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Atmospheric Residence Time of CH₃Br Estimated from the Junge Spatial Variability Relation

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The atmospheric residence time for methyl bromide (CH₃Br) has been estimated as 0.8 ± 0.1 years from its empirical spatial variability relative to C₂H₆, C₂Cl₄, CHCl₃, and CH₃Cl. This evaluation of the atmospheric residence time, based on Junge's 1963 general proposal, provides an estimate for CH₃Br that is independent of source and sink estimates. Methyl bromide from combined natural and anthropogenic sources furnishes about half of the bromine that enters the stratosphere, where it plays an important role in ozone destruction. This residence time is consistent with the 0.7-year value recently calculated for CH₃Br from the combined strength estimates for its known significant sinks.

Chlorine and bromine atoms are primarily responsible for the stratospheric ozone depletion observed since the late 1970s (*1*). Therefore, anthropogenic production of many organochlorine and organobromine compounds has been internationally banned since January 1996 under the terms of the 1987 Montreal Protocol and its subsequent revisions. In the United States, the criterion for regulation for each compound under the Clean Air Act of 1990 is a calculated ozone depletion potential (ODP) of ≥0.2, relative to CFC-11 (CCl₃F) as 1.0. Approximately half of the organobromine that reaches the stratosphere is carried there by CH₃Br for which an ODP of 0.39 has recently been estimated (*2*), down from 0.6 given in the 1994 Scientific Assessment of Ozone Depletion (*1*). A highly significant factor in ODP estimates is the atmospheric residence time (τ) for each compound, and the latest estimate for CH₃Br (*2*) uses a sink strength τ estimate of 0.7 years (*3*). However, this estimate relies on several removal sinks (gas-phase reaction with the OH radical, oceanic hydrolysis, and terrestrial reactive deposition), each with its own geographic and temporal variability. Given the uncertainties in these atmospheric processes, an estimate of τ independent of particular sources and

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sinks is highly desirable. Such an independent approach was proposed by Junge in 1963 (*4*) based on an inverse relation between τ and the spatial variability (defined as the spatial distribution's standard deviation in mixing ratio divided by the mean mixing ratio), and elaborated theoretically since (*5–8*). However, the Junge relation has not previously been applied to a spatial measure of variability for determination of τ, presumably because of the lack of the necessary data on the variabilities of comparison compounds with known residence times. We have now used the empirical variabilities in the mixing ratios of ethane (C₂H₆), perchloroethylene (C₂Cl₄), chloroform (CHCl₃), and methyl chloride (CH₃Cl) in 3936 air samples collected during the NASA PEM-Tropics-A (Pacific Exploratory Mission) aircraft flights in 1996 to estimate τ for CH₃Br.

The qualitative intuition that the longer a compound lasts in the atmosphere the more likely it is to be uniformly distributed was first put into a quantitative relation in 1963 by Junge (*4*), who noted that "If the space and time distribution of sources and sinks were the same for *all* gases, the time and space variations of all constituents would be similar and the amplitudes would be proportional to τ⁻¹" (p. 2). Although these hypothetical requirements are unlikely to ever be rigorously met for any set of compounds, it is still a

useful gendanken experiment. Insufficient data on atmospheric residence times or spatial variations existed at the time to do more than state a general agreement with empirical observations. In 1974, Junge (*9*) compiled available data and deduced the approximate relation τ × σ = 0.14, in which σ is the relative standard deviation, that is, the standard deviation in the mixing ratio of a gas divided by the mean mixing ratio of that gas. He also investigated a numerical model that produced the result σ = 0.0216 × τ⁻⁰·⁹⁵. In 1983 M. Hamrud investigated the effects of different spatial arrangements of sources and sinks on the relation between τ and spatial variability in a two-dimensional numerical model (*10*). He found that the preexponential factor varied between 0.05 and 0.5 and the exponential term between −0.63 and −0.91. These numerical investigations provide strong evidence that a relation between τ and spatial variability should exist in a suitable atmospheric data set, without establishing any best choice for numerical evaluation.

Various attempts have been made to derive a relation between τ and variability (mostly temporal) from first principles (*5–8*). With an assumed uniform sink distribution for species X, the highest mixing ratio of an individual measurement, [X]ᵢ, will be set by the shortest transit time from the source (or alternatively the shortest average transit time from a number of sources). The lowest [X]ᵢ will be set by the longest transit time from the source. The mean value of all [X]ᵢ will be set by the average transit time. If two or more compounds have identical source distributions, then the range of [X]ᵢ around its mean value (for each compound) will be determined by the magnitude of the decay constant for that compound. Further, if the removal rate is proportional to the mixing ratio (as for hydroxyl-initiated oxidation), and the compound is in approximately steady state in the atmosphere, the decay constant, and therefore the variability, will be inversely proportional to τ.

In the real atmosphere, sources emit into a preexisting background of X that includes contributions from many different transit times. Junge accounted for this by estimating variability as deviations from a mean value. Additionally, some removal processes occur only at the surface (oceanic and terrestrial), while even hydroxyl-initiated oxidation is far from uniform in either space or time within the troposphere. However, Junge's result is empirical and not theoretical, and it is likely that some of these problems are averaged out in the PEM-Tropics-A data set. With several thousand air samples collected over a wide geographic area, the spatial history of the air parcels becomes essentially stochastic.

As in any investigation of the relation between τ and spatial variability, some ac-

count must be taken of the experimental limitations on our ability to measure variability. A relative quantity such as variability should not be sensitive to the absolute accuracy of the measurement. However, we must be able to resolve the variability within the experimental precision. If the error in the measurement has a statistically normal character, then the contribution of precision to the measured variability should drop off as $(\sqrt{n})^{-1}$. We consider here a data set of 3973 whole air samples that were taken during PEM-Tropics-A and subsequently analyzed by gas chromatography. The samples were taken during flights between 24 August and 5 October 1996 (11). Fourteen samples collected during takeoffs or landings were removed because very large mixing ratios for C_2Cl_4, C_2H_6, and propane (C_3H_8) were obtained. These samples do not have the spatially random character of the others because all airplane flights must begin and end at airports. The 23 samples collected on flight number 21 of the P-3 aircraft between New Orleans and Wallops Island, Virginia, were also removed because they were taken over the continental United States. The latitude, longitude, and altitude for each of the remaining 3936 samples are shown in Fig. 1. Under the specific conditions discussed here, it seems reasonable that we could resolve variability in the set of measurements at least as large as the relative precision of individual measurements.

Four compounds were used in the analysis of τ_{CH_3Br}: C_2H_6, C_2Cl_4, $CHCl_3$, and CH_3Cl (Fig. 2). The analytical system used was capable of quantifying around 100 hydrocarbons, 25 halocarbons, and 10 alkyl nitrates when encountered at mixing ratios such as those observed during the landing in New Orleans. The average mixing ratio of most hydrocarbons is much lower in the Southern Hemisphere, and variability estimates require that measurements near the detection limit be infrequent. Only 34 compounds were archived for PEM-Tropics-A. Of the 10 hydrocarbons, 19 halocarbons, and 5 alkyl nitrates measured, 5 of the halocarbons and all of the alkyl nitrates were found to have dominant sources at the equatorial ocean surface such that their mixing ratios within the equatorial boundary layer were an order of magnitude larger than elsewhere. These 10 are therefore considered unsuitable for this type of analysis over the entire data set. More than 600 samples were collected below 900 hPa, the variability calculated for CH_3Br in this subset was 0.10, which is similar to the value of 0.086 calculated for the entire data set (Table 1). All five of the compounds used in the Junge-type analysis showed increased variability below 900 hPa, driven by continental outflow from the United States. In the Southern Hemisphere, the empirical variability below 900 hPa (0.052 for CH_3Br in 354 sam-

ples) was lower for all five compounds than between 400 and 800 hPa (0.080 for CH_3Br in 1486 samples). Of the other 24 compounds quantified, 4 hydrocarbons were below their analytical detection limit in a majority of samples and were therefore excluded. Of the remaining 20 compounds, 5 hydrocarbons have τ's substantially shorter than the average tropospheric mixing time within a hemisphere (about 1 month) and were therefore considered unsuitable for spatial analysis. The rest of the compounds were defined as
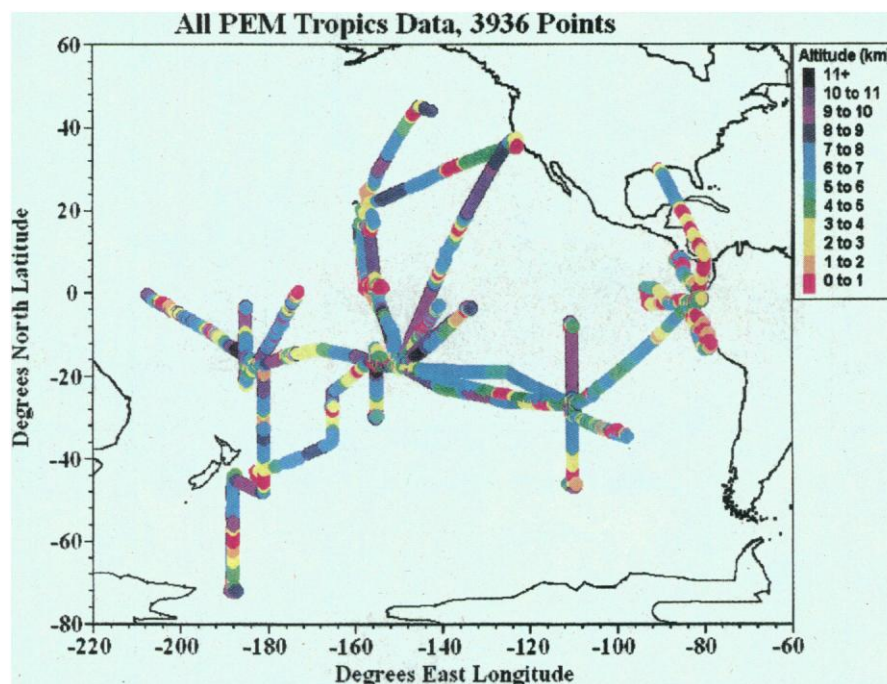

Fig. 1. All PEM-Tropics-A Data, 3936 points. Each circle represents the spatial location of one sample. The colors represent altitude.
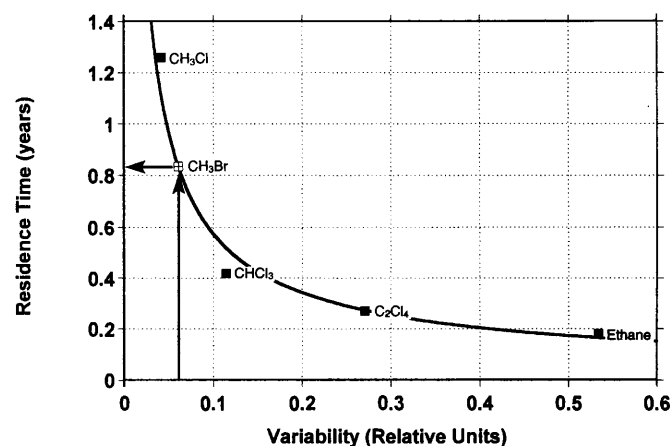

Fig. 2. All Southern Hemispheric data, 2935 points. Residence time (in years) versus the variability (the standard deviation divided by the mean) for all samples collected in the Southern Hemisphere less 12 takeoff and landing samples. A least-squares best fit of the data to a power series gives $\tau = 0.10 \times$ (variability)$^{-0.74}$ ($r^2 = 0.97$) and predicts $\tau_{CH3Br} = 0.83$ years.

Table 1. The empirical variability and mean values of the five compounds shown in Figs. 2 and 4 and their calculated residence times (see text).

Compound	Southern Hemispheric variability (mean)*	All PEM-Tropics-A data variability (mean)*	Residence time (years)
CH_3Cl	0.041 (565)	0.044 (563)	1.26
CH_3Br	0.060 (8.57)	0.086 (8.80)	
$CHCl_3$	0.114 (6.04)	0.146 (6.18)	0.42
C_2Cl_4	0.270 (1.43)	0.412 (1.58)	0.27
Ethane	0.534 (408)	0.517 (421)	0.18

*Unitless (parts per trillion by volume).

suitable if they had a variability that was at least as large as the relative precision of an individual measurement.

We estimate our analytical precision as 1 to 3% with the range representing differing apparatus sensitivities and ambient mixing ratios for different compounds. Of the 15 compounds remaining after the preceding analysis, C_2H_6 had the largest variability, 0.52 over the entire data set. Our analytical precision of about 1% for C_2H_6 makes a negligible contribution to this variability. The next four largest variabilities are 0.41, 0.15, 0.086, and 0.044 for the compounds C_2Cl_4, $CHCl_3$, CH_3Br, and CH_3Cl, respectively. The
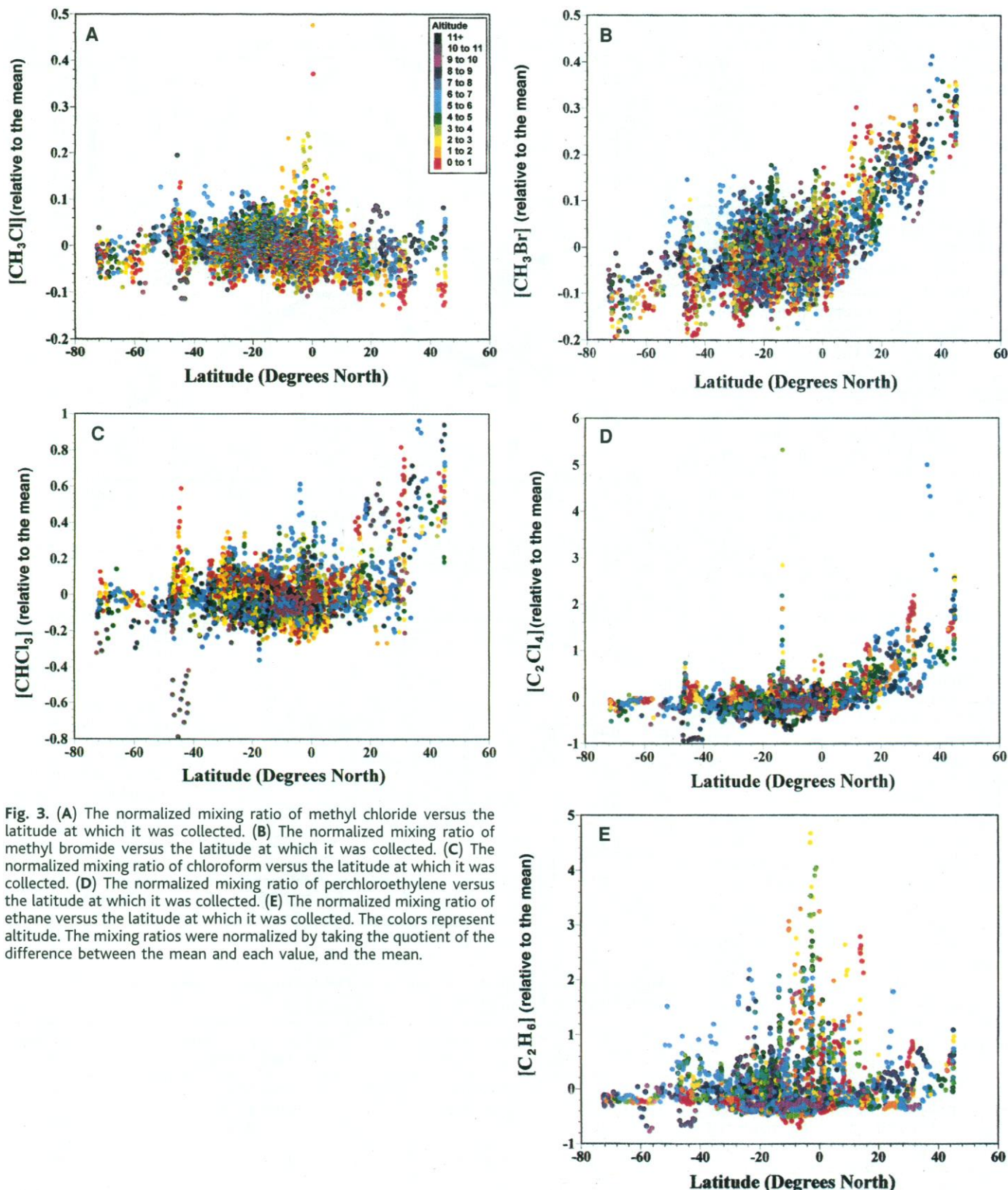

Fig. 3. (A) The normalized mixing ratio of methyl chloride versus the latitude at which it was collected. (B) The normalized mixing ratio of methyl bromide versus the latitude at which it was collected. (C) The normalized mixing ratio of chloroform versus the latitude at which it was collected. (D) The normalized mixing ratio of perchloroethylene versus the latitude at which it was collected. (E) The normalized mixing ratio of ethane versus the latitude at which it was collected. The colors represent altitude. The mixing ratios were normalized by taking the quotient of the difference between the mean and each value, and the mean.

10 remaining halocarbons all have τ's estimated to be longer than that of CH₃Cl. The halocarbon with the next longest residence time is 1,1,1-trichloroethane (CH₃CCl₃) with 4.8 years (12). Assuming the Junge relation holds, using Fig. 2 we estimate that a precision of 0.6% is needed to resolve the variability in a compound with τ = 4.8 years. Our estimated analytical precision for CH₃CCl₃ is closer to 2%. The other compounds measured (CFC-11, -12, -113, -114, Halon-1211, -1301, -2402, HCFC-22, and CCl₄) all have estimated τ's longer than that of CH₃CCl₃ and analytical precisions greater than 0.6%. Therefore, we restricted our analysis to the five compounds shown in Fig. 2.

The residence times for C₂H₆, C₂Cl₄, CHCl₃, and CH₃Cl were plotted as a function of each compound's empirical spatial variability in the Southern Hemisphere (Fig. 2 and Table 1). A least-squares best fit of a power series to the data is also presented. The value of τ for each compound was estimated on the assumption that the only sink for each is reaction with the OH radical, normalized to a global hydroxyl concentration of 9.7×10^5 molecules·cm⁻³ as estimated by Prinn et al. (12); an average tropospheric temperature of 277 K as estimated by Prather and Spivakovsky (13); and rate constants taken from the Jet Propulsion Laboratory (JPL) 1997 review (14). Such a treatment of τ is most appropriate when hydroxyl-initiated oxidation makes up the bulk of the total sink for a compound and when τ is longer than the average vertical mixing time for the troposphere (because average horizontal mixing is faster). These two conditions are well satisfied for CH₃Cl and CHCl₃. For C₂Cl₄ and C₂H₆, reaction with OH is their primary sink, but their τ's are similar to the tropospheric mixing time (~1 month). Thus, this treatment of τ is not ideal but is a reasonable approximation. The τ of 0.27 years for C₂Cl₄ is consistent with previous estimates based on seasonal variations and global source strength (15).

The tropospheric residence time of CH₃Br is more difficult to estimate from source and sink information than for the other gases. Biogenic sinks have been reported for marine surface waters and soils as well as an abiotic sink in soils (16). Combined, these sinks are thought to be as large as the hydroxyl-initiated oxidation sink, for which a hydroxyl-only τ of 1.6 years is predicted. The most recent sink strength analysis suggests that τ_CH₃Br = 0.7 years (0.6 to 0.9) (3). In this study a range of mixing ratios was observed for each compound at all altitudes (Fig. 3, A to E). These results highlight the facts that the vast majority of samples were collected in locations remote from sources, and that sinks were quite uniformly distributed (17). We consider this a prerequisite for a spatial

Junge-type analysis because it means that on average we are effectively equidistant from all sources. This helps decouple the empirical variability from individual source strengths and emission ratios. Using the Junge relation we estimate τ_CH₃Br, on the basis of the fit shown in Fig. 2 and its empirical variability in the Southern Hemisphere, as 0.83 years.

Many more air samples were collected in the Southern Hemisphere than the Northern Hemisphere (Fig. 1). In addition, the mixing barrier between the hemispheres is the intertropical convergence zone (ITCZ), which was located around 10°N during PEM-Tropics-A, so that only about 500 samples were acquired in the meteorological Northern Hemisphere. Figure 3, A to E, shows all measurements (normalized to their mean values) of the five compounds used in this analysis as a function of latitude and altitude and gives a picture of the spatial variability. A cursory inspection shows that the variability increases in the series CH₃Cl, CH₃Br, CHCl₃, C₂Cl₄, and C₂H₆. Three compounds (CH₃Br, CHCl₃, and C₂Cl₄) show increasingly elevated mixing ratios north of 10°N. However, the gradient does not extend into the Southern Hemisphere. Only CH₃Br has a mean value that varies with latitude in the Southern Hemisphere. These observations are reasonable considering the sources, sinks, and residence times of each species in question. A significant part of the total variability in

CH₃Br (Fig. 3B), CHCl₃ (Fig. 3C), and C₂Cl₄ (Fig. 3D) is the result of the higher average values in the Northern Hemisphere. Although this represents part of the intrinsic spatial variability that we are trying to estimate, the lower overall coverage in this region may make their relative contribution unreliable. When τ is plotted versus variability for all samples collected during PEM-Tropics-A (with 37 points removed, see above), the Junge relation still holds and predicts τ_CH₃Br = 0.73 years (Fig. 4). An analysis of the sensitivity of the results to different estimates of τ for each of the other four compounds suggests that a ±30% change in τ_CH₃Cl, τ_CHCl₃, τ_C₂Cl₄, or τ_C₂H₆ would result in a change in τ_CH3Br of ±15, 10, 3, and 1%, respectively. Our overall evaluation from its empirical atmospheric variability is τ_CH₃Br = 0.8 ± 0.1 years.

The Junge-type relation developed above can be used to estimate τ for compounds measured by other research groups during the PEM-Tropics-A mission. Seventeen research groups performed about 130 discrete measurements on two aircraft (11). In addition, a large number of physical parameters were archived. Most of these data are inimical to the specific analysis presented here. Only three compounds meet the combined requirements of the hydroxyl-initiated sink, primarily remote sources, and τ between 60 and 500 days: a measurement of C₂Cl₄ by Singh et al. (NASA Ames Research Center), a measure-

Table 2. The predicted lifetimes (in years) based on our power-series fits for selected compounds measured by other groups, along with the number of measurements. The predicted lifetimes based on JPL hydroxyl-initiated oxidation rate constants are shown for comparison. SH, Southern Hemisphere.

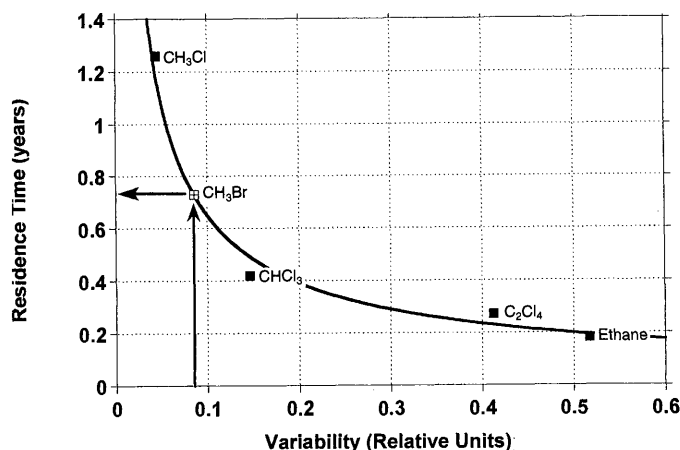| Compound	No. of data points	Global prediction*	SH data points	SH prediction*	JPL prediction*
C₂Cl₄	1227	0.23	1049	0.30	0.27
CH₂Cl₂	625	0.30	382	0.31	0.38
CO	13921	0.23	9618	0.19	0.16

*In units of years.

Fig. 4. All PEM Tropics Data A, 3936 points. Residence time (in years) versus the variability (the standard deviation divided by the mean) for all samples collected during PEM Tropics less 14 takeoff and landing samples and P-3 flight number 21. A least-squares best fit of the data to a power series gives τ = 0.12 × (variability)⁻⁰·⁷³ (r^2 = 0.99) and predicts τ_CH3Br = 0.73 years.

ment of dichloromethane (CH_2Cl_2) performed by Atlas et al. (National Center for Atmospheric Research), and a measurement of CO by Sachse et al. (NASA Langley Research Center) (11). The CO data were averaged over 1-min intervals to approximate the spatial range of the other measurements; the variability was calculated directly from this set (Table 2). Based on the curve generated by our data and the empirical variabilities of these three gases, the predicted values for τ are in reasonable agreement with the accepted values for these compounds. This corroboration adds confidence to our predicted value for τ_{CH_3Br}, because the other data sets were collected by independent research groups over sampling intervals and spatial ranges incongruent with our set.

Considering the more complete latitudinal coverage in the Southern Hemisphere and the more remote location of those samples, we believe the Southern Hemispheric prediction more closely simulates the assumptions necessary for application of the Junge relation to spatial variability estimates. The question of whether the variability has a seasonal signal could not be addressed by this data set but may be accessible in the future. A more complete latitudinal profile including the Northern Hemisphere might improve this analysis. Nonetheless, it seems unlikely that the residence time of CH_3Br lies outside the range 0.7 to 0.9 years.

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17. In this context, a recently discoveryed biological sink for CH_3Br in the polar oceans is not thought to be present for the other four compounds. The distribution and seasonality of this sink is still highly uncertain, and some portions of the ocean may also be a source of CH_3Br. Regardless, no evidence for a large sink in the southern boundary layer was seen in this data set (Fig. 3B, and discussion in paragraph 6). If a large oceanic sink were affecting the variability of CH_3Br in a nonspatially uniform manner, it would be expected to increase its empirical variability relative to the other four compounds. Therefore, any correction due to this effect would have to subtract from its stated variability and thus increase our residence time prediction.
18. We acknowledge the hard work and commitment to excellence exhibited by the science team at the University of California at Irvine and all members of the PEM Tropics mission. Funding was provided by NASA grant NAG-1-1777.

Water as a Dense Icelike Component in Silicate Glasses

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Density and Brillouin-scattering measurements of hydrous andesite glasses at ambient conditions showed that dissolved water has a concentration-independent partial molar volume of 12 ± 0.5 cubic centimeters per mole and a bulk modulus of 18 ± 3 gigapascals. Dissolved as hydroxyl ions or as molecular water, water has volume properties similar to those of ice VII, the densest form of ice. These properties point to hydrogen bonding as an important factor in water dissolution, and they indicate that changes of water speciation are driven by the entropy and not by the volume of the system. Water in a concentration greater than 1 percent by weight also causes a marked decrease of the shear modulus of the glass.

Water is an important component of naturally occurring silicate glasses and melts. As a light oxide, it influences the density of the melt, which affects the rate of magma ascent. The effects of water on volume properties are generally not well known, however. For glasses, reported partial molar volumes of water range from 0 to 22 cm^3/mol at room pressure (1), and elastic properties have not been investigated. Here, we show that, in conjunction with density measurements, Brillouin scattering can be used to determine the elastic moduli of hydrous glasses. Because the elastic moduli are related to the bonding within a substance, these measurements provide structural information on water dissolution and speciation.

Because of the importance of water in andesitic lavas, we investigated a glass whose composition was similar to that of andesitic Montagne Pelée lavas that formed 650 years before the present in the last pumice eruption (2). Glasses made from the lavas (ME1311 in Table 1) would have been opaque, so we investigated hydrous iron-free glasses that had been used in viscosity measurements (3). After synthesis from oxide and carbonate mixtures, the starting glass (Table 1) was

hydrated with up to 3.5 weight % H_2O at high pressure and high temperature in an internally heated vessel. The anhydrous natural and synthetic materials had the same viscosity, and analyses of the water content indicated that water dissolution was homogeneous in the synthetic glasses (3).

The Brillouin-scattering measurements (Table 2) were made with a setup similar to that previously described (4), whereby the light scattered by the sample from the single-mode 200-mW beam of an Ar^+ laser tuned to 514.5 nm was analyzed by a six-pass tandem Fabry-Pérot interferometer and was recorded with a photon-counting multichannel detector. The longitudinal (V_p) and shear (V_s) sound velocities were determined to within 30 m/s from spectra recorded in about 5 min with a platelet geometry. These results were then used to determine (to within 1%) the index of refraction (n) from experiments that were performed with a backscattering geometry. The investigated samples were doubly polished thin sections that were previously used to record infrared (IR) spectra before and after viscosity measurements (3).

A first series of measurements was made on samples that were recovered after hydration at high pressure, which were thus densified permanently (5). A second series was made on samples whose densities had relaxed to the room-pressure values while being heated during the viscosity measurements (3); as shown from Archimedean measurements of the density (ρ), the latter samples were less

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