy on the control of ozone destroying chemicals.

Stratospheric bromine is 30 - 120 times more efficient than stratospheric chlorine in destroying ozone on a per atom basis and the major source of stratospheric bromine is methyl bromide.

Methyl bromide is not currently regulated under the Clean Air Act amendment of 1990.

Reductions in emissions of methyl bromide would contribute effectively to the restoration of the ozone layer.

PHASE-OUT: Effective January 1, 1996, it shall be unlawful for any person to produce or consume, or import for consumption, methyl bromide in the United States, except where such person can be demonstrated that any such production or consumption does not result in destruction of the stratospheric ozone layer.

METHYL BROMIDE

PURPOSE: To provide for the phase-out of production and consumption of methyl bromide.

FINDINGS: The Congress finds the following:

The stratospheric ozone layer which protects all living things from harmful ultraviolet radiation from the sun has been significantly depleted in nearly all areas of the globe due to the action of halogenated chemicals.

Recently, the United Nations/World Meteorological Organization International Ozone Trends Scientific Assessment Panel reported that the depletion is occurring twice as rapidly as had previously been measured or predicted; is persisting into the warmer months of the year, and has reached significant levels even in summer.

These findings necessitate a reappraisal of both domestic and international policy on the control of ozone destroying chemicals.

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Reductions in emissions of methyl bromide would contribute effectively to the restoration of the ozone layer.

PHASE-OUT: Effective January 1, 1996, it shall be unlawful for any person to produce or consume, or import for consumption, methyl bromide in the United States, except where such person can be demonstrated that any such production or consumption does not result in destruction of the stratospheric ozone layer.

how per a source?
alga?
production?

**A Literature Survey of
Atmospheric Methyl Bromide
and Stratospheric Ozone**

Prepared for

**The Methyl Bromide Industry Panel
Chemical Manufacturers Association**

by

N.D. Sze and M.K.W. Ko

November 14, 1991

**Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, MA 02139**

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APPENDICES

- APPENDIX A: Definition of ozone depletion potential (ODP), chlorine and bromine loadings, atmospheric lifetime
- APPENDIX B: AER Presentation before MBGC on May 14, 1991
- APPENDIX C: Aerodyne report on kinetic data.
- APPENDIX D: AER one-dimensional photochemical transport model

1. Executive Summary

This report summarizes a review of published information, particularly with regard to observational data for methyl bromide (CH_3Br) and its atmospheric chemistry and budgets (sources and sinks). The measured tropospheric abundance reported by several groups ranges from 10 to 20 pptv (1 pptv = 1 part in 10^{12} by volume) or corresponds to a global burden of 160 to 320 kilotons. With this level of abundance, CH_3Br is currently the dominant form of organic bromine of importance to the stratospheric bromine budget. It remains unclear, however, whether the range in the observed abundances reflects the true temporal and spatial variations or differences in measurement techniques or calibrations. Intercalibration of data between various measurement groups will help to resolve this issue.

One of the pertinent issues concerns the origins of atmospheric CH_3Br . Despite WMO reports (1985; 1989) that CH_3Br is predominantly anthropogenic, the present study reveals considerable controversy on this issue. We note that there is evidence suggesting that ocean may be the major, if not the dominant, source of atmospheric CH_3Br . In order to resolve this important issue, the following are required:

- (a) information on the global production/emission of CH_3Br for the past ~10 years;
- (b) accurate determination of the global removal rate or the atmospheric lifetime of CH_3Br ; 1-2 yrs?
- (c) systematic and coordinated measurements of CH_3Br at selected sites in the next few years;
- (d) model simulations of time evolution of atmospheric CH_3Br abundance based on our best knowledge of (a) and (b);
- (e) comparison of models with observed abundance of CH_3Br .

The atmospheric lifetime is a calculable quantity based on our knowledge of removal mechanisms for CH_3Br . If we assume that tropospheric OH is the principal sink for CH_3Br , we calculate a lifetime of 1.6 years. Because of the uncertainty in both the mean concentration of tropospheric OH and the rate constant for the reaction of OH with CH_3Br , we estimate that the lifetime has an uncertainty range of about a factor of 4. An accurate measurement of the rate constant for the reaction of OH with CH_3Br will help narrow this uncertainty range. Other removal processes appear to be unimportant except possibly for the reaction with atomic chlorine. The relatively short lifetime of CH_3Br (~1.6 year as estimated by models) makes it possible to experimentally determine its lifetime over the next few years.

lifetime
6.4 yrs
unc - 6.4 yrs

Accurate determination of atmospheric lifetime is not only important for quantifying the atmospheric budget for CH_3Br but is also crucial for calculating the ozone depletion potential (ODP). Scientists, and policy makers, rely on computer modeling to assess the impact of chemicals on stratospheric ozone depletion. The concept of ODP was introduced to characterize the relative potential of a trace gas to deplete stratospheric ozone (Appendix A). Using the AER one-dimensional model, we calculate a value of 0.6 for the ODP of CH_3Br with an uncertainty range of at least a factor of 10. The large uncertainty in ODP is due, in part, to the uncertainty in lifetime and, in part, to the uncertainties in stratospheric bromine chemistry. Our theoretical and experimental knowledge about atmospheric bromine is less well-developed than atmospheric chlorine. Thus, model predictions concerning bromine impact should be viewed with caution. The calculated ODP values depend on the model calculated concentration of BrO . Although model predictions of BrO appear to be consistent with *in situ* measurements (Brune et al., 1988), measurements of HBr (Park et al., 1989) indicate that the concentration of HBr may be 20 times larger than model predictions. Interpretation of the results is not straight-forward. However, when taken at face value, they appear to be in serious conflict with predicted total bromine loading and the BrO/HBr ratio. This apparent discrepancy implies that there may be a missing source for stratospheric bromine, and/or that the chemical scheme in the model is incomplete or that the kinetic data used is in error. Among other possibilities, a revised chemistry scheme that predicts a larger concentration of HBr in harmony with the Park et al. measurements could lead to a downward revision of the ODPs of all brominated species. Current models need to be improved with kinetics data governing certain key reactions and reliable data on emission rates, and their predictions will have to be confirmed by atmospheric observations (e.g., CH_3Br , HBr , BrO).

Park
? - what observational data drive here?

2. Introduction

On February 21, 1991, Dr. Kurylo of NASA briefed the Methyl Bromide Global Coalition (MBGC) of the potential contribution of CH_3Br to stratospheric ozone loss. He also mentioned that the current view of CH_3Br is that about 50-75% of emissions may be of anthropogenic origin (WMO, 1985; 1989). In response to Dr. Kurylo's briefing, members of the MBGC, CMA and AER staff identified the following issues pertinent to establishing an adequate scientific basis for possible future policy decisions relating to the atmospheric release of CH_3Br :

1. What are the atmospheric budgets/origins of CH_3Br ?
2. How good are the observational data for atmospheric CH_3Br , particularly with regard to defining a secular trend?

3. What is the ODP value and the uncertainty range calculated for CH₃Br?
4. How robust is the tropospheric chemistry of CH₃Br and the stratospheric bromine chemistry?

After a series of discussions with members of MBGC, AER was asked to undertake a highly focussed project to provide a partial assessment of the above issues. The project consists of two main tasks:

Task I: Literature review for data on:

- a) Laboratory kinetics
- b) Field measurements
- c) Removal mechanisms

Task II: Modeling

- a) Calculation of atmospheric lifetime
- b) Calculation of ODP

Regarding Task I(a), AER engaged the services of Aerodyne Research, Inc. (ARI), a firm specializing in laboratory kinetic measurements, to critically review the kinetic data on CH₃Br and selective bromine mechanisms in the stratosphere. The results, to be discussed in section 3.2, are based on a report prepared by ARI which is included as Appendix C of this report.

A report presented to MBGC details the findings of Tasks I and II presented in sections 3 and 4, respectively (see Appendix B for a complete set of viewgraphs). The report also contains four appendices which are intended to describe and clarify certain definitions, approaches, and methodology adopted in this study.

3. Atmospheric Budget of CH₃Br

3.1 Sources of CH₃Br

Although the WMO reports (1985; 1989) stated that 50-75% of atmospheric methyl bromide (CH₃Br) may be of anthropogenic origin, the underlying reasons and evidence leading to this conclusion were not clearly established. In what follows, we review past published work regarding atmospheric sources of CH₃Br.

Wofsy et al. (1975) estimated a source of 76 kiloton yr⁻¹ for CH₃Br based on a tropospheric concentration of 10 pptv (1 pptv = 1 part in 10¹² by volume) and the removal rate as set by the reaction OH + CH₃Br. This source, they noted, exceeds Klingman's (Klingman, 1974) estimate for the total amount of CH₃Br produced industrially in 1974 by about a factor of 4. They contacted Plonka of Dow Chemical, who is of the opinion that only 25% of the industrial bromine is released to the atmosphere, mainly as a by-product of fumigation. Based on this, Wofsy et al. concluded that CH₃Br is most likely of natural origin, with the sea providing 75-95% of atmospheric CH₃Br. A later paper by Singh et al. (1983) who measured CH₃Br in and over the Eastern Pacific Ocean essentially confirms this view. Their measurements indicate that ocean water over the eastern Pacific (40°N to 32°S latitude) is approximately 250% supersaturated with CH₃Br and they estimate an oceanic source strength of 300 kiloton yr⁻¹, almost a factor of 4 larger than Wofsy et al.'s estimates. Note that Singh et al.'s estimate of the source strength is based on a higher tropospheric concentration of CH₃Br of 23 pptv.

*Wofsy et al. have
not been
measured*

* Penkett et al. (1985), however, argued that the predominant source of CH₃Br in the atmosphere is anthropogenic rather than natural. They apparently arrived at this conclusion by noting that annual production of CH₃Br in 1972 was estimated to be about 300 kiloton yr⁻¹. And they further assumed, following Wofsy et al.'s estimates, that about 1/4 of the production (75 kilotons) was emitted to the atmosphere. Using the rate for the reaction OH + CH₃Br, an estimated OH concentration of $4 \times 10^5 \text{ cm}^{-3}$ and a CH₃Br global abundance of 226 kilotons (or ~14 pptv) inferred from their measurements, Penkett et al. estimated a total emission (i.e., natural and anthropogenic) of 90 kilotons yr⁻¹, which, along with estimates of industrial release, would imply an anthropogenic contribution of about 83 percent. Penkett et al.'s estimate of the 1972 CH₃Br industrial production of 300 kiloton yr⁻¹ was based on information from Wofsy et al (1975) which actually stated that the total (natural and anthropogenic) source is 75 kilotons/year. This issue, which is fundamental to the understanding of the origins and atmospheric budgets of

CH₃Br, and may have important implications for formulating any future control strategies, must be resolved by scientific methods.

We summarize the source estimates by various investigators in Table (1).

3.2 Removal processes

According to present ideas (Wofsy et al., 1975; Yung et al., 1980; Cicerone, 1981), CH₃Br is principally removed by:



in the troposphere.

The rate constant for (1) is given by

$$k = 7.6 \times 10^{-13} \exp(-890/T \pm 200/T).$$

This rate is uncertain by a factor of about 2 at a mean tropospheric temperature of 278°K (see Appendix C). A re-measurement of this rate constant is important for a more accurate determination of the atmospheric lifetime of CH₃Br. Using the AER one-dimensional model (see Appendix D), the calculated lifetime for CH₃Br due to (1) is 1.6 years. The same model calculates a lifetime for CH₃CCl₃ of about 6.5 years, in good agreement with that derived from the atmospheric lifetime experiment (Prinn et al., 1987).

Other known removal processes include stratospheric photolysis,



The uv-absorption cross-sections appear to be quite well determined. Since photolysis is restricted to the stratosphere where the region consists of about 10% of total air mass, (2) cannot be an important sink for CH₃Br, although it can still affect the calculated ODP value which partly depends on the rate at which bromine atoms are released from stratospheric CH₃Br. We calculate a lifetime of 50 years due to (2).

Methyl bromide also reacts with NO₃,



The rate constant for (3) is about $2 - 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ at 298°K. We calculated a lifetime for CH_3Br due to (3) of about 40 years or longer. Thus, (3) is unlikely to be an important sink for CH_3Br unless our model significantly underestimates the concentration of tropospheric NO_3 .

Recently, work by Keene et al. (1990) suggests that atomic chlorine may be released heterogeneously from seasalt (NaCl) in the marine boundary layer. Their model predicts concentrations of atomic chlorine approaching that of OH within the marine boundary layer. If we adopt Keene et al's predicted Cl concentration, then the reaction of Cl with CH_3Br



would yield a lifetime of about 1-3 years. The rate constant for (4) has been experimentally studied by Tschuikow-Roux et al. (1988) and is about a factor of 10 faster than that for (1). However, it should be noted that there are considerable uncertainties in modeling tropospheric Cl . The proposed mechanism (Keene et al., 1990) of generating large quantities of reactive chlorine from seasalt is quite speculative and substantially more experimental and modeling work is needed to ascertain its role in the removal of CH_3Br and other halomethanes and haloethanes, including the HCFCs, HFCs and CHF_2Br , a proposed substitute for halons (Talukdar et al., 1991).

3.3 Atmospheric measurements and trends

Atmospheric measurements of CH_3Br have been reported by several groups. In table (2), we summarize their measurements according to location, year, and measurement period. Note that most of the measurements of CH_3Br in remote regions indicate concentrations of around 10-15 pptv except for Singh et al. (1983) who reported an average concentration of 23 pptv. It is not clear whether the difference is due to differences in experimental techniques, calibrations or if it reflects real spatial and temporal variations of CH_3Br . Cicerone et al. (1988) reported that there is no clear evidence of a temporal trend although a trend as large as 0.1 ppt/month cannot be ruled out. Salawitch et al. (1988) have reviewed CH_3Br data and argued that CH_3Br has probably increased significantly, perhaps by a factor of 2, in the past ten years. Model simulation of CH_3Br trends with reliable emission data will help resolve this important issue.

Handwritten notes:
 Central
 time
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4. Stratospheric Bromine Chemistry

4.1 Stratospheric sources of bromine

Once bromo-methanes (e.g., CH_3Br , halons) enter the stratosphere, they may be photo-decomposed to release bromine atoms. Specifically, for CH_3Br , the following



are expected to lead to ultimate release of Br atoms into the stratosphere. A review of the kinetic data for the above processes are given in Appendix C.

4.2 Partitioning of Bromine Atoms

A schematic diagram for stratospheric bromine chemistry is given in figure 1. Once released by the organic bromine molecule, the bromine atom is transformed into various species indicated in figure 1. The aggregates of the species, Br, BrO, Br_2 , BrCl, BrNO₃, HOBr and HBr, are referred to as the total inorganic bromine, or the BrX species. The exact partitioning of BrX into its components depends on altitude, the rate data for the formation and decomposition rate of each species, and the local concentrations of species such as NO₂, O₃, OH and H₂CO which actively participate in stratospheric bromine chemistry. As we will discuss in section 4.3, BrO and Br are the most reactive forms of BrX that directly participate in the catalytic cycles of ozone removal. One key question in determining the ODP of brominated species is what portion of BrX is in the form of BrO in the lower stratosphere. In our model calculations, BrO is predicted to be one of the major forms (about 40%) of BrX at those altitudes.

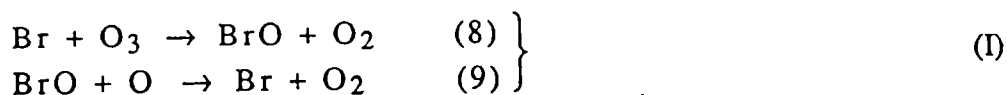
Br is reactive form in stratosphere. Measurement of BrO.

The existence of BrO in the lower stratosphere (~18-20 km) is confirmed by Brune et al (1988) and Toohey et al (1990) who reported concentrations of about 8 ± 2 pptv. The model calculated concentration of BrO is in rough agreement with the measured values. However, measurement of HBr reported by Park et al (1989) indicates a concentration of 20 ± 6 pptv at 28 km. Our model calculates a value of 1 pptv at the same altitude, about a factor of 20 less than the observation. This large discrepancy between the model result and observation is suggestive of

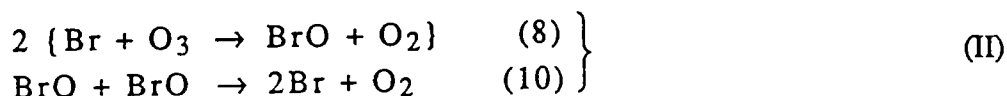
possible missing elements in our present understanding of the bromine chemistry. It should also be noted that the comparison between models and observations as a means for model validation is not straightforward. More HBr data from different locations and times of year are needed to test models.

4.3 Bromine catalyzed ozone removal

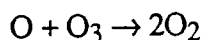
The bromine atoms released from bromo-methanes may participate in a number of catalytic cycles leading to ozone removal. Wofsy et al. (1975) introduce the following cycles involving Br and BrO with odd oxygen (O, O₃)



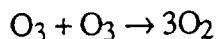
and



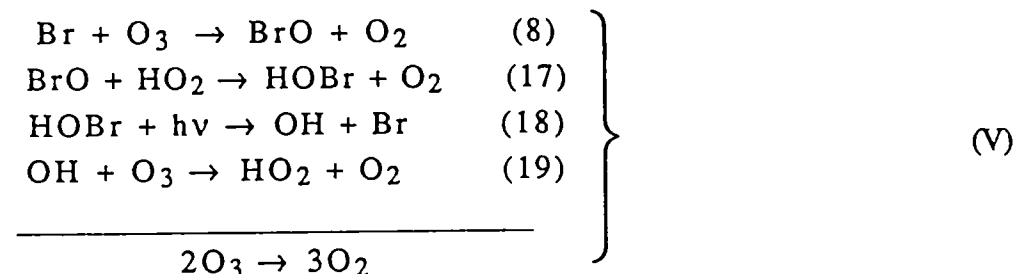
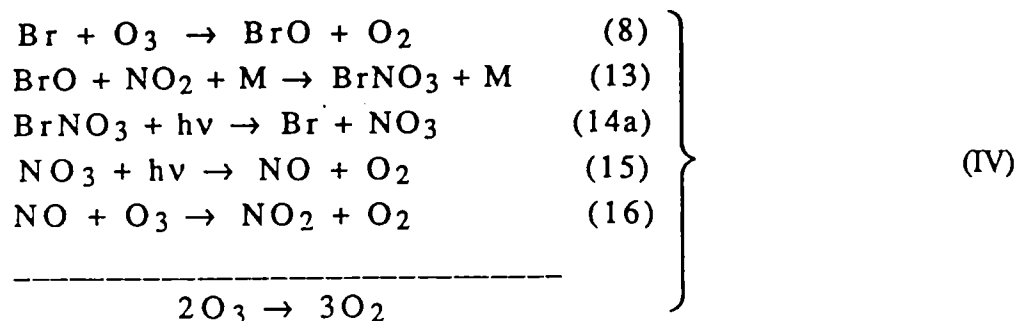
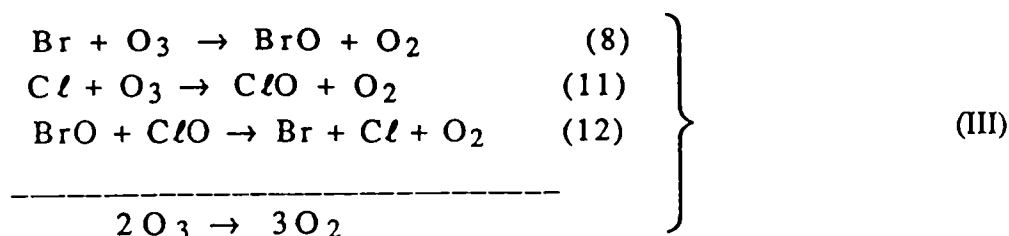
The sequence (I) is equivalent to



The sequence (II) is equivalent to



Studies after 1975 suggested that O₃ may also be removed through the coupling of different classes of radicals (e.g., HO_x, ClO_x, NO_x). Yung et al. (1980) proposed that the following catalytic cycles involving coupling of BrO with reactive chlorine, nitrogen and hydrogen species could also lead to ozone depletion:



4.4 Key uncertainties

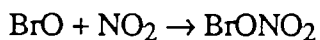
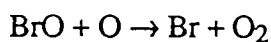
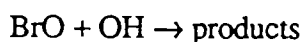
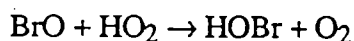
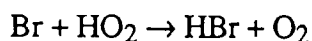
Note that cycles (I) through (V), discussed in the previous section, all involve the BrO radical. Since there are no measurements reported for many other bromine species in the lower stratosphere, observational support for stratospheric bromine chemistry is relatively weak, especially compared to that of chlorine. Although model calculations indicate that the impact of bromine on ozone on a per molecule basis is about an order of magnitude larger than that due to chlorine, there is a lack of data to validate these model results.

There are large uncertainties associated with rate data for certain key bromine reactions. For instance, in order for sequence (IV) to be operative as an ozone depletion cycle, BrNO₃ must photo-dissociate into Br and NO₃. However, no measurements have been made (De More et al., 1990) regarding the different possible photolysis products. If alternative dissociation paths exist, such as



then sequence IV will become a null cycle (i.e., no impact on ozone removal). There is a need to ascertain the photolysis products from $\text{BrNO}_3 + h\nu$. By analogy, the recommended quantum yield for ClNO_3 photolysis is taken to be 0.9 for the $\text{Cl} + \text{NO}_3$ channel and 0.1 for the $\text{O} + \text{ClNO}_2$ channel (Margitan, 1983; Burrow et al., 1988). It should be noted that this value is based on analysis of six independent studies carried out over a ten year period that showed conflicting results.

Other key reactions for which rate constants are uncertain by at least a factor of two include:



Accurate determination of the kinetic data for the aforementioned processes will help narrow the range of calculated values for ozone depletion potential of various bromo-methanes including CH_3Br .

Recent work on bromine chemistry is mostly directed towards its potential contribution to the observed ozone depletions over the polar regions (McElroy et al., 1986; Rodriguez et al., 1986; Anderson et al., 1989; Ko et al., 1989; Solomon et al., 1990). The current consensus is that, based on observed *in situ* concentrations of BrO and ClO, up to 25% of the observed stratospheric polar ozone depletion may be attributed to bromine chemistry (Anderson et al., 1990).

Scientists and policy makers rely on computer modeling to assess the impact of chemicals on stratospheric ozone depletion. Unfortunately, our theoretical and experimental knowledge about atmospheric bromine is much less well-developed than atmospheric chlorine. Thus, model

predictions concerning bromide impact should be viewed with caution. Current models need to be improved with kinetics data governing certain key reactions and reliable data on emission rates, and their predictions will have to be confirmed by atmospheric observations (e.g., CH₃Br, HBr, BrO).

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Table 1. Estimated Sources of Methyl Bromide

Investigators	Total Source strength (kt/yr)	Origin	
		Mostly Natural	Mostly Anthropogenic
Wofsy et al. (1975)	~76	X	
Singh et al. (1983)	~300*	X	
Penkett et al. (1985)	~90		X
WMO/NASA (1985; 1989)	~100		X

*estimate based on oceanic source

Table 2. Tropospheric abundance of CH₃Br

Time period	Location	Remarks	Result
1979-1981 Singh et al	Point arena, 39°N	4-6 samples per month	20 pptv (mean) 10-30 pptv
1980, May Singh et al	Houston St. Louis Denver Riverside	1 week 1 week 1 week 1 week	45-278 pptv 7-125 pptv 23-227 pptv 43-1033 pptv
March 81	Staten Island Pittsburgh Chicago	1 week 1 week 1 week	27-671 pptv 27-62 pptv 21-96 pptv
December, 1981 Singh et al	ship cruise 40°S to 40°N Pacific coast along the America	20 days cruise	19 pptv in South 26 pptv in north up to 50 pptv near 30°N
1982, 1983 Penkett et al	ship cruise 80°N to 80°S	Atlantic UK to Antarctica	10 pptv in south 15 pptv in north
March/April 1983 Berg et al	Arctic	surface to 8 km	11 pptv (mean) 7-24 pptv
1983 Rasmussen et al	Arctic	weekly sampling for 1 year, 30 samples	10 pptv
1985-1987 Cicerone et al	Alaska Mauna Loa Cape Kumukahi Samoa New Zealand	750 samples	11 pptv 10.8 pptv 11.4 pptv 10.2 pptv 9.6 pptv

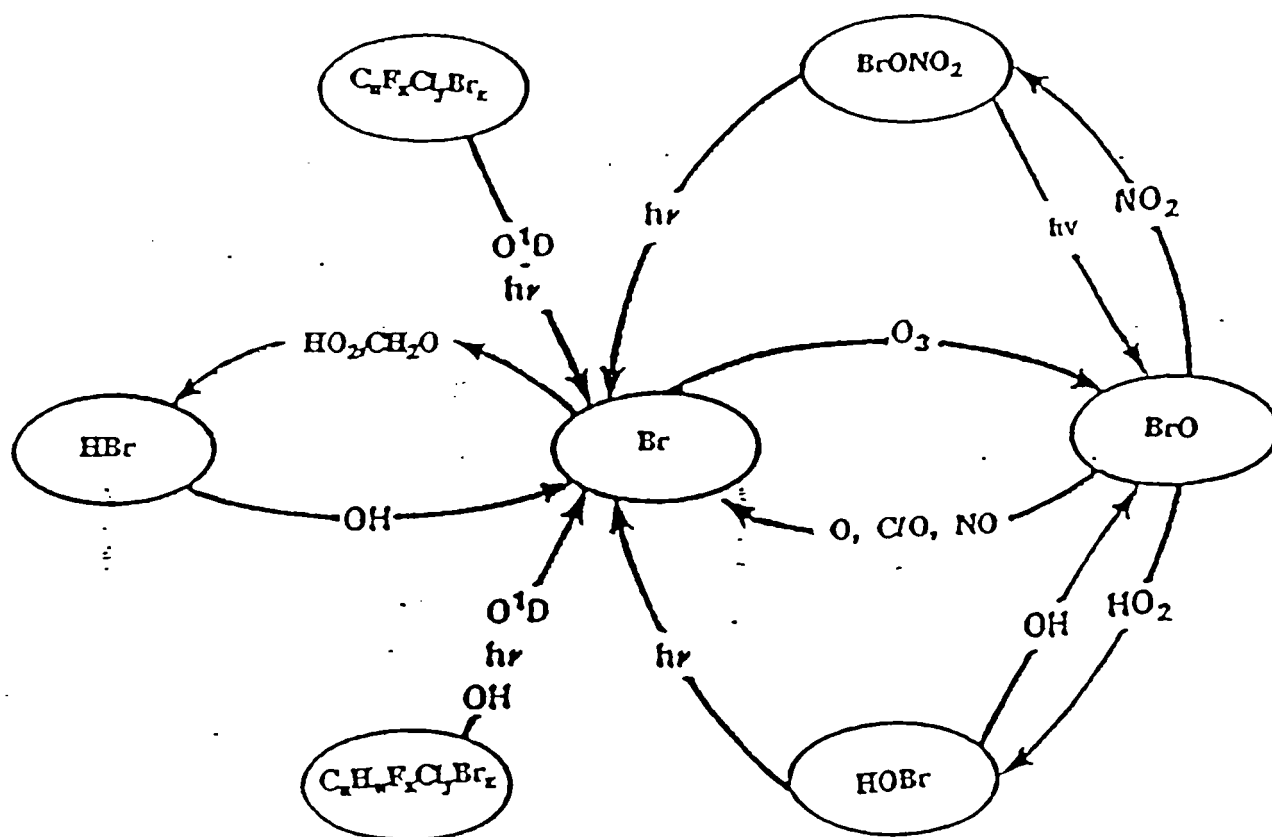


Figure 1. Bromine Cycle

Appendix A

Definitions of atmospheric lifetimes, bromine and chlorine loadings and ozone depletion potential

Atmospheric Lifetime

The atmospheric lifetime of a trace gas provides indications of how rapidly the atmospheric burden will increase if the gas is emitted into the atmosphere; and how fast the gas will be removed from the atmosphere once the emission stopped. The lifetime defined below is the so-called e-folding lifetime. It is the decay time constant that corresponds to the time period in which the atmospheric burden will decrease by 63% if there is no emission.

The atmospheric burden of a gas is given by the equation

$$\frac{dN}{dt} = E - \frac{N}{\tau} \quad (A1)$$

where N is the burden, E is the emission rate and τ is the atmospheric lifetime. The parameters are related to certain observables in the following special cases :

- (1) If the burden at $t=t_0$ is N_0 , and $E = 0$, then, $N(t) = N_0 e^{-t/\tau}$ showing that τ is the e-folding lifetime.
- (2) If E is constant in time, and $N(t_0) = 0$, then $N(t) = E\tau(1 - e^{-t/\tau})$. Note that a steady state is achieved when the emission is balanced by removal resulting in a steady state burden given by

$$N_{ss} = E\tau$$

- (3) If values of the burden and emission are available from observation over a sufficient long period of time, τ can be derived from the data using equation (A1).

Alternatively, the atmospheric lifetime of a compound X can be calculated using photochemical models that incorporate the removal mechanisms (e.g., reaction with OH) with measured rate constants and the calculated trace gases (e.g., OH) that react with X . These values can be partially validated by comparison of the model calculated results with corresponding observed quantities.

Bromine and Chlorine Loadings

The impact on ozone from bromine and chlorine containing chemicals, among other factors, is proportional to the concentration of bromine and/or chlorine atoms released by the organic chemicals in the stratosphere. The concentration of stratospheric bromine (chlorine) atoms can be estimated from the concentration of the organic chemical in the troposphere as given by the following equation

$$\text{bromine (chlorine) loading} = f \times n$$

where f is the concentration of the chemical in the troposphere and n is the number of bromine (chlorine) atoms per molecule.

Ozone Depletion Potential

The amount of stratospheric ozone decrease caused by addition of chlorine and bromine containing chemicals depends on the spatial and temporal distributions of the reactive forms of bromine and chlorine as well as the bromine and chlorine loadings. The fraction of reactive forms relative to total loadings is determined by the adopted photochemical scheme with rate data taken from De More et al. (1990). The actual decrease in ozone due to specific emission of a chemical can be calculated using photochemical models. A model may be viewed as a depository of current knowledge and information that provides the basis and capability to simulate the present day atmosphere and to predict future changes.

The ozone depletion potential (ODP) is a measure of the potency of halocarbon specie in removing ozone on a per pound emitted basis relative to CFC-11. The ODP for a chemical Y is calculated using the numerical model as follows. The model is first used to calculate the ozone content in the present day atmosphere. A separate simulation is performed in which the addition of CFC-11 at E kiloton/year is included. The percent change in ozone content between the two simulations is calculated to be A%. The simulation is repeated again with addition of chemical Y at E kiloton/year. The calculated change in ozone relative to the present day atmosphere is B%. Then, ODP for chemical Y is B/A. Note that ODP does not depend on the absolute emission rate. To the extent that ODP depends on bromine (chlorine) loadings, it is also proportional to atmospheric lifetime. Thus, if every factor remains identical, then a shorter lifetime will imply a lower ODP.

References

DeMore, W.B., S.P. Sanders, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara (1990) Chemical kinetics and photochemical data for use in stratospheric modeling. *JPL Publication 90-1*, Jet Propulsion Laboratory, Pasadena, CA.

Appendix B

Atmospheric Methyl Bromide and Stratospheric Ozone

Presented to

The Methyl Bromide Panel
Chemical Manufacturers Association

Prepared by

N.D. Sze
M.K.W. Ko

Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, Massachusetts 02139

Outline of Presentation

- Summary of Issues
- Budget and Sources of Atmospheric Methyl Bromine
 - Atmospheric Lifetime
 - Sources of Methyl Bromine
- Review of Atmospheric Measurements
 - Burden
 - Trend
- Potential Impact on Stratospheric Ozone and Ozone Depletion Potential
 - Stratospheric Bromine Chemistry
 - Model Determined Values of ODP
- Sources of Uncertainties on Ozone Depletion Potential
 - Atmospheric lifetime of methyl bromine and bromine loading
 - Bromine-ozone relation
- Recommendations

Summary of Issues

1. Atmospheric budgets/origins of CH₃Br
2. Preliminary model calculation of ozone depletion potential (ODP)
3. Sources of major uncertainties
4. Recommendations

Issue #1

Atmospheric Budgets/Origins of CH₃Br

		<u>Uncertainty Range</u>
Concentration (ppt)	~12	10 - 20
Burden (kiloton)	~189	159-315
Lifetime (yr)	~1.6	.7 - 2.5
Annual removal rate (kiloton/yr ⁻¹)	~118	63 - 450

Issue #2

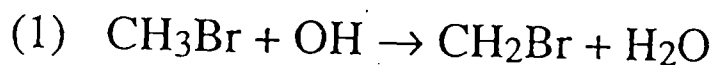
Preliminary Model Calculation of Ozone Depletion Potential (ODP)

$$\text{ODP} = 0.6 \quad \left\{ \begin{array}{l} \text{Uncertainty range} \\ .15 - .8^{(1)} \\ .26 - .9^{(2)} \\ .07 - 1.2^{(3)} \end{array} \right.$$

- (1) due only to uncertainty in stratospheric bromine chemistry
- (2) due only to uncertainty in atmospheric lifetime
- (3) combined uncertainty

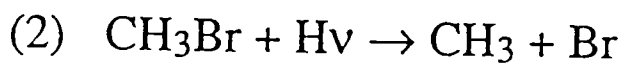
Removal Processes for CH₃Br

$$\text{Total Lifetime } \frac{1}{\tau_T} = \sum_{i=1}^n \frac{1}{\tau_i}$$



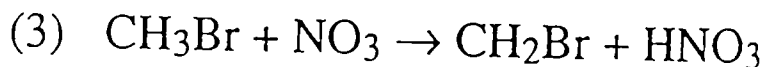
$$k = 7.6 \times 10^{-13} \exp\left(-\frac{890}{T}\right) \text{ cm}^3 \text{ s}^{-1}$$

$$\tau_{\text{OH}} = 1.6 \text{ years}$$



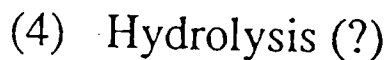
$$\lambda = 210 - 290 \text{ nm}$$

$$\tau_{\text{hv}} \approx 50 \text{ years}$$



$$k \approx 2-3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$$

$$\tau_{\text{NO}_3} > 40 \text{ years}$$



Sources of Methyl Bromide

Investigators	Source strength (kt/yr)	Origin	
		Natural	Anthropogenic
Wofsy et al. (1975)	~76	X	
Singh et al. (1983)	~300*	X	
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WMO/NASA (1985; 1989)	~100		X

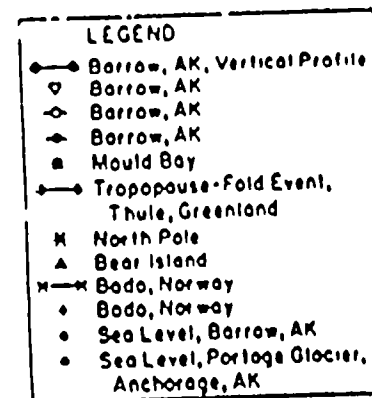
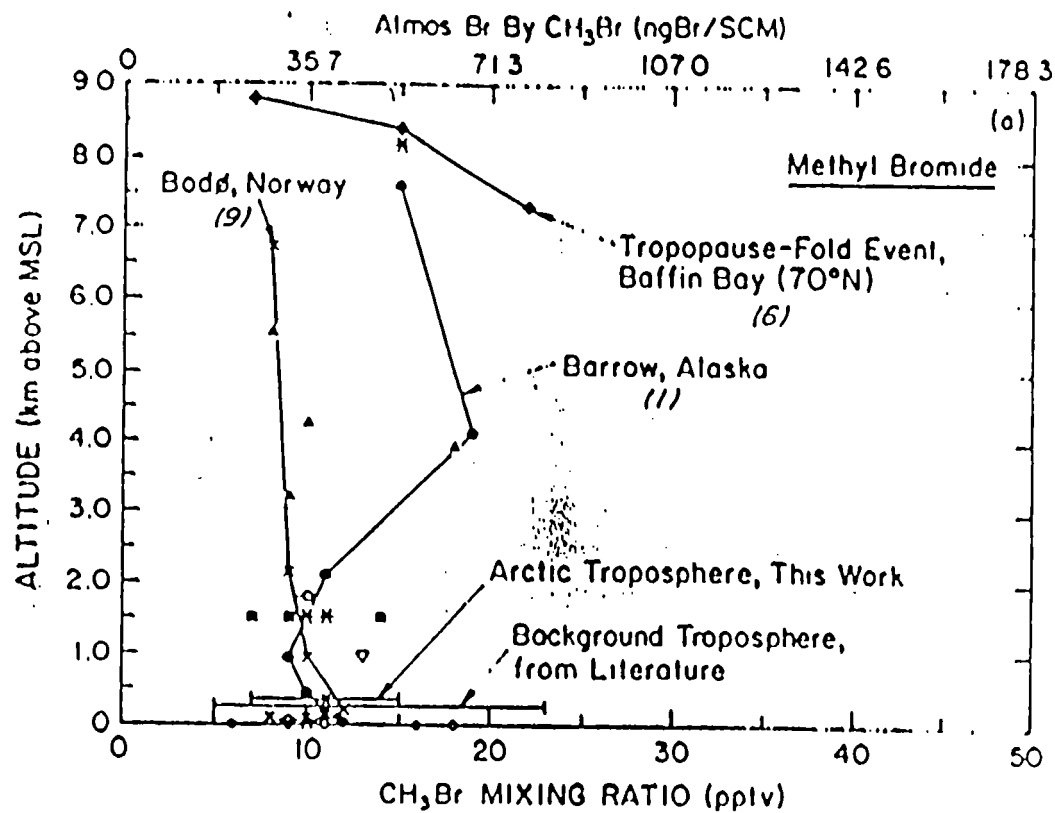
*estimate based on oceanic source

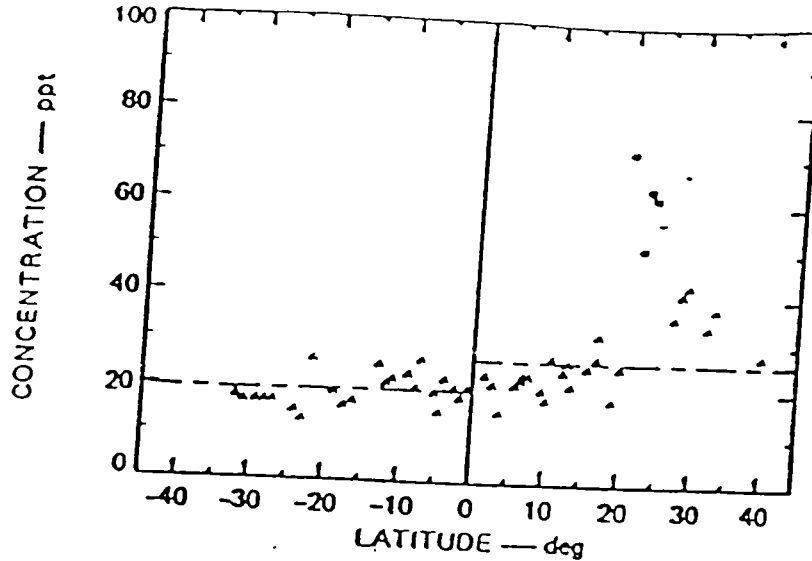
Atmospheric Measurements

Tropospheric abundance of CH₃Br

Time period	Location	Remarks	Result
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1980, May Singh et al	Houston St. Louis Denver Riverside	1 week 1 week 1 week 1 week	45-278 pptv 7-125 pptv 23-227 pptv 43-1033 pptv
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March/April 1983 Berg et al	Arctic	surface to 8 km	11 pptv (mean) 7-24 pptv
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1985-1987 Cicerone et al	Alaska Mauna Loa Cape Kumukahi Samoa New Zealand	750 samples	11 pptv 10.8 pptv 11.4 pptv 10.2 pptv 9.6 pptv

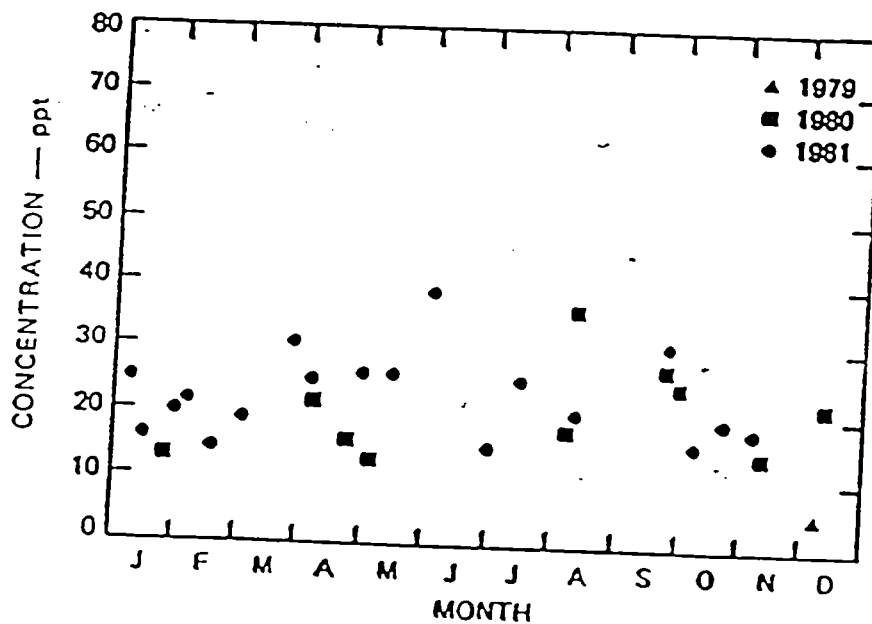
** Anthropogenic source*





(b) METHYL BROMIDE

Fig. 3. Latitudinal distribution of methyl halides. Dashed lines indicate weighted hemispheric averages. Darkened squares are excluded from these averages for statistical reasons. Positive latitudes are °N; negative latitudes are °S.



(b) METHYL BROMIDE

Fig. 4. Methyl halide concentrations at Point Arena (39°N). Each data point is an average of 4 to 6 samples.

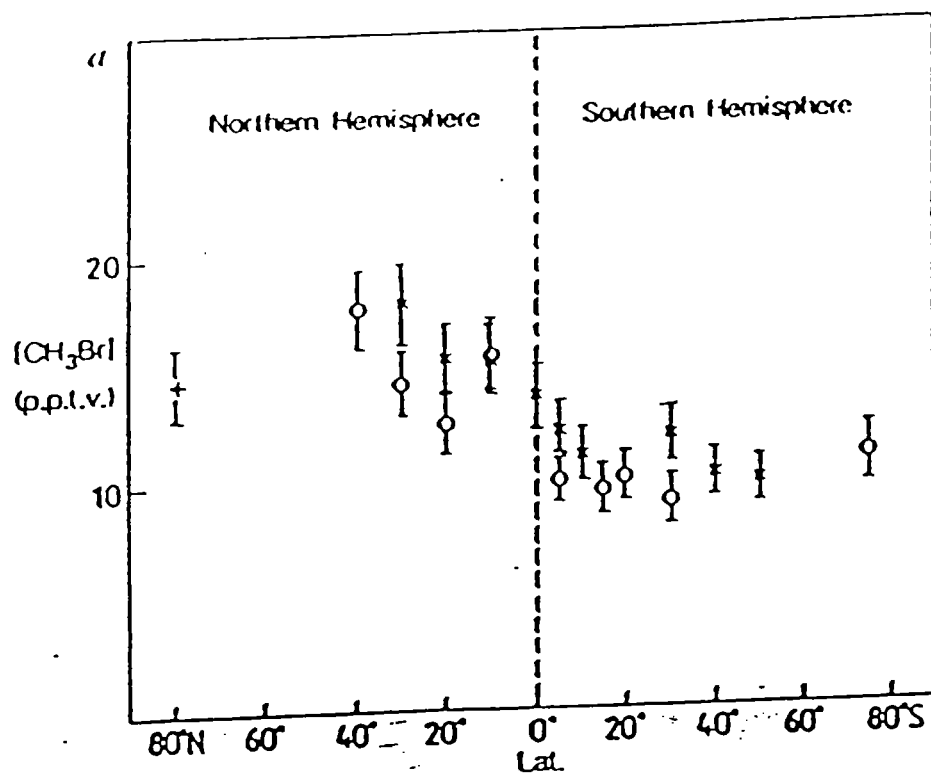


Fig. 1 Longitudinal transects of the concentrations of four bromine compounds: *a*, CH_3Br ; *b*, CH_2Br_2 ; *c*, CHBr_3 ; *d*, CF_3Br . O, 1982 voyage via Cape Town; x, 1983 voyage via Rio; +, values collected on other experiments.

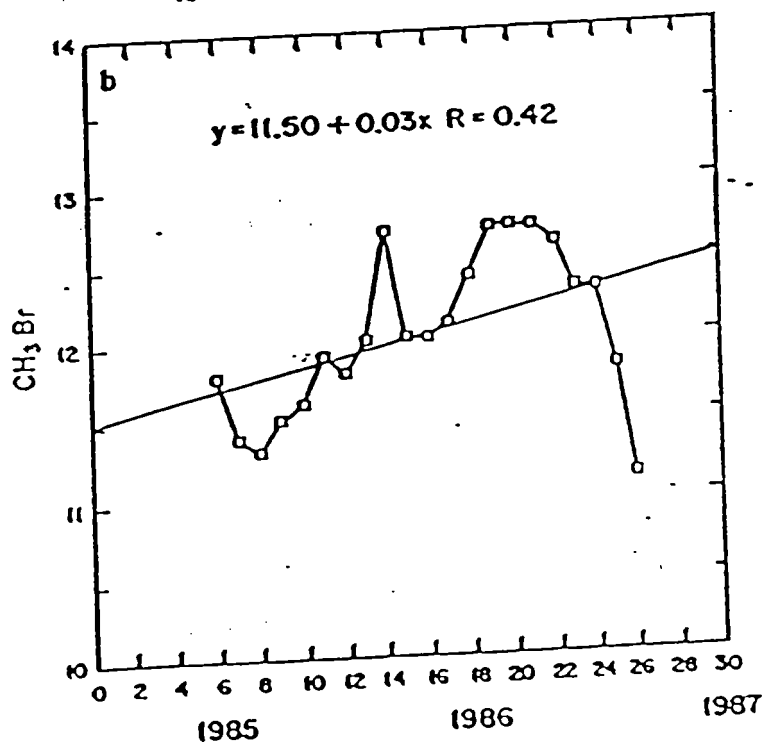
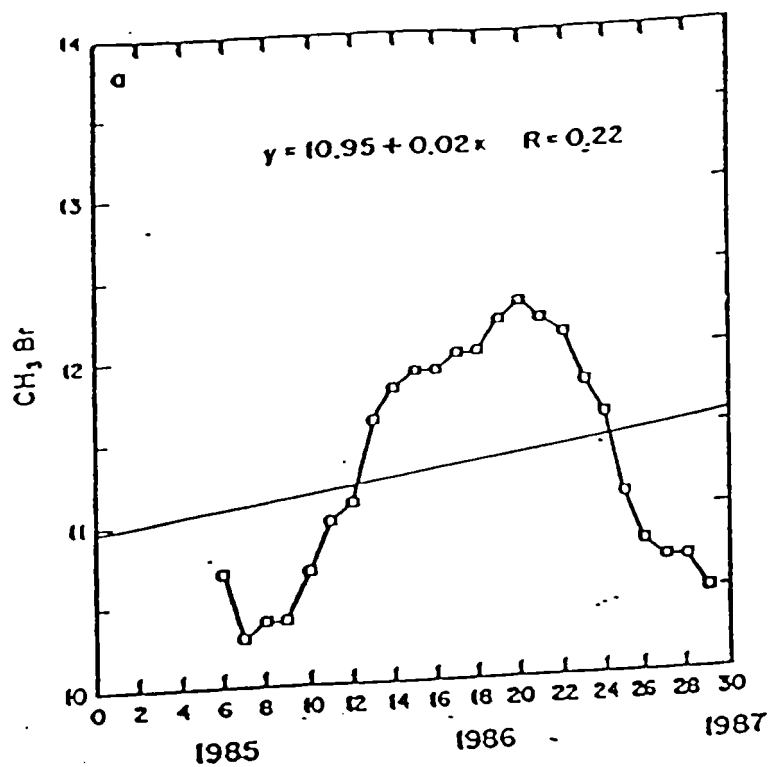
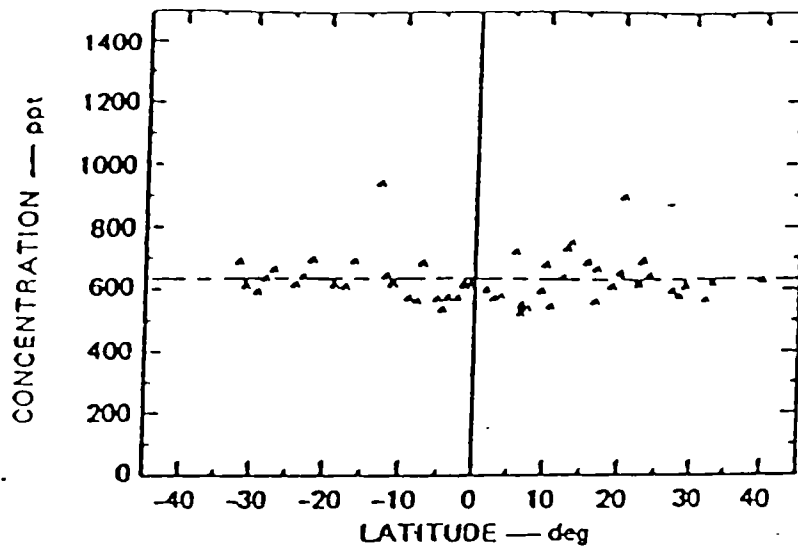


Fig. 1. Twelve-month running averages of CH_3Br mole fractions ($\text{ppt} = 10^{-12}$) measured at (a) Point Barrow, Alaska, and (b) Cape Kumukahi, Hawaii, during a 34-month period that began in January 1985. Equations for regression-line fits to the data are displayed in each panel; slopes are measured in ppt per month. R values are correlation coefficients.

Trend

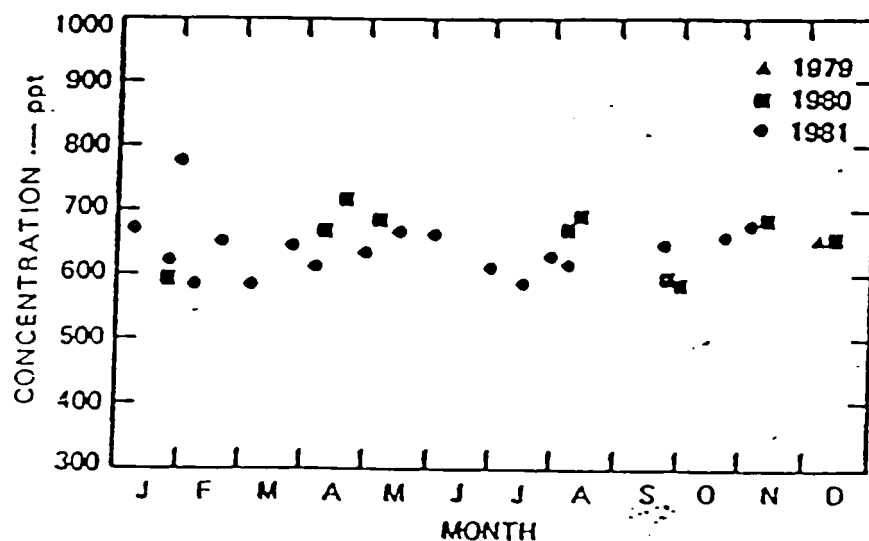
The only data that discusses trend is from the monitoring at five sites. Cicerone et al. reported that there is no clear indication of a temporal trend although a trend as large as 0.1 pptv/month cannot be ruled out.

From the budget point of view, current concentration of 12 pptv implies that a source of 118 kilotons/year is needed to maintain concentration. An additional 34 kilotons/year will cause a 1 pptv/year increase in concentration.



(a) METHYL CHLORIDE

Fig. 3. Latitudinal distribution of methyl halides. Dashed lines indicate weighted hemispheric averages. Darkened squares are excluded from these averages for statistical reasons. Positive latitudes are °N; negative latitudes are °S.



(a) METHYL CHLORIDE

Fig. 4. Methyl halide concentrations at Point Arena (39°N). Each data point is an average of 4 to 6 samples.

TABLE 2. Independent Existence of High Methyl Chloride and Methyl Iodide Concentrations in Seawater

Latitude*	Surface Seawater Concentration, ng/l		
	CH ₃ Cl	CH ₃ Br	CH ₃ I
22.68	41.8	3.7	0.9
20.19	18.1	1.5	1.0
-8.68	10.6	1.5	3.2
-8.99	22.5	2.9	2.4
-9.50	9.8	1.2	6.8
-11.70	8.7	1.9	4.2
-12.83	10.6	1.1	3.7
-16.93	26.7		3.5

*Positive latitude is °N; negative latitude is °S.

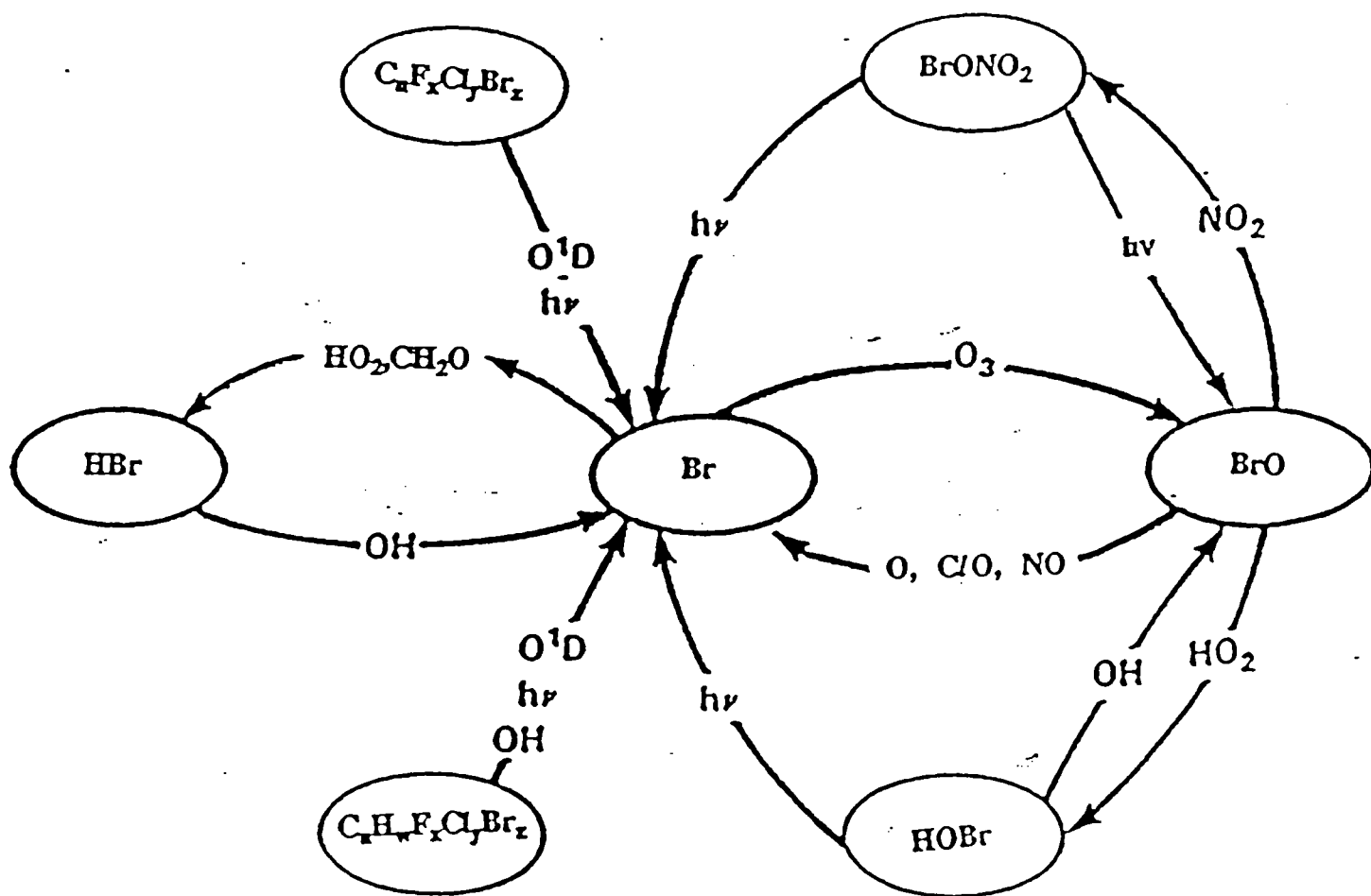
TABLE 3. Estimated Oceanic Methyl Halide Source Strength

Chemical Name	Average Concentration		Ocean Supersaturation, %	Extrapolated Ocean to Air Flux, 10 ⁻⁷ g cm ⁻² yr ⁻¹	Global Oceanic Source, Tg/yr	Estimated Atmospheric Residence Time From Oceanic Source Alone, years*
	Seawater ng/l	Air, ppt				
Methyl chloride	11.5	633	275	13.3	4.9	1.2
Methyl bromide	1.2	23	250	0.9	0.3	1.2
Methyl iodide	1.6	2	336	1.4	0.5	0.09
	1.0		210	0.9	0.3	0.15

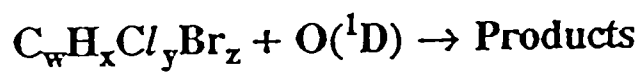
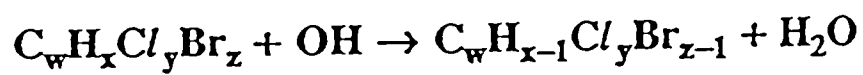
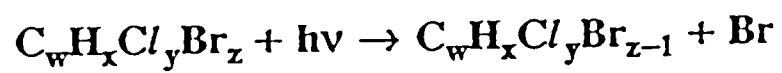
*Assuming the air and seawater concentration to be representative of troposphere and oceans, respectively. See text for discussion.

Stratospheric Bromine Chemistry

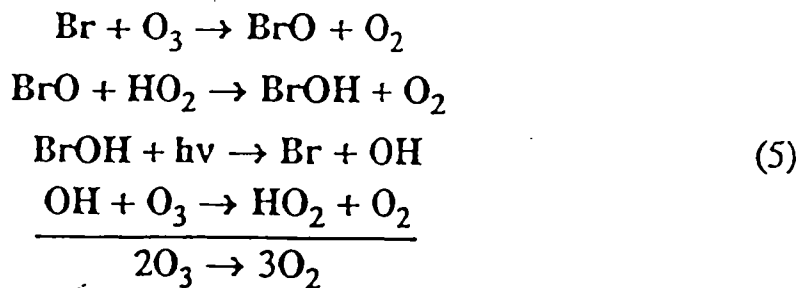
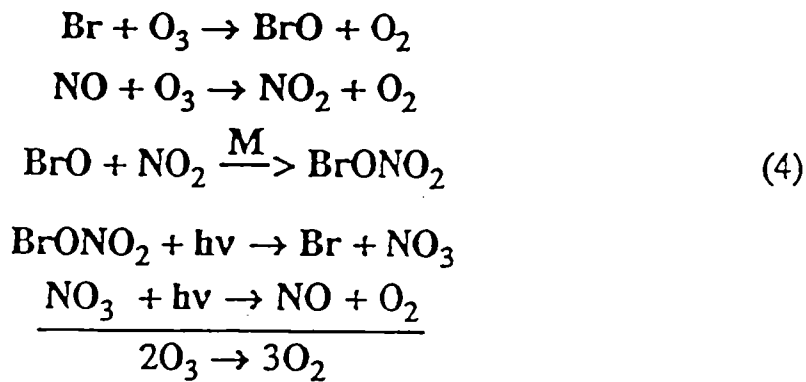
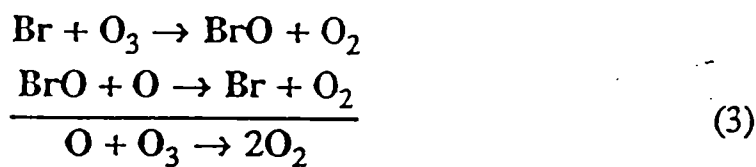
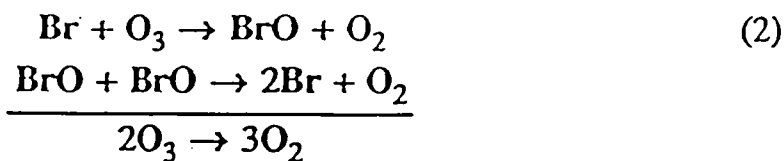
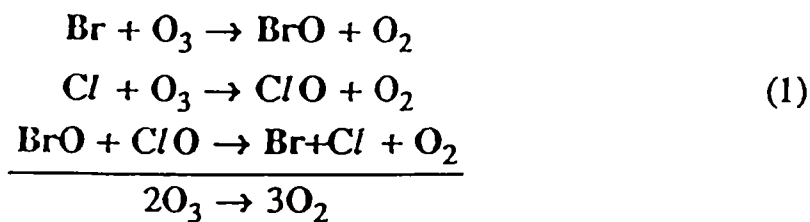
BROMINE CYCLE



Stratospheric Sources of Bromine

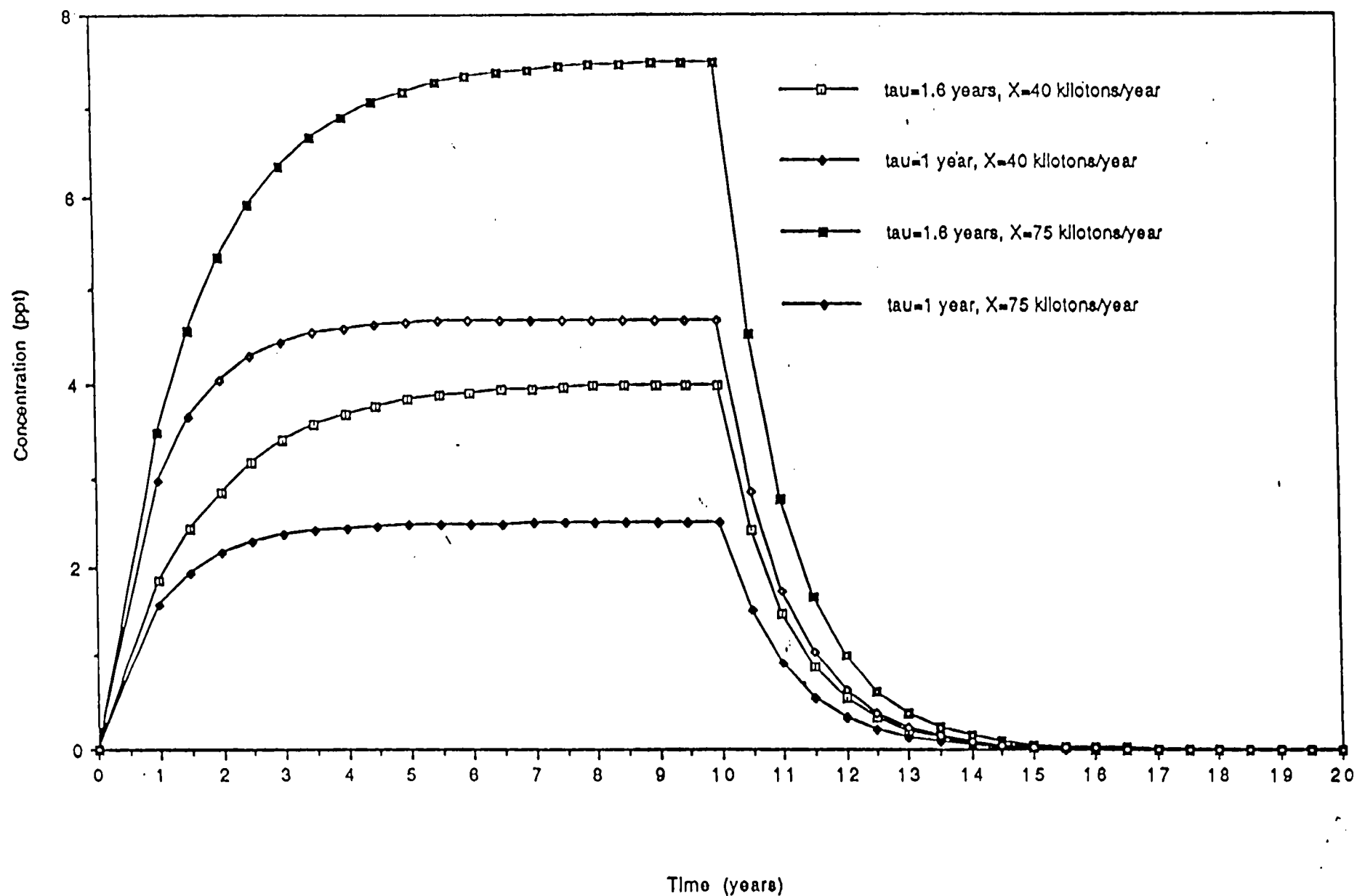


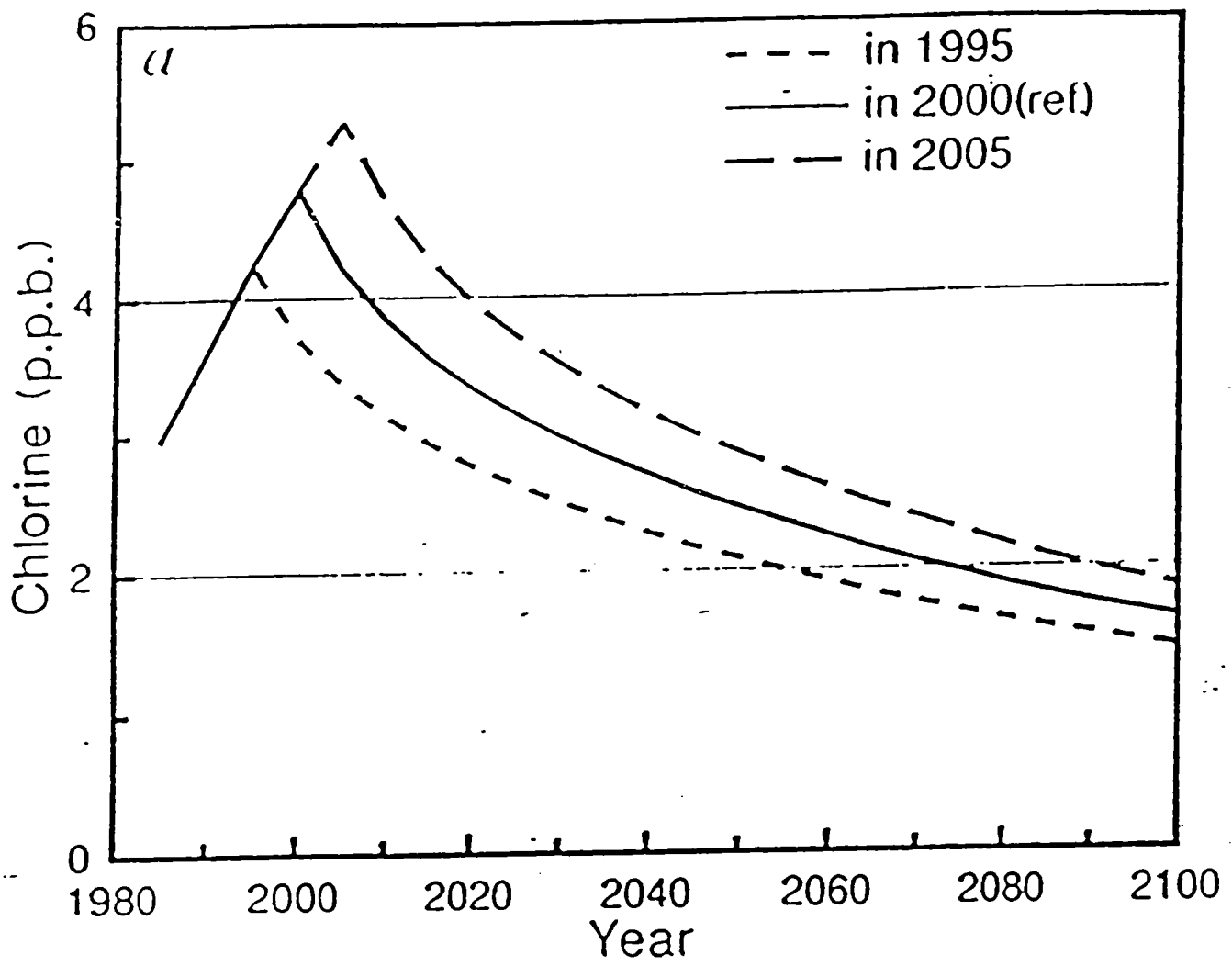
Bromine Catalyzed O₃ Depletion



Time Dependent Calculations and Trends

Effect of Lifetime (Tau) and Emission Rate on Methyl Bromide Burden.
Emission Rate Is X For the First 10 Years and 0 After.





Recommendations

Reduce the uncertainties in the Ozone Depletion Potential by validating the atmospheric lifetime of methyl bromine and the bromine-ozone relation

Issue #1: Atmospheric budget and origin:

Laboratory kinetic measurements:

Kinetics of methyl bromine to determine lifetime

Field measurements:

Burden, trend, and intercalibration

Modeling:

Tropospheric chemistry

tropospheric OH

tropospheric chlorine chemistry

*Simulation of burden and trend from emission data
using 1-D and 2-D models*

Issue #2: Bromine-ozone relation

Laboratory kinetic measurements:

Bromine chemistry

Modeling:

Heterogeneous chemistry

Appendix C

EVALUATION OF THE ATMOSPHERIC CHEMICAL KINETICS OF METHYLBROMIDE

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May 1991

EVALUATION OF THE ATMOSPHERIC CHEMICAL KINETICS OF METHYL BROMIDE

ABSTRACT

Reaction rate constants and photodissociation cross sections of potential importance in determining the atmospheric lifetime of methyl bromide (CH_3Br) have been reviewed and evaluated. Reactions with OH , Cl , $\text{O}(^1\text{D})$, $\text{O}(^3\text{P})$, HO_2 and NO_3 have been considered along with ultraviolet photodissociation.

INTRODUCTION

Methyl bromide is a trace constituent of the Earth's atmosphere with both natural and anthropogenic sources. The major interest in atmospheric methyl bromide has focused on its role as a source for stratospheric Br and BrO , which participate in the halogen catalyzed destruction of the stratospheric ozone layer. Initial modeling studies of this effect by Wofsy et al. (1975) and Yung et al. (1980) restricted atmospheric destruction of CH_3Br to reaction with hydroxyl radicals (OH) and photodissociation. Quite recent models designed specifically to calculate the atmospheric lifetimes of halocarbons still restrict CH_3Br degradation to these two processes (Prather and Spivakovsky, 1990; Prather, 1991). National Institute of Standards and Technology (NIST) staff have concluded that these two processes will also dominate the atmospheric degradation of hydrogen containing bromocarbon compounds including CH_2Br_2 (Gann et al., 1990).

Grogjean (1991) has just published an analysis of the tropospheric chemistry of methyl bromide. He concludes that the reaction with OH is slow and reactions with O_3 and NO_3 are negligible. He suggests that the loss for the lower troposphere is upward diffusion or deposition. He also concludes that CH_3Br is not formed within the atmosphere. Methyl bromide may also play a minor role in the springtime destruction of tropospheric ozone in the arctic, although bromoform (CHBr_3) rather than CH_3Br is believed to be the major driver for that recently discovered phenomena (Barrier et al., 1988).

This short report will document and evaluate chemical kinetic and photodissociation processes which may influence the atmospheric lifetime of CH_3Br . It also contains a brief analysis of the photochemistry and reaction kinetics of active stratospheric bromine species such as Br , BrO , BrONO_2 , HOBr and HBr .

PHOTODISSOCIATION OF CH_3Br

The weakest bond in methyl bromide is the C-Br bond, with a dissociation energy at 298°K of 292 ± 8 kJ/mole or 69.8 ± 2 kcal/mole (Tschuikow-Roux and Paddison, 1987). This corresponds to a possible photodissociation threshold of only 410 nm. However, measurable absorption does not begin until about 290 nm in the near ultraviolet, ensuring that CH_3Br photodissociation does not occur below the stratosphere. Photoabsorption cross sections for CH_3Br have been measured by Robbins (1976), Molina et al. (1982), Uthman et al. (1978) and Gillotay and Simon (1988). The agreement between these studies is very good.

Gillotay and Simon extended the previous room temperature measurements down to 209 K. A plot of their room temperature data compared to Robbins data is shown in Figure 1. A tabular comparison of 295 K data from three of the measurements along with selected lower temperature data from Gillotay and Simon (1988) is presented in Table 1. The data of Molina et al. do extend to 290 nm with a measured cross section of $3 \times 10^{-24} \text{ cm}^2$ at 298 K for that wavelength.

It is probably a safe assumption that the photoabsorption cross sections shown in Figure 1 and Table 1 lead to a breaking of the C-Br bond with unit quantum yield. However, the C-H bonds in CH_3Br have a dissociation energy at 298 K of 425 ± 4 kJ/mole indicating that photoabsorption at wavelengths of 282 nm or shorter could also break the C-H bond. Which bond is broken may be immaterial under stratospheric photochemical conditions.

REACTION KINETICS OF CH_3Br

Methyl bromide is a stable, saturated compound and can be expected to react only with free radical or electronically excited species. Current

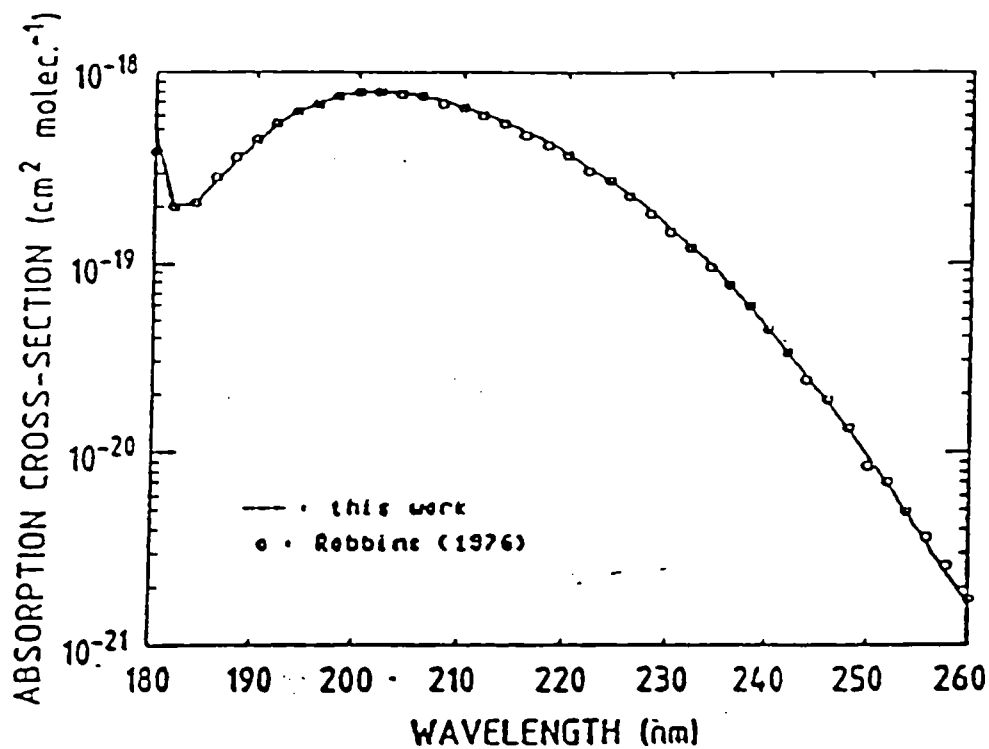


Figure 1. CH_3Br absorption cross-section of with respect to wavelength between 180 and at 260 nm, at 295 K from Gillotay and Simon (1988).

TABLE 1 - CH₃ Br absorption cross-section: experimental values at 295 K, 227 K and from Gillotay and Simon (1988) compared with the values of Robbins (1976) and of Molina et al. (1982)

λ (nm)	σ (λ) 10^{21} (cm molec. ⁻¹) This work				Robbins (1976)	Molina et al. (1982)
	295K	255K	227K	209K	295K	295K
180	500	500	500	500	391	
182	198	198	198	198	197	
184	208	208	208	208	211	
186	271	271	271	271	284	
188	346	346	346	346	358	
190	439	439	439	439	447	441
192	529	529	529	529	544	
194	620	620	620	620	626	
196	691	691	691	691	692	
198	760	760	760	760	768	
200	791	791	791	791	796	785
202	797	797	797	797	797	
204	793	793	793	793	778	
206	767	767	767	767	757	
208	727	727	727	727	695	
210	666	666	666	666	657	649
212	614	613	613	613	597	
214	559	558	558	556	547	
216	493	495	494	490	476	
218	442	436	434	433	420	
220	377	374	369	366	375	360
222	324	321	315	312	310	
224	276	275	261	259	270	
226	230	228	213	216	223	
228	188	188	181	177	182	
230	154	151	146	144	146	145
232	124	121	118	114	121	
234	98.7	95.2	90.8	88.6	96.1	
236	76.5	73.4	69.9	65.8	76.4	
238	59.5	55.2	51.6	49.7	58.7	
240	44.7	41.7	39.0	37.9	44.2	41.1
242	33.5	30.2	28.9	27.6	33.0	
244	25.0	22.5	20.7	19.4	23.8	
246	18.2	16.2	14.7	14.2	18.7	
248	13.1	11.3	10.4	9.80	13.4	
250	9.57	8.13	7.31	6.75	8.48	9.49
252	6.86	5.68	4.99	4.47	7.04	
254	4.87	3.88	3.43	3.15	4.95	
256	3.36	2.72	2.32	2.02	3.58	
258	2.35	1.90	1.49	1.29	2.60	
260	1.64	1.37	1.08	0.88	1.72	1.63

models of the troposphere and stratosphere have identified OH, HO₂, NO₃, Cl, O and O(¹D) as the primary reactive radicals which drive atmospheric oxidation. The available reaction rate data for these species with CH₃Br will be evaluated below.

In evaluating the reaction kinetics of CH₃Br I have accessed several data bases and evaluated data compilations, including the NIST Chemical Gas Kinetic Data Base (Release 2) (NIST, 1990), NASA's stratospheric chemical kinetics and photochemical data evaluation (DeMore et al., 1990), IUPAC's atmospheric chemistry kinetic and photochemistry data evaluation (Atkinson et al., 1989), a recent review of OH/organic compound kinetics (Atkinson, 1989), and reviews/evaluations of HO₂ kinetics (Lloyd, 1974; Kaufman and Sherwell, 1983) and O atom kinetics (Herron and Huie, 1973; Herron, 1988).

OH Reaction

The reaction of CH₃Br with OH is presumed to proceed by hydrogen atom abstraction:



The reaction has been studied experimentally by Howard and Evenson (1976) at 296 K and Davis et al. (1976) between 245-375 K. These studies agree very well at room temperature. The IUPAC evaluated rate constant (Atkinson et al., 1989) of:

$$k = 7.6 \times 10^{-13} \exp(-890 \pm 200/T) \text{ cm}^3/\text{s} \quad (2)$$

was also adopted in Atkinson's OH/organics review (Atkinson, 1989). NASA's stratospheric evaluation of the same data (DeMore et al., 1990) yielded a slightly different rate constant representation of:

$$k = 6.8 \times 10^{-13} \exp(-850 \pm 200/T) \text{ cm}^3/\text{s} . \quad (3)$$

Cohen and Benson (1987) have published a theoretical evaluation of the OH/CH₃Br reaction which is in reasonable accord with the data.

Either the IUPAC or NASA evaluated rate can be used in current models since they are essentially equivalent, with Equation 2 yielding 2.81×10^{-14} and Equation 3 yielding $2.92 \times 10^{-14} \text{ cm}^3/\text{s}$ evaluated for the mean tropospheric temperature of 270 K.

* The NASA evaluation gives an uncertainty factor in the room temperature (298 K) rate of $x/\div 1.25$. The temperature dependence uncertainty ($E/R \pm \Delta E/R$) is stated as (-850 ± 200) . At 270 K this is an uncertainty range of 4.4 just due to exponential factor uncertainty.

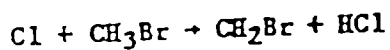
The IUPAC evaluation gives a room temperature uncertainty range of $3.8 \times 10^{-14} \pm 0.1$ leading to an uncertainty range of 4.7×10^{-14} to 3.0×10^{-14} . They also estimate the ($E/R \pm \Delta E/R$) as (-890 ± 200) . At 270 K this is also an uncertainty range of 4.4.

Given the above, it is clear that an uncertainty in the 270 K rate of a range of factor of 5 can be justified. (E g. approximately an uncertainty factor of $x/\div 2.2$.)

It should be noted, however, that the reaction with OH could be even slower than indicated by the two experimental measurements. Recent experience with the $\text{CH}_4 + \text{OH}$ reaction rate (Vaghjiani and Ravishankara, 1991) has shown that slow, low temperature rates can easily be biased by sample impurities. The $\text{CH}_3\text{Br} + \text{OH}$ rate constant should be remeasured with updated techniques over the 300-240°K range relevant to the troposphere and stratosphere.

Cl Reaction

The reaction of CH_3Br with ground state atomic chlorine:



(4)

has been experimentally studied by Tschulkow-Roux et al. (1988) over the temperature range of 273 to 368 K. The rate constant determined was:

$$k = (3.16 \pm 0.63) \times 10^{-11} \exp(-1205 \pm 69/T) \text{ cm}^3/\text{s}$$

(5)

This is the only measurement for this reaction I could locate, so comparative data evaluation is impossible. This group measured comparable rate constants for several other halocarbon compounds. The rate expression is reasonable given the nature and thermochemistry of the reaction.

O Reaction

The reaction of ground state atomic oxygen, $O(^3P)$, with CH_3Br :



is nearly thermoneutral and can be expected to possess a significant activation barrier. Three groups (Wilson and O'Donovan, 1968), (Herron and Huie, 1969) and (Westenberg and deHaas, 1975) have measured the rate constant at elevated temperatures (350-1000 K). The most recent NIST evaluation by Herron (1988) recommends:

$$k = 3.3 \times 10^{-11} \exp(-3900/T) \text{ cm}^3/\text{s} \quad (7)$$

which extrapolates to 1.8×10^{-17} at 270 K. Herron suggests this rate constant has an overall error factor of 3 over the temperature range of 400-1500 K. It may be more uncertain at atmospheric temperatures.

NO_3 Reaction

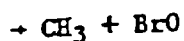
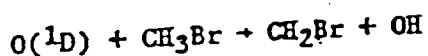
The reaction of CH_3Br with the nitrate radical has been measured at 298 K in a competitive reaction with toluene by Carlier et al. (1987). The absolute rate depends on the choice of the NO_3 + toluene rate and is quoted as either $(1.57 \pm 0.11) \times 10^{-17}$ or $(3.05 \pm 0.21) \times 10^{-17}$ in Wayne et al. (1990). I estimate a 270°K rate of $1.5 \times 10^{-17} \text{ cm}^3/\text{s}$ based on this single determination. The reaction products have not been determined, but are probably HNO_3 and CH_2Br .

HO₂ Reaction

Chemical thermodynamic and molecular dynamic considerations suggest that the hydroperoxyl radical will react at a negligible rate with CH₃Br at atmospheric temperatures. A survey of HO₂ kinetics reviews (Lloyd, 1974; Kaufman and Sherwell, 1983) suggests strongly that saturated hydrocarbon or halocarbon compounds are quite unreactive with HO₂.

O(¹D) Reaction

Singlet atomic oxygen, O(¹D), is produced in the photodissociation of atmospheric ozone. While no measurement of its reaction rate with CH₃Br was located in the literature, measurements with CH₃F, CH₃Cl and CF₃Br have been made (Gillespie et al., 1977; Force and Wiesenfeld, 1981) these studies suggest that O(¹D) can react readily with CH₃Br:



Based on the reaction rate of $1.9 \times 10^{-10} \text{ cm}^3/\text{s}$ measured for CH₃Cl (Force and Wiesenfeld, 1981), I estimate a rate for CH₃Br + O(¹D) of $2.0 \times 10^{-10} \text{ cm}^3/\text{s}$. O(¹D) reaction rates generally have little or no temperature dependence.

REACTION KINETICS OF ACTIVE BROMINE COMPOUNDS

A few comments on the current state of the reaction kinetics of active stratospheric bromine compounds (Br, BrO, BrONO₂, HOBr and HBr) are listed below.

Key reactions probably involve Br + O₃, H₂CO, HO₂; HBr + O and OH and BrO + O, NO, ClO and NO₂(+H). The reaction of BrO with O₃ is not believed to occur at atmospheric temperatures. The photodissociation of BrONO₂ and BrO are also of interest. The status of these reactions as reflected in the 1990 NASA evaluation has been assessed and noted below.

Comments on Br Atom Reactions

The NASA 298 K uncertainty factors for the HO_2 and H_2CO reactions with Br are 2.0 and 1.3, respectively. Relatively large temperature dependence uncertainties of -600 ± 600 and -800 ± 200 make these reactions considerably more uncertain at stratospheric temperatures. $\text{Br} + \text{O}_3$ is in better, but no great shape (1.2 and -800 ± 200).

Comments on BrO Reactions

$\text{BrO} + \text{O}$, NO , and ClO have NASA $f(298)$'s of 3.0, 1.15 and 1.25, respectively. Their temperature dependent uncertainties are listed as 0 ± 250 and -260 ± 130 for O and NO . The three ClO channels are listed as -430 ± 200 (OClO), -220 ± 200 (ClOO) and -170 ± 200 (BrCl).

The reaction of $\text{BrO} + \text{HO}_2$ is quite uncertain, with an $f(298)$ of 3, as are the products, but HOBr is possible. Nothing seems to be known about HOBr photochemistry.

The termolecular reaction of $\text{BrO} + \text{NO}_2$ has recently been reinvestigated (Danis, et al., Chem. Phys. Lett. 167, 450-456, 1990). They measured a low pressure limit of k_0 at room temperature that is 20% lower than NASA's 1990 evaluation. Their value of n ($k = k_0^{300} [T/300]^{-n}$) is also lower (2.0 vs. 3.8 ± 1.0 for NASA). This reaction clearly needs a reevaluation.

Comments on HBr Reactions

The reactions of OH and O with HBr are reasonably well known, with NASA $f(298)$'s of 1.2 and 1.3, respectively.

Comments on Photolysis Reactions

The BrO photodissociation spectrum is reasonably well known and has been evaluated by NASA (1990).

The BrONO₂ cross section has only been measured once, in 1978, and then only at room temperature. The BrO + NO₂ + H kinetics suggest the possibility of more than one BrNO₃ isomer, so more than one photodissociation cross section may be required. Nothing is known about the BrONO₂ photodissociation products. By analogy with ClONO₂ a best working guess would be 90% Br + NO₃ and 10% O + BrNO₂.

No measurements of HOBr photodissociation properties are presently available.

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Appendix D

Description of the AER one-dimensional photochemical transport model

Results from the AER 1-D model have been described in several publications (Fisher et al, 1990; Rodriguez et al, 1988; Ko and Sze, 1983; Sze and Ko, 1980). The model simulates the vertical distribution of about 50 species interacting through over 150 elementary reactions. The species included in the model are given in table 1. The kinetic data are based on the recommendation of the NASA-JPL panel (DeMore et al, 1990).

The model simulates the vertical distribution of the species by parameterizing transport in terms of a vertical eddy diffusion formalism. It calculates the distributions of the source gases (N_2O , CH_4 , organic chlorine species and organic bromine species), the corresponding radical species (oxygen, nitrogen, hydrogen, chlorine and bromine) and ozone, taking into account all the photochemical and radiation couplings and feedbacks among the species. Calculated distributions of the species have been extensively compared to available observations for validation.

While the utility of the 1-D model is somewhat limited by its inability to simulate the latitudinal and seasonal behavior of the trace gases, it remains a useful tool for obtaining first order assessment of various effects. The parallel effort at AER of continuous updating both the 1-D and 2-D models assures us that results from the 1-D model are properly interpreted.

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Table D-1. Summary of Chemical Species Included in AER 1-D Model

Fixed species

M	Bulk air density calculated from ideal gas law
O ₂	Set equal to 21% of M
H ₂ O	Stratospheric values parameterized from the LIMS observation Tropospheric values calculated from seasonally varying relative humidity determined from climatology

Long-lived species

N₂O
 CH₄, H₂, CO
 CH₃Cl, CH₃CCl₃, CCl₄
 CFC-11, CFC-12, HCFCs, HFCs
 CF₂O, CFC₂O, CCl₂O
 CH₃Br, Halon-1301, Halon-1211
 NO_y = N + NO + NO₂ + NO₃ + 2 x N₂O₅ + HNO₃ + ClNO₃ + HNO₄
 Cl_y = Cl + ClO + ClNO₃ + HCl + HOCl + OClO + 2 x Cl₂O₂
 Br_y = Br + BrO + BrNO₃ + HBr + HOBr + 2 x Br₂
 O_x = O + O(¹D) + O₃

Radical species

Oxygen	O, O(¹ D)
Hydrogen	H, OH, HO ₂ , H ₂ O ₂
Methyl	CH ₃ O ₂ , CH ₂ O, CH ₃ OOH
Nitrogen	N, NO, NO ₂ , NO ₃ , N ₂ O ₅ , HNO ₃ , ClNO ₃ , HNO ₄
Chlorine	Cl, ClO, ClNO ₃ , HCl, HOCl, OClO, Cl ₂ O ₂
Bromine	Br, BrO, BrNO ₃ , HBr, HOBr, Br ₂

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1/3/1

0215777 Enviroline Number: *91-006602
ATMOSPHERIC CHEMISTRY OF TOXIC CONTAMINANTS. 4. SATURATED HALOGENATED
ALIPHATICS: METHYL BROMIDE, EPICHLORHYDRIN, PHOSGENE,
GROSJEAN DANIEL DANIEL GROSJEAN & ASSOC, VENTURA, CA,
AIR & WASTE MANAGEMENT ASSN J, JAN 91, V41, N1, P56(6)
THE ORIGINAL DOCUMENT IS AVAILABLE FROM BOWKER

1/3/2

0214563 Enviroline Number: *91-005388
ATMOSPHERIC CHEMISTRY OF TOXIC CONTAMINANTS 1. REACTION RATES AND
ATMOSPHERIC PERSISTENCE,
GROSJEAN DANIEL DGA INC, VENTURA, CA,
AIR & WASTE MANAGEMENT ASSN J, OCT 90, V40, N10, P1397(6)
THE ORIGINAL DOCUMENT IS AVAILABLE FROM BOWKER

1/3/3

0211056 Enviroline Number: *91-001880
NON-DESTRUCTIVE METHOD FOR ESTIMATING METHYL BROMIDE RESIDUES IN APPLES
DURING AERATION FOLLOWING FUMIGATION,
SELL CHARLES R. AND ; MOFFITT HAROLD R. USDA, YAKIMA, WA,
PESTICIDE SCIENCE, 1990, V29, P19(9)
THE ORIGINAL DOCUMENT IS AVAILABLE FROM BOWKER

1/3/4

0205314 Enviroline Number: *90-002862
METHYL BROMIDE RESIDUES IN FUMIGATED MANGOS,
STEIN EDUARDO R. AND ; WOLFENBARGER DAN A. SUBTROPICAL AGRICULTURAL
RESEARCH LAB, WESALCO, TX,
J AGRICULTURAL & FOOD CHEMISTRY, NOV-DEC 89, V37, N6, P1507(3)
THE ORIGINAL DOCUMENT IS AVAILABLE FROM BOWKER

1/3/5

0197561 Enviroline Number: 89-001631
IN VITRO METHYLATION OF DNA BY THE FUMIGANT METHYL BROMIDE,
STARRATT ALVIN N. AND ; BOND EDWIN J. AGRICULTURE CANADA,
J ENV SCIENCE & HEALTH-PESTICIDES FOOD CONTAMINANTS & AGRI WASTES, 1988,
VB23, N5, P513(13)

File 292:GEOBASE 1980 - JAN 92
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✓ 7/3/1

0870558 91J-13641

Atmospheric chemistry of toxic contaminants. 4. Saturated halogenated aliphatics: methyl bromide, epichlorhydrin, phosgene

Grosjean, D.

DGA, Inc., Suite 205, 4526 Telephone Rd, Ventura, CA 93003, USA

Journal - Air & Waste Management Association 1991. v 41(1) pp 56-61

Language: English

7/3/2

0857813 91J-10206

Atmospheric chemistry of toxic contaminants 1. Reaction rates and atmospheric persistence

Grosjean, D.

Daniel Grosjean & Assoc. Inc., Suite 205, 4526 Telephone Road, Ventura, CA 93003, USA.

Journal - Air & Waste Management Association 1990. v 40(10) pp 1397-1402

Language: English

7/3/4

0743706 89J-00829

Measurements of atmospheric methyl bromide and bromoform

Cicerone, R. J. ; Heidt, L. E. ; Pollock, W. H.

National Centre for Atmospheric Research, Boulder, CO, USA

Journal of Geophysical Research 1988. v 93(D4) pp 3745-3749

Language: English

ISSN 0148 - 4184

7/3/6

0504725 86B-1522

Brominated organic species in the Arctic atmosphere.

BERG, W. W.; HEIDT, L. E.; POLLOCK, W.; SPERRY, P. D.; CICERONE, R. J.; GLADNEY, E. S.

Nat. Center for Atmospheric Research, P.O.Box 3000, Boulder, Colorado 80307, USA.

Geophysical Research Letters 1984. v 11(5) pp 429-432.

Language: English

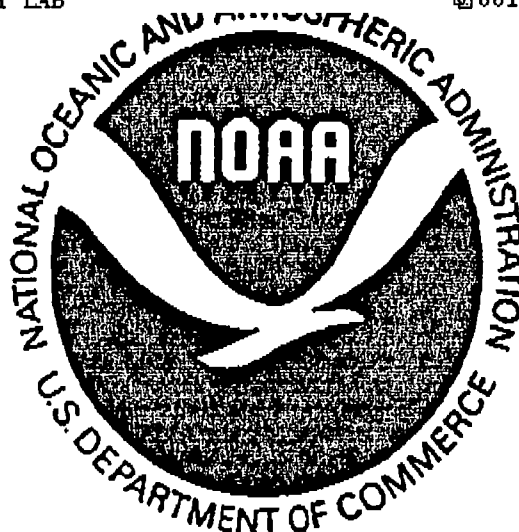
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ISSN 0190 - 6928

Dr. Ralph J. Cicerone
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Chemistry
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AERONOMY LABORATORY FACSIMILE COVER SHEET

DATE: 2/21/92PAGE: 1 OF 2

FROM

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SUSAN SOLOMON

TELEPHONE NUMBER

(303) 497-3483

RAPIFAX NUMBER

FTS 320-5373; Commercial (303) 497-5373

VERIFY NUMBER

FTS 320- ; Commercial (303) 497-

TO

NAME

Katie McGinty

TELEPHONE NUMBER

RAPIFAX NUMBER

(202) 224-0880PRELIMINARY

ADDITIONAL REMARKS:

Attached you'll find our analysis of the cumulative probability distribution functions for ODP's for HCFC-22, CH_3CCl_3 , CH_3Br , and CFC-113, done in the same way as in UNEP (1991). Please keep these confidential for now, since we are still checking the numbers. But you can see that present understanding suggests that:

- ① the probability of CH_3Br 's ODP being under 0.2 appears to be under 10% using the UNEP analysis.
- ② CH_3Br 's ODP is between those of CH_3CCl_3 and CFC-113, and is closer to the latter than the former. Let's talk by phone before the meeting, if possible.

DRAFT

NOT FOR
DISTRIBUTION

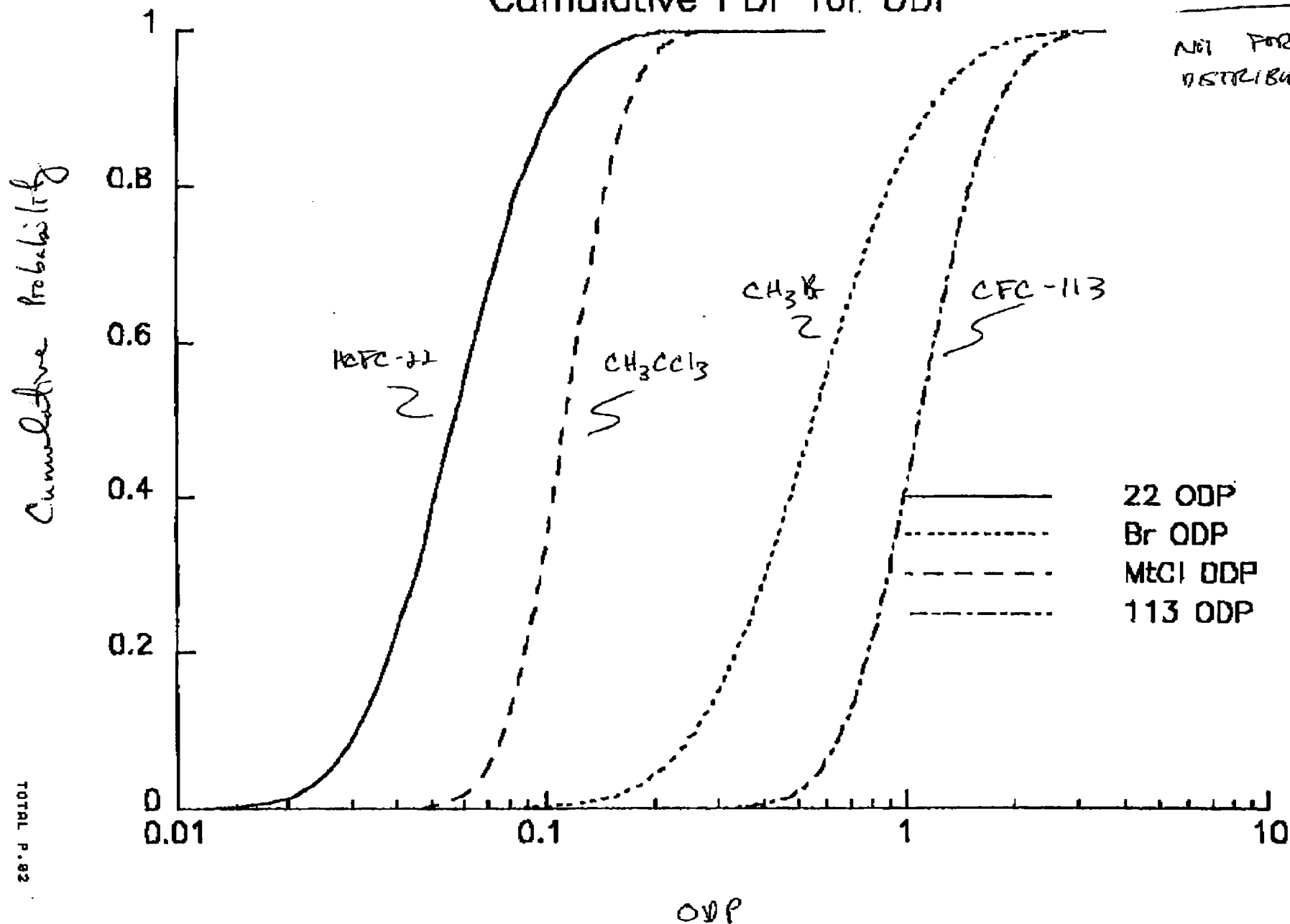
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ERL AERONAUT LAB

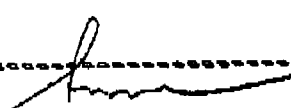
0002

Cumulative PDF for ODP



**Aeronomy Laboratory**

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FROM: Dr. Susan Solomon 
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TO: Katie McGinty
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DATE: February 24, 1992

Page 1 of 11

Dear Katie,

Attached please some material relevant to the ODP for CH₃Br and its uncertainties. It is an extension of the material in Solomon et al. (1992) and UNEP (1991) and includes a detailed propagation of error terms. The bottom line is that the probability of CH₃Br's ODP being below 0.2 is at most 11.2% and likely to be closer to a few percent. You probably want to look at Table 2, which compares CH₃Br to two other compounds which have already been regulated, namely CFC-113 and methyl chloroform. This analysis shows that the probability that CH₃Br's ODP lies between the two, closer to CFC-113 than methyl chloroform. I will come to the meeting Wednesday with a few extra copies of this material.

It appears that an error was made in evaluating the uncertainty in the rate constant for OH+CH₃Br at 277K in the Sze and Ko summary of the ODP for CH₃Br, as discussed in the following. Correct analysis significantly narrows the uncertainty.

Any comments on the attached are welcome.

-Susan Solomon

*P.S. Looking forward to seeing you on
Wed. —*

Extension of semi-empirical ODP method to CH₃Br and its uncertainties (after Solomon et al., 1992 and UNEP, 1991)

S. Solomon and M. J. Mills, NOAA Aeronomy Laboratory

1. Formalism for semi-empirical ODP estimate

Following Solomon et al. (J. Geophys. Res., vol. 97, 825-842, 1992), the ODP for brominated compounds can be defined as:

$$\text{BODP} = \tau_x / \tau_{\text{CFC-11}} \cdot M_{\text{CFC-11}} / M_x \cdot k_x / 3 \cdot A \cdot B \cdot C$$

where τ_x is the atmospheric lifetime of the species considered, $\tau_{\text{CFC-11}}$ is the atmospheric lifetime of the reference gas, $M_{\text{CFC-11}}$ and M_x are the molecular weights of CFC-11 and the species considered, k_x is the number of bromine atoms in the molecule, A is an efficiency factor that quantifies the effectiveness of bromine for ozone loss, B is the fraction of total observed loss that takes place in region considered (1 for the global case) and C is a factor that describes the fractional stratospheric dissociation of CH₃Br compared to the reference gas where the ozone loss occurs. In Solomon et al. (1992), polar regions were emphasized in deducing values of A, B and C. The values of $M_{\text{CFC-11}}$, k_x , and M_x are known essentially exactly.

Like model estimates, the semi-empirical approach requires knowledge of the lifetimes. It makes use of observations rather than models to constrain the factors A, B, and C.

2. Estimates of A, B, and C

Work presented subsequent to the publication of Solomon and co-workers [in particular, UNEP (1991) and McCormick et al. (in press, Geophys. Res. Lett., 1992)] confirms that the bulk of atmospheric ozone destruction takes place in the lowest part of the stratosphere where bromine is particularly effective at destroying ozone. Here the global BODP is deduced by using values of A and B appropriate to a global average. (Hence B is taken to be 1).

Solomon et al. (1992) assumed that the fractional dissociation of CH₃Br would be at least equal to that of CFC-11 within the stratosphere since both have short stratospheric lifetimes. Airborne measurements of CH₃Br and CFC-11 confirm that this is true (Figures 1 and 2 attached show that the fractional dissociation of CH₃Br is actually slightly greater than that of CFC-11, consistent with its somewhat shorter stratospheric lifetime). A multiplicative factor (C) has been introduced in the above equation to account for this. C is taken to be 1.0 with an uncertainty factor of 10%, recognizing that Figures 1 and 2 imply that this will lead to a slight underestimate for the ODP.

Solomon et al. showed that observations of ClO, BrO, and OClO reveal that the value of A is approximately 40 in the polar lower stratosphere. Measurements obtained during the AASE II aircraft mission confirm and expand earlier findings from AAOE and AASE I showing that ClO abundances in the lower stratosphere at middle latitudes are higher than gas-phase model predictions. Since the rate-limiting step governing the bulk of the ozone loss due to bromocarbons is the reaction between ClO and BrO, this finding increases the sensitivity of the lower stratosphere to ozone loss due to bromine. A value for A of 40 is

assumed in the following analysis, with an uncertainty factor of 50% and is considered conservative.

3. Lifetimes

The value of $\tau_{\text{CFC-11}}$ is assumed to be 55 years with an uncertainty of 30%, following UNEP (1991). The NASA CFC lifetime panel suggests that the uncertainty is about 15%, from both model studies and release data; hence, the number adopted here is conservative.

The only remaining uncertainty is that associated with the lifetime of CH_3Br , determined by the following reaction:



There are two uncertainties in the lifetime of CH_3Br : the rate constant for this reaction at about 277K and the globally averaged OH concentration.

a) rate constant at 277K

The document by Sze and Ko states that the range in this rate constant at 277K is a factor of 4 (or $\pm 200\%$). This is incorrect and results from an incorrect application of uncertainty factors in kinetic rate studies. One must be careful to consider that rate constants are almost always known with minimum uncertainty at room temperature (298K). As noted in JPL (1990) (attached), the uncertainty at a temperature T cannot be evaluated from the expression $A\exp(-B/T)$, as was apparently done in the document by Sze and Ko.

Rather, one must use the following equation (from JPL, 1990, attached):

$$\text{uncertainty}(T) = \text{uncertainty}(298) * \exp[\Delta E/R (1/T - 1/298)]$$

JPL (1990) reports a rate constant for OH with CH_3Br of $6.8 \times 10^{-13} \exp(-(850 \pm 200)/T)$, with an uncertainty factor at 298K of 25%. Application of the above equation to the uncertainty factors given in JPL (1990) shows that the uncertainty in the rate constant for $\text{OH} + \text{CH}_3\text{Br}$ at 277K is 32%. Proper evaluation of the IUPAC rate constants gives a similar value.

A new study by Ravishankara and co-workers suggests $(2.17 \pm 0.28) \times 10^{-12} \exp(-(1280 \pm 100)/T)$, with an uncertainty at 277K of about 16%.

b) globally averaged OH concentration

The study by Prinn et al. (in press, JGR, 1992) has made use of CH_3CCl_3 data to constrain the globally averaged OH concentration. They find $8.1 \pm 0.9 \times 10^5$ molecules/ cm^3 (including the hydrolysis of CH_3CCl_3 in the ocean). This value is adopted here.

4. Analysis of the ODP and related statistical uncertainties

The attached figures show cumulative probability distributions for the ODP for CH_3Br calculated with these parameters, assuming both the JPL (1990) rate constant and assuming the Ravishankara et al. rate constant as discussed above. This uncertainty analysis follows the same approach as that given in UNEP (1991). The ODPs for HCFC-22, CFC-113, and CH_3CCl_3 are included for comparison. The figures show the statistical probability that the ODP will be below a certain value and indicate that the ODP for CH_3Br lies between those of CFC-113 and CH_3CCl_3 . The tables on the next page summarize the inputs and the results.

Table 1. Summary of uncertainties considered in generating the figures.

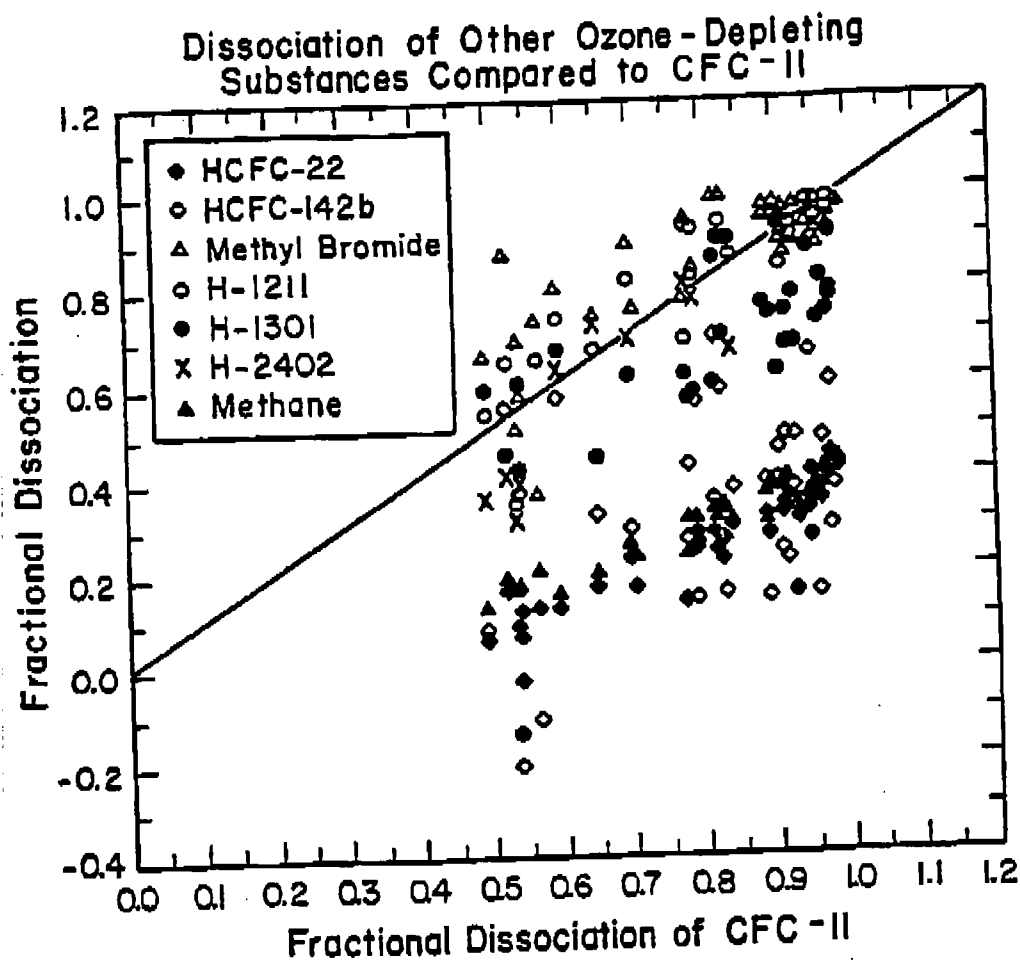
Factor	Value	Uncertainty ($\pm$) and source
Global average OH	8.1×10^5	0.9×10^5 (from Prinn et al.)
$\tau_{\text{CFC-11}}$	55 years	30% (UNEP, 1991)
A	40	50% (Solomon et al., 1992)
C	1.0	10%
k for $\text{CH}_3\text{Br} + \text{OH}$	JPL (1990)	32% at 277K
	Ravishankara	16% at 277K
$\tau_{\text{CH}_3\text{CCl}_3}$	5.7 years	12% (from Prinn et al.)
$\tau_{\text{CFC-113}}$	110 years	30% (UNEP, 1991)

Table 2. Probability that the ODP is below a particular value for each gas. Two sets of values are given for CH_3Br . The first set is based on the JPL (1990) reaction rate constant. The set in parentheses is based on Ravishankara's rate constant.

Gas	ODP	Probability that the ODP is below this value	
CFC-113	3.0	nearly 100%	
	2.0	94%	
	1.0	42%	
	0.5	2%	
	0.2	nearly zero	
	0.1	nearly zero	
CH_3Br	3.0	nearly 100%	(nearly 100%)
	2.0	99.5%	(99%)
	1.0	94%	(83%)
	0.5	65%	(35%)
	0.2	11%	(2%)
	0.1	less than 1%	(nearly zero)
CH_3CCl_3	3.0	nearly 100%	
	2.0	nearly 100%	
	1.0	nearly 100%	
	0.5	nearly 100%	
	0.2	97%	
	0.1	34%	
HCFC-22	3.0	nearly 100%	
	2.0	nearly 100%	
	1.0	nearly 100%	
	0.5	nearly 100%	
	0.2	nearly 100%	
	0.1	88%	

Value of C from
stratospheric measurements

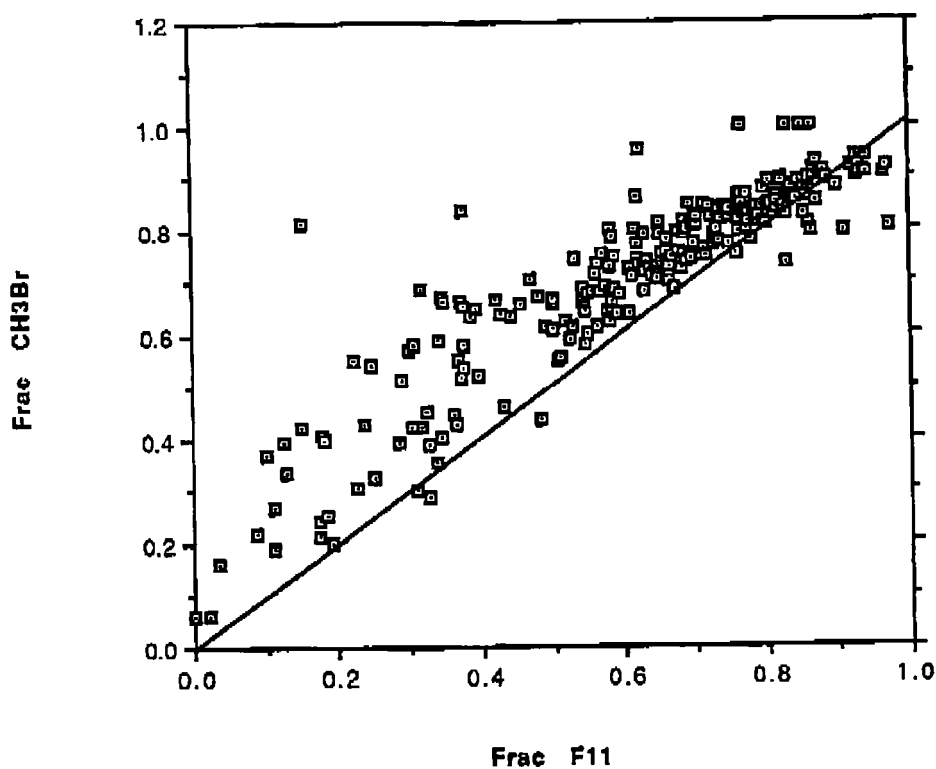
AASE I



Value of C

AASE II

AASE II October, 1991 - January, 1992



JPL Publication 90-1

Solomon
Uncertainty
in k

Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

Evaluation Number 9

NASA Panel for Data Evaluation:

W.B. DeMore
S.P. Sander
Jet Propulsion Laboratory

D.M. Golden
SRI International

M.J. Molina
Massachusetts Institute of Technology

R.F. Hampson
M.J. Kurylo
National Bureau of Standards

C.J. Howard
A.R. Ravishankara
NOAA Environmental Research Laboratory

January 1, 1990

NASA

National Aeronautics and
Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Uncertainty
in kUncertainty Estimates

For second-order rate constants in Table 1, an estimate of the uncertainty at any given temperature may be obtained from the following expression:

$$f(T) = f(298) \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

An upper or lower bound (corresponding approximately to one standard deviation) of the rate constant at any temperature T can be obtained by multiplying or dividing the value of the rate constant at that temperature by the factor f(T). The quantities f(298) and $\Delta E/R$ are, respectively, the uncertainty in the rate constant at 298 K and in the Arrhenius temperature coefficient, as listed in Table 1. This approach is based on the fact that rate constants are almost always known with minimum uncertainty at room temperature. The overall uncertainty normally increases at other temperatures, because there are usually fewer data and it is almost always more difficult to make measurements at other temperatures. It is important to note that the

Uncertainty in k

uncertainty at a temperature T cannot be calculated from the expression $\exp(\Delta E/RT)$. The above expression for $f(T)$ must be used to obtain the correct result.

The uncertainty represented by $f(T)$ is normally symmetric; i.e., the rate constant may be greater than or less than the central value, $k(T)$, by the factor $f(T)$. In a few cases in Table 1 asymmetric uncertainties are given in the temperature coefficient. For these cases, the factors by which a rate constant are to be multiplied or divided to obtain, respectively, the upper and lower limits are not equal, except at 298 K where the factor is simply $f(298 \text{ K})$. Explicit equations are given below for the case where the temperature dependence is $(E/R + a, -b)$:

For $T > 298 \text{ K}$, multiply by the factor

$$f(298 \text{ K})e^{[a(1/298-1/T)]}$$

and divide by the factor

$$f(298 \text{ K})e^{[b(1/298-1/T)]}$$

For $T < 298 \text{ K}$, multiply by the factor

$$f(298 \text{ K})e^{[b(1/T-1/298)]}$$

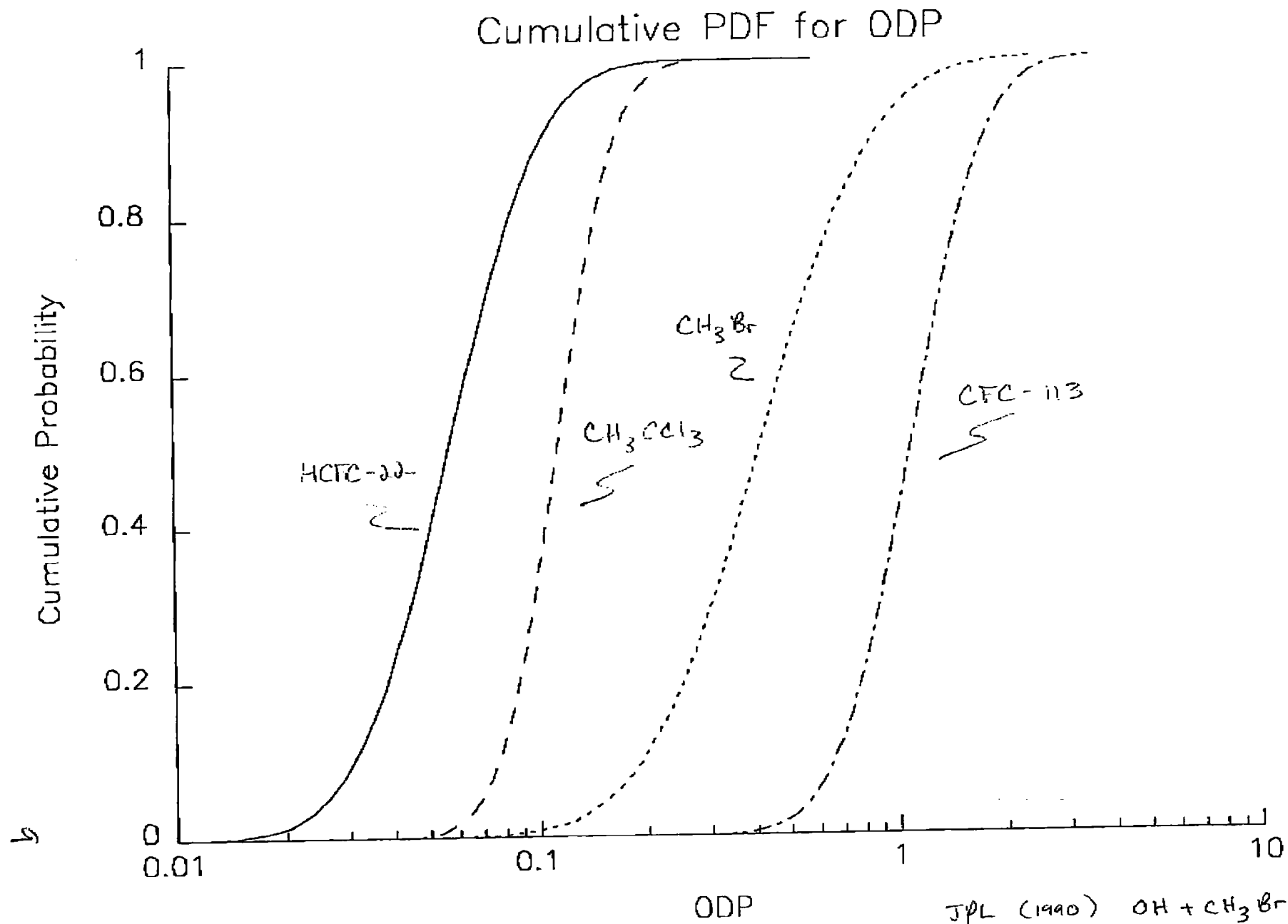
and divide by the factor

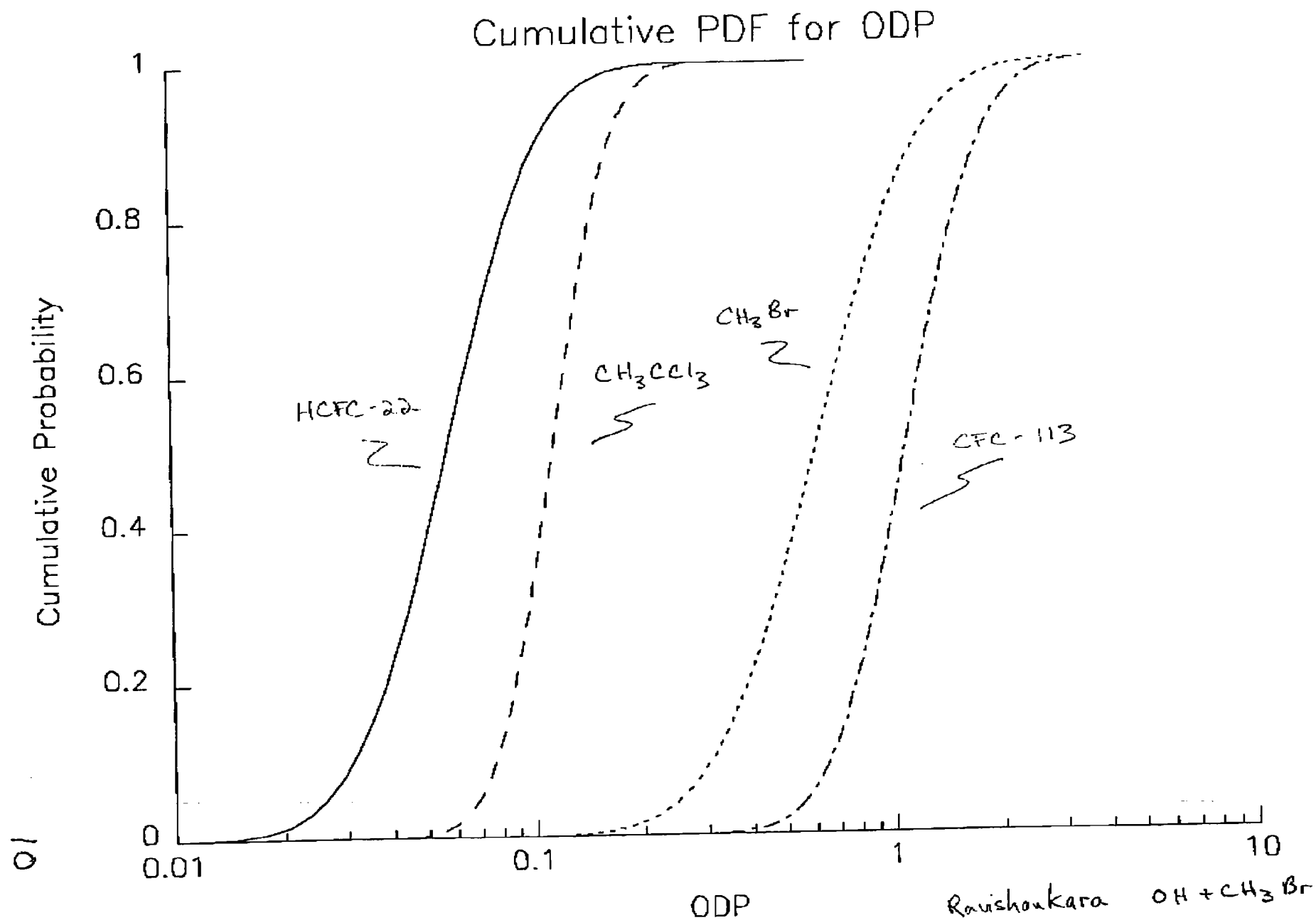
$$f(298 \text{ K})e^{[a(1/T-1/298)]}$$

Examples of symmetric and asymmetric error limits are shown in Figure 1.

For three-body reactions (Table 2) a somewhat analogous procedure is used. Uncertainties expressed as increments to k_0 and k_∞ are given for these rate constants at room temperature. The additional uncertainty arising from the temperature extrapolation is expressed as an uncertainty in the temperature coefficients n and m .

The assigned uncertainties represent the subjective judgment of the Panel. They are not determined by a rigorous, statistical analysis of the data base, which generally is too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experiments, and the potential for systematic errors. There is obviously no way to quantify these "unknown" errors. The spread in results among different techniques for a given reaction may provide some basis for an uncertainty, but the possibility of the same, or compensating, systematic errors in all the studies must be recognized. Furthermore, the probability distribution may not follow the normal, Gaussian form. For measurements subject to large systematic errors, the true rate constant may be much further from the recommended value than would be expected based on a Gaussian distribution with the stated uncertainty. As an example, the recommended rate constants for the reactions $\text{HO}_2 + \text{NO}$ and $\text{Cl} + \text{ClONO}_2$ have changed by factors of 30-50, occurrences which could not have been allowed for with any reasonable values of σ in a Gaussian distribution.





**Aeronomy Laboratory**

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FROM: Dr. Susan Solomon
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TO: Katie McGinty
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DATE: February 25, 1992

Page 1 of 2

Dear Katie,

FYI, I sent our analysis of the uncertainty in the CH₃Br ODP out to the following individuals yesterday:

Yourself
Steve Seidel (EPA)
Bob Watson (NASA)
Nien Dak Sze (AER, Inc.: the scientists hired by the CH₃Br manufacturers)

I included Dr. Sze in the interest of scientific honesty and fairness. Obviously, I could have just brought the document to the meeting and distributed it, giving them no chance to study it. I chose not to do that. I wear contacts, and have to look myself in the mirror every morning.

Anyway, there have, as you might guess, been a few flurried phone calls this morning. The bottom line is as follows: a) they are extremely embarassed by the fact that a substantial error was made in their analysis and that this may become clear in front of their sponsors and b) they have offered no substantive criticism of our analysis. Tomorrow I am sure that they will come in and try to 'nickle and dime' my numbers by saying, for example, that maybe Dr. Prinn's estimate of the uncertainty in OH

(which I adopted) is too small, etc. I can easily rebut such discussions, but clearly this is the tack they will take.

Suggestions for you and the Senator:

- 1) If possible, we may want to avoid actually coming out and saying that they made an error. It is clear that they did make an error, but maybe backing them into a corner is bad strategy. This will embarrass them into fighting harder and probably isn't necessary.
- 2) One strategy that could be useful would be for the Senator to wait and watch the scientists thrash around for a while arguing about the magnitudes of various uncertainties and then ask the following question: "Do any of the scientists think it is likely (greater than 50% probability) that the ODP of CH₃Br is really less than that of methyl chloroform?" The answer to this question is clearly NO by any standard. Thus, if methyl chloroform releases have been regulated then applying the same standard implies that methyl bromide should also be.

This is going to be a whole lot of fun.

-Susan Solomon

We must know hormone
is significant -- otherwise
it wouldn't be
regulating hormones

Is there any evidence for
the possibility that

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SANTA BARBARA • SANTA CRUZ

F. SHERWOOD ROWLAND
DONALD BREN PROFESSOR OF CHEMISTRY
DEPARTMENT OF CHEMISTRY
IRVINE, CALIFORNIA 92717
(714) 856-6016

DATE:

FEB. 26, 1992

TO:

KATIE MCGINTY ALSO FOR MIKE KURYLO

FAX NO:

202-224-0580

FROM:

F. SHERWOOD ROWLAND
UNIVERSITY OF CALIFORNIA, IRVINE

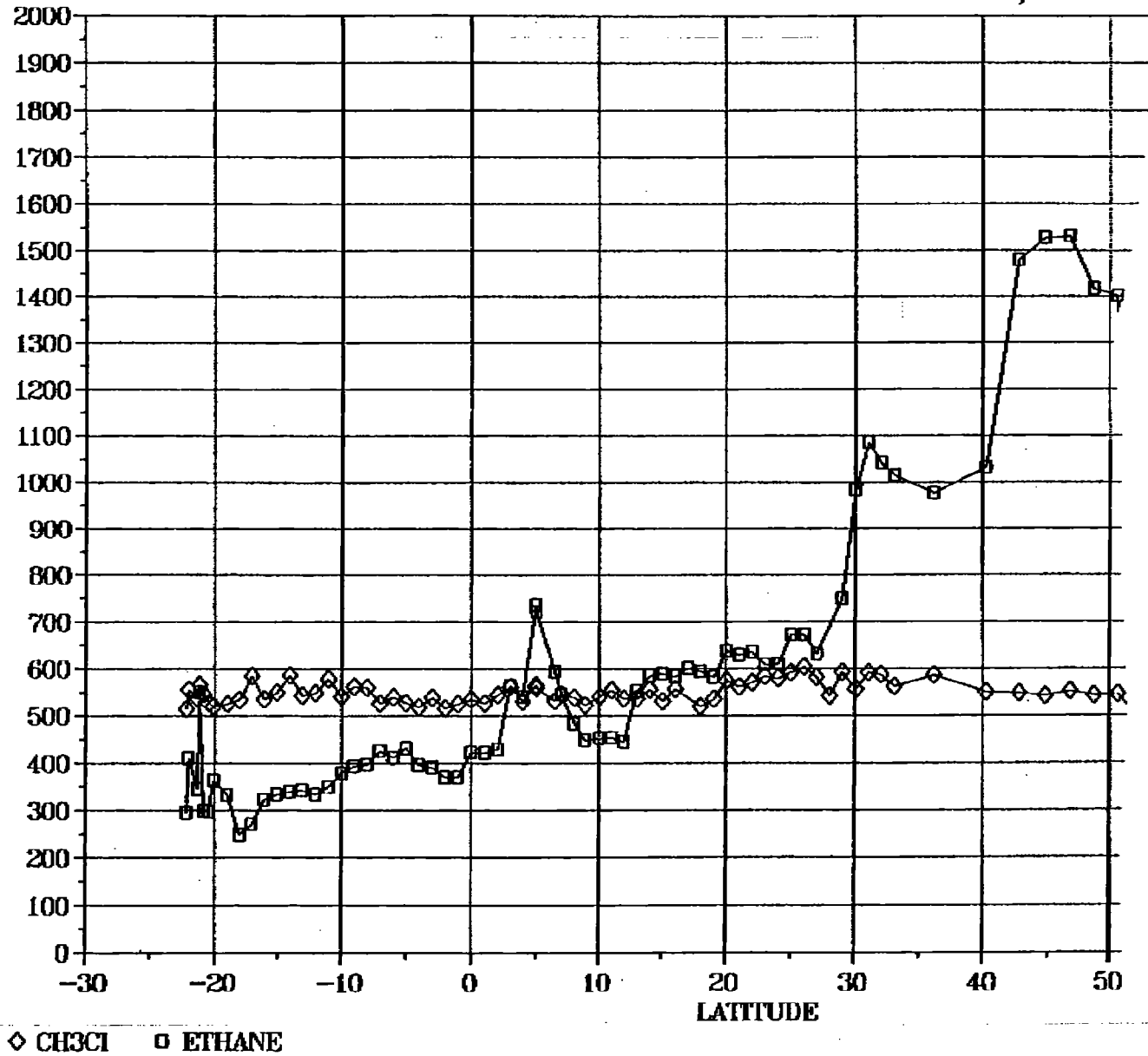
FAX NO.

714-725-2905

RE:

THIS GRAPH SHOWS C_2H_6 AND CH_3Cl
IN THE SAME SAMPLES. CH_3Cl LITTLE
CHANGE; ETHANE (NORTHERN HEMISPHERE
CHIEF SOURCE) FALLS OFF RAPIDLY.

AASE-II MISSIONS 8 & 10 LATITUDE PROFILE @ >30,000ft



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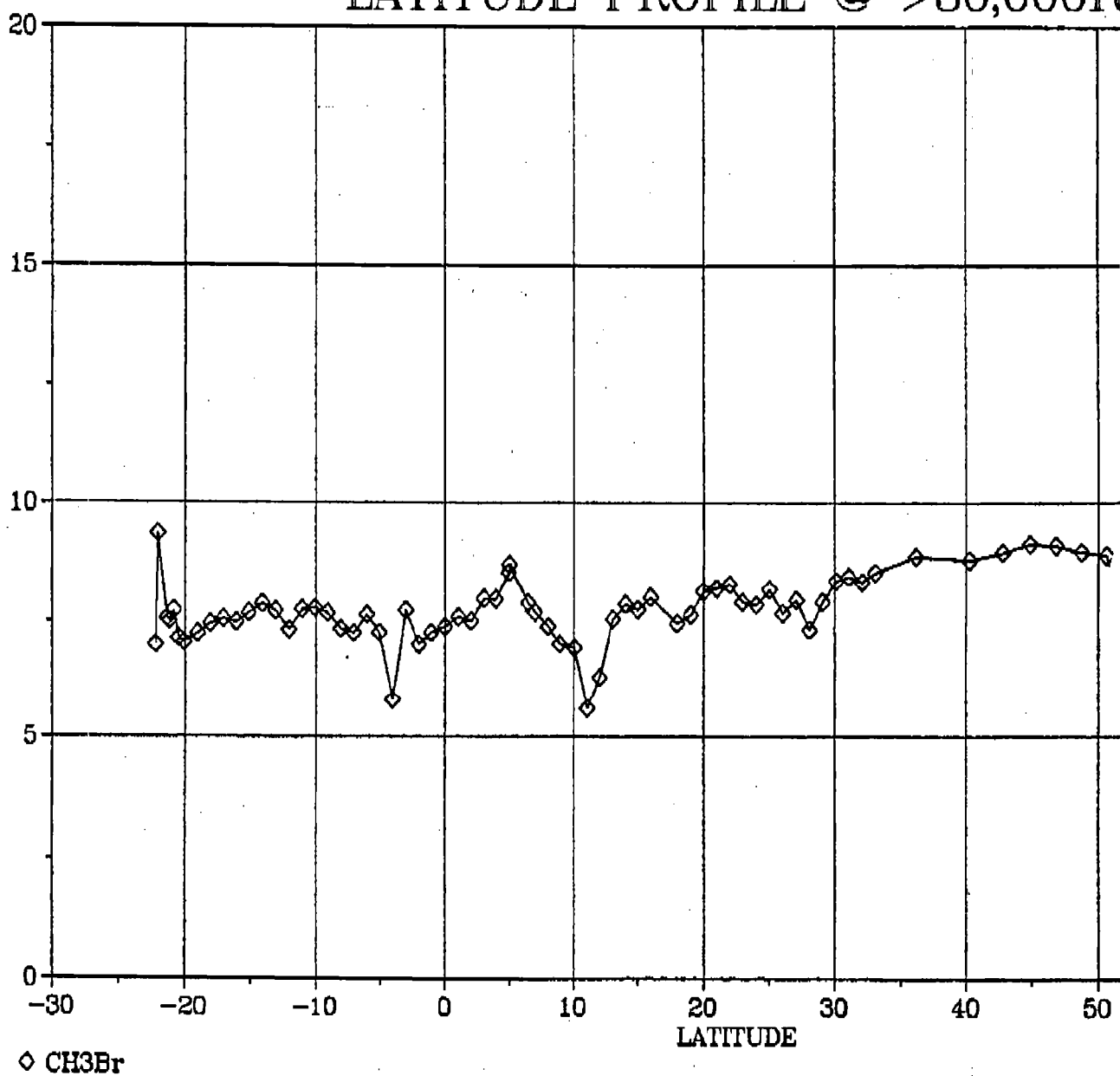
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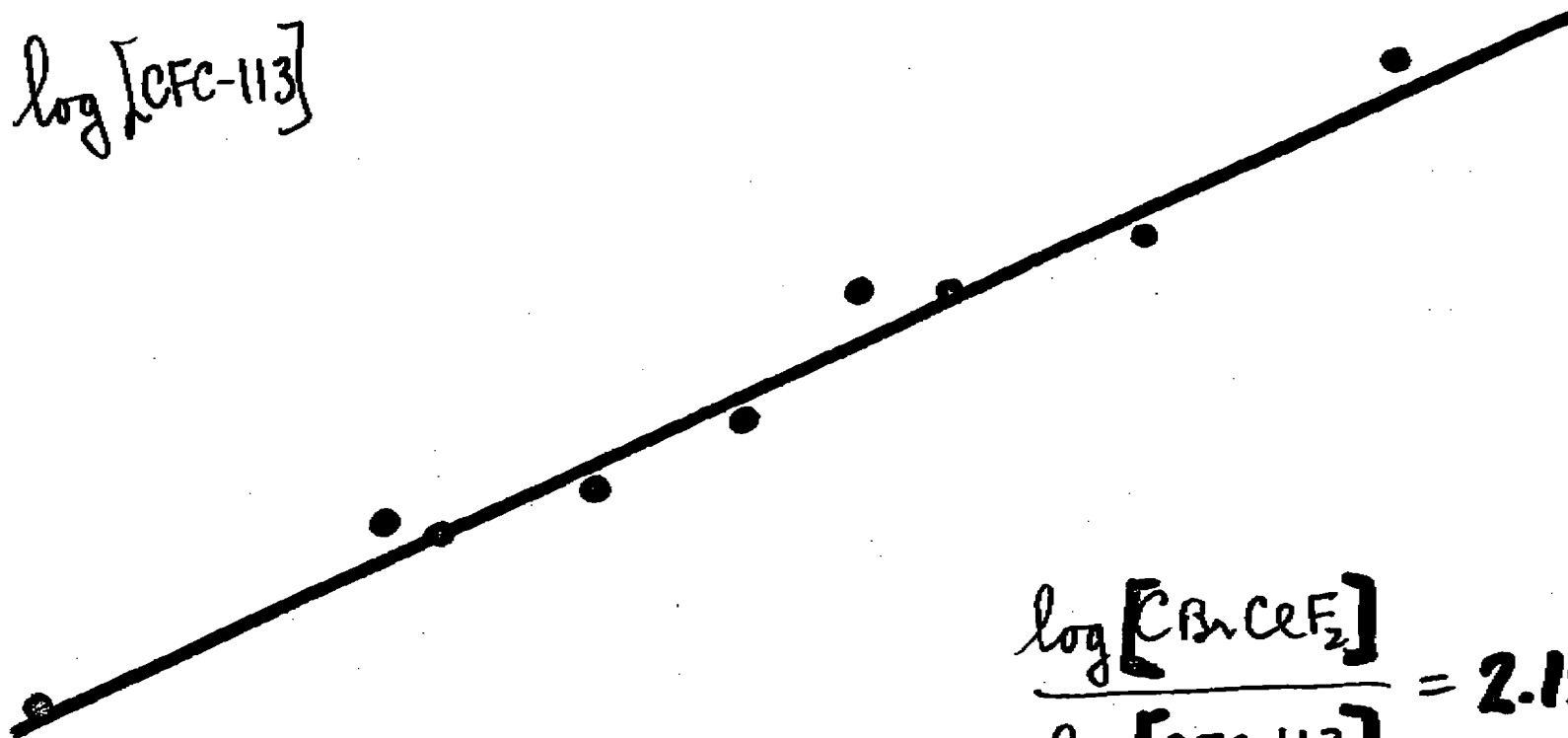
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FASTER THAN CFC-11 (HIGHER #S).

AASE-II MISSIONS 8 & 10
LATITUDE PROFILE @ >30,000ft



AASE-2 MISSION 10

$\log [\text{CFC-113}]$



$$\frac{\log [\text{CBrClF}_2]}{\log [\text{CFC-113}]} = 2.19$$

$$r^2 = 0.95$$

**CORRELATION OF
MIXING RATIOS FROM
9 SAMPLES AT 39,200'
OVER NORTHERN CANADA**

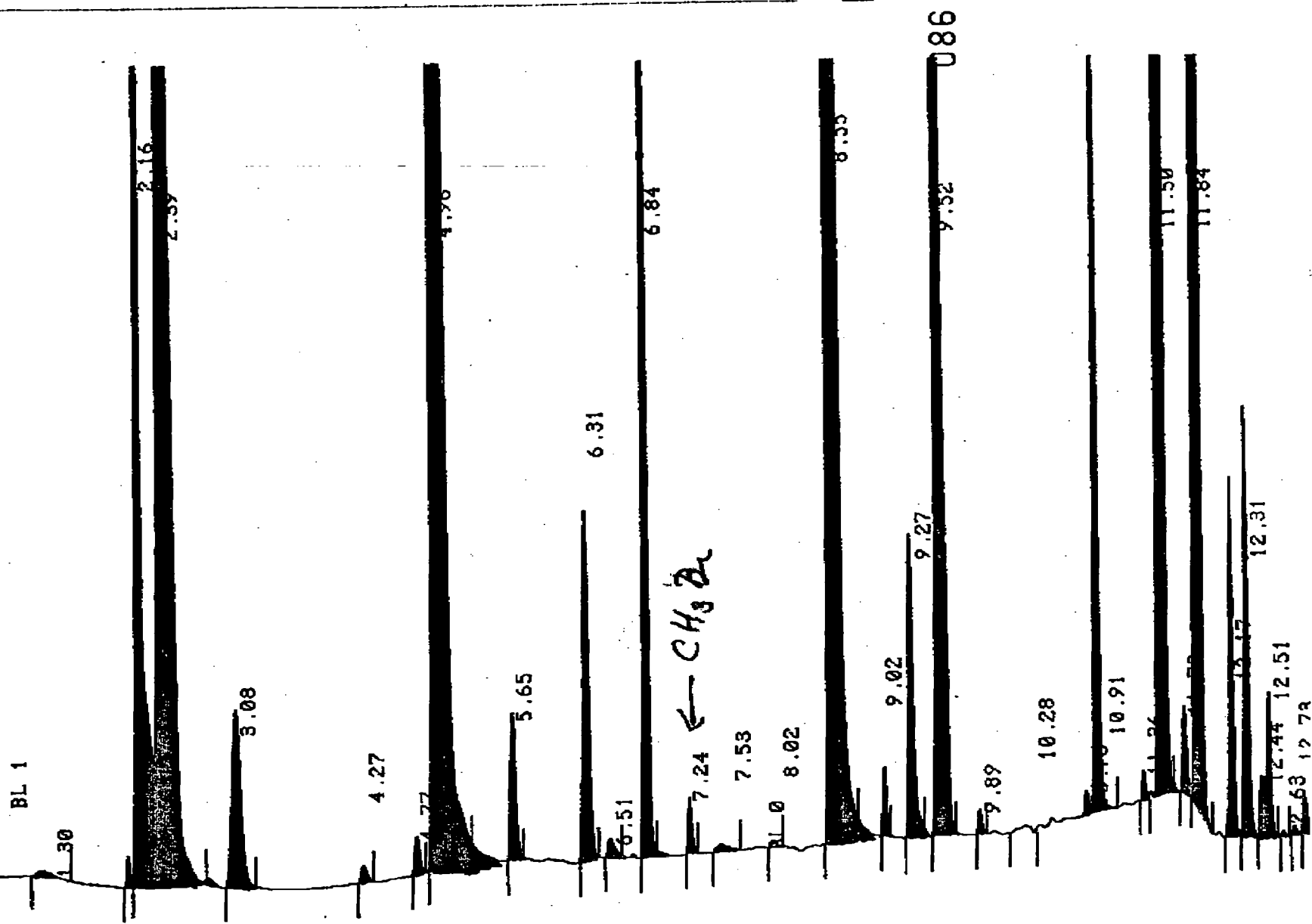
$\log [\text{CBrClF}_2]$

MORE
RAPID
LOSS
IN
STRATO-
SPHERE



CBnClF_2	- -	2.19	(HALON-1211)
CH_3Br	= -	1.69	CH_3CCl_3
CBnF_3	= -	1.39	(HALON-1301)
CCl_4	= -	1.30	CCl_3F (CFC-11)
	= -	1.07	CH_3Cl
	= -	1.00	$\text{CCl}_2\text{FCClF}_2$ (CFC-113)
	= -	0.83	CCl_2F_2 (CFC-12)
N_2O	= -	0.73	
	= -	0.65	CHClF_2 (HCFC-22)
	= -	0.51	$\text{CClF}_2\text{CClF}_2$ (CFC-114)

CHANNEL A A101199.RAW INJECT 02/16/92 13:00:09



MISSION 10 TROPO 20,000'
1190 20,000'

10 MISSION

can't measure OH concentrations
directly, cause too transient.

Using CH_3OCl , as a proxy?

I don't know abt. pt. of
ocean SINK.

Sherry's data is a source
guess.

145

Can we assume the greatest uncertainty
on all g 's - where
does that get us?
How compare w/ what currently
regulate.

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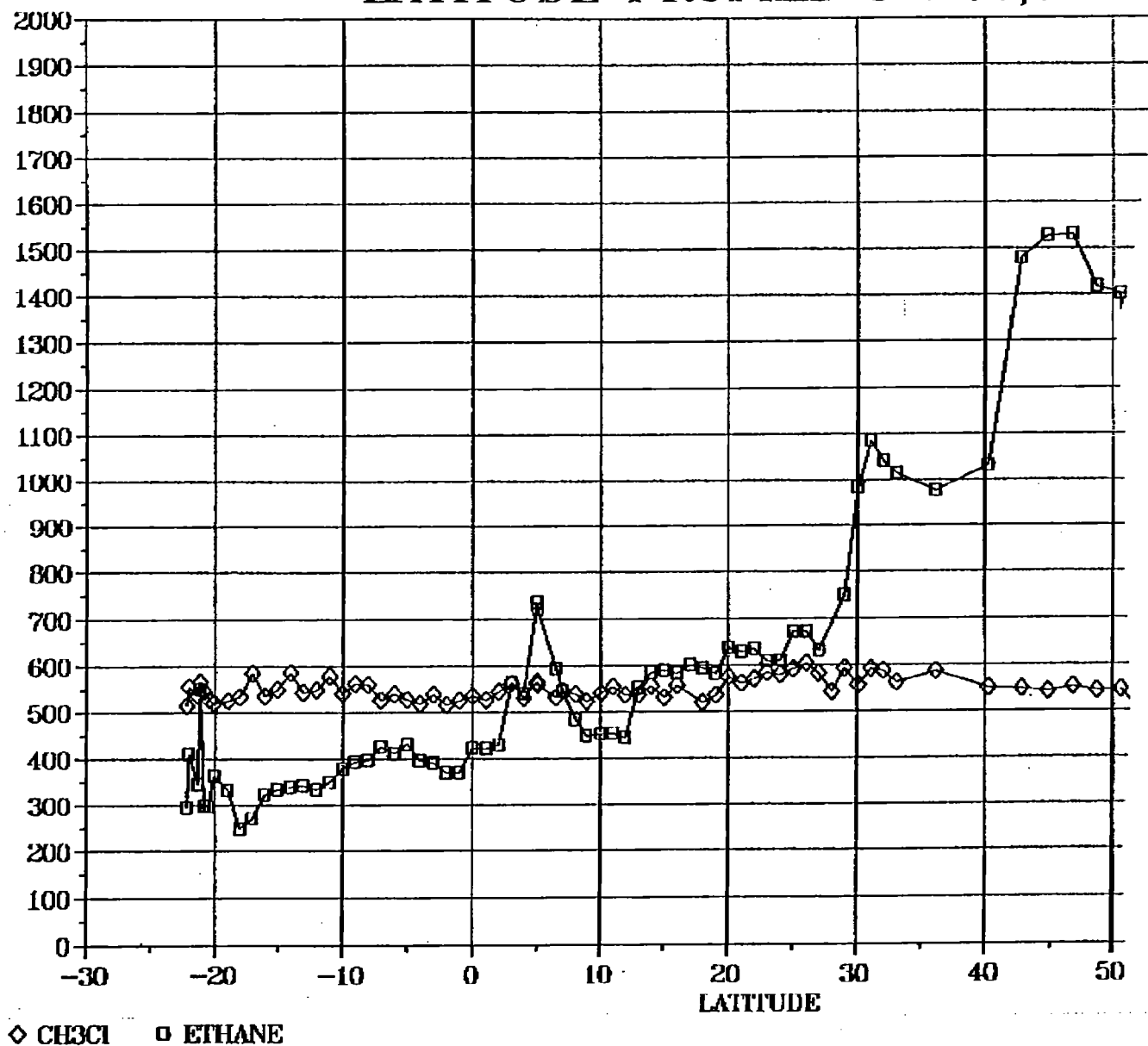
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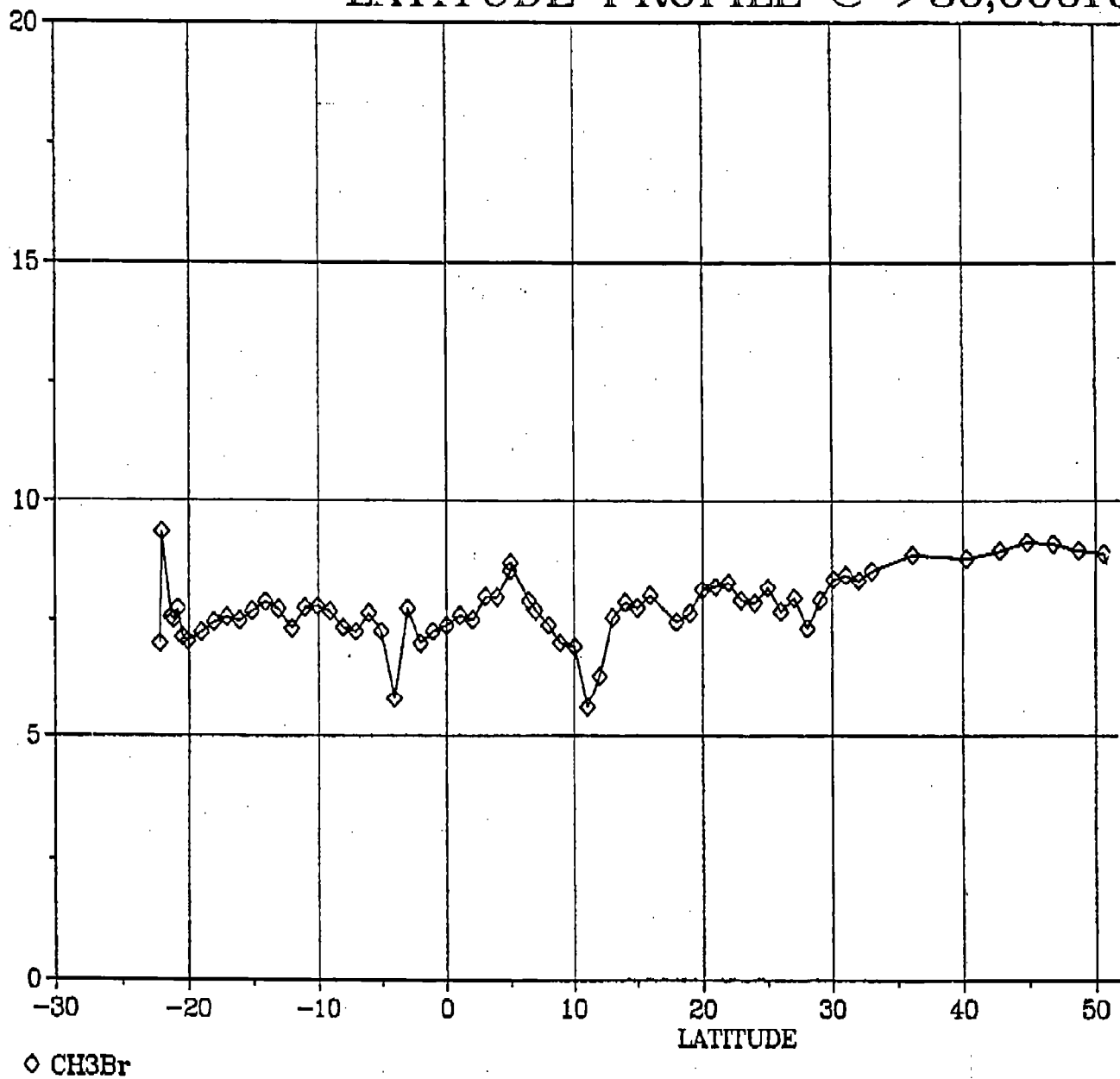
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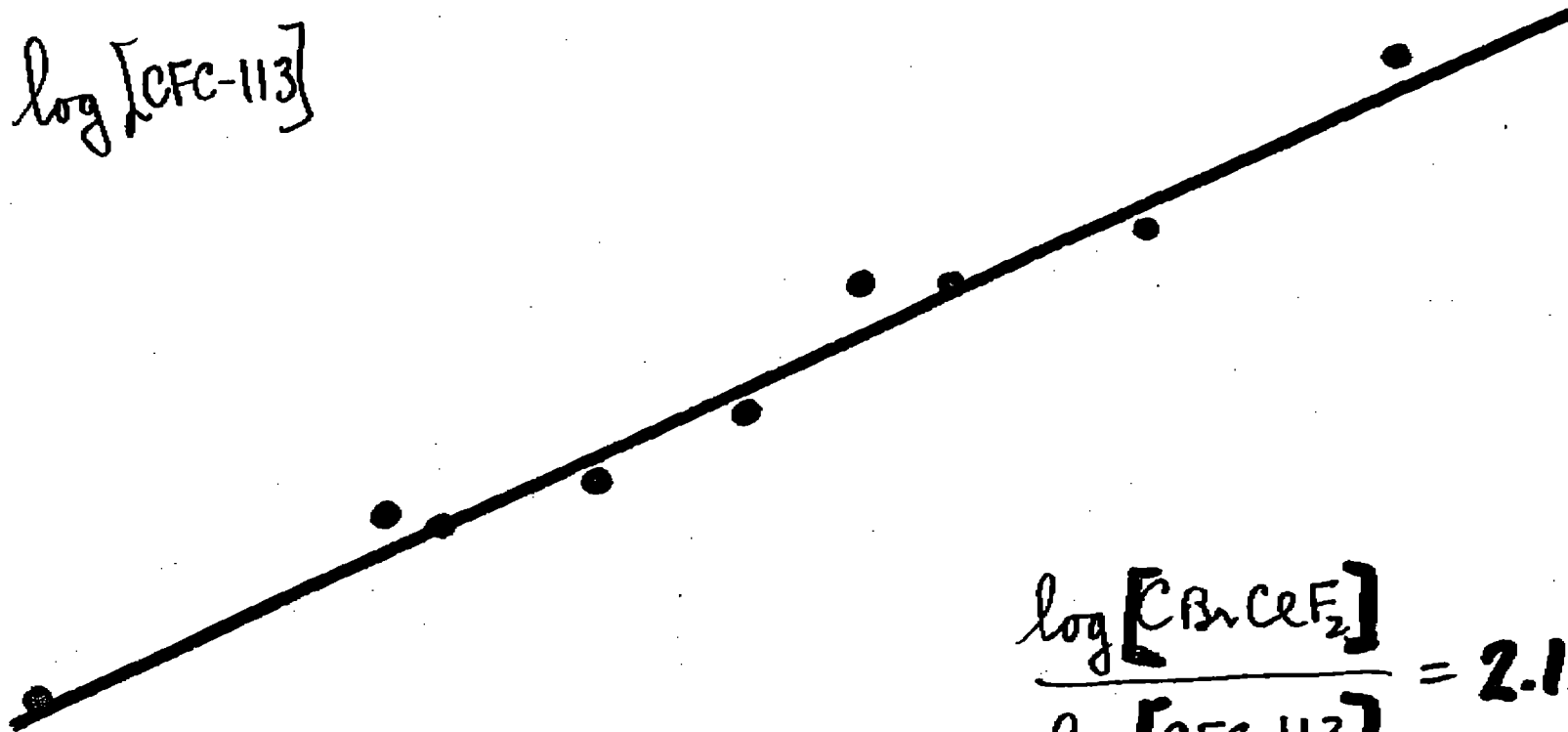
Could be
a problem
w/ Rowland's
data

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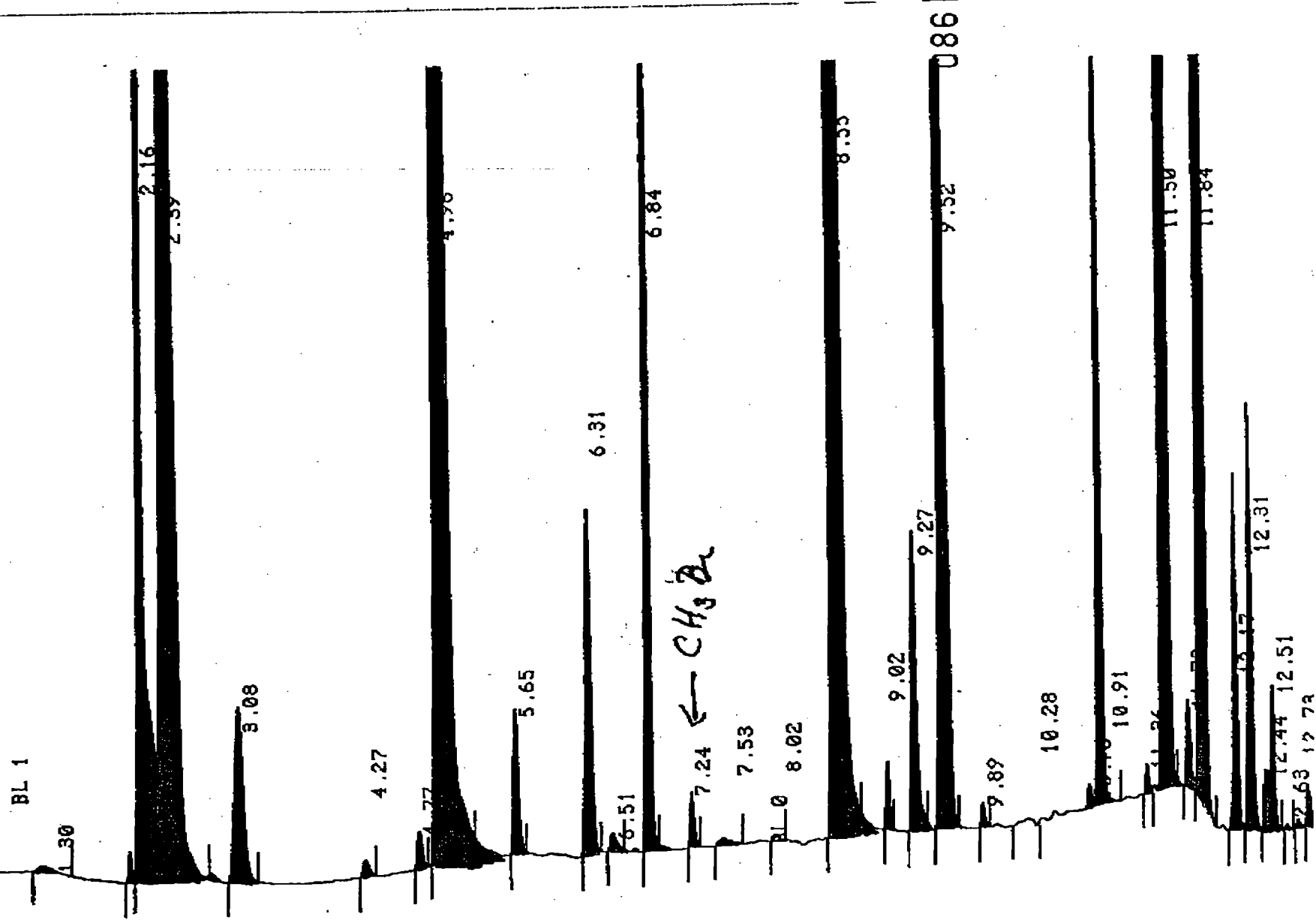
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