permuted the rates but rejected the permutation if the number of peaks did not agree with that for their data. They found that this conditioning did not affect the results, as would be expected on the basis of the relative insensitivity of the number of peaks to the stochastic structure of the series [see S. M. Stigler, *Am. Stat.* **40**, 111 (1986)]. Indeed, insofar as there is any relation between the distribution of the number of peaks and the stochastic or periodic structure of the series, it is inappropriate to condition on the number of peaks if the goal is to learn about the relative likelihood of different alternative models. In some of the other studies reported (*9*), the series of peaks has been culled to limit attention to "significant" peaks before applying the randomization test. If this culling were based only on information in adjacent stages it would be essentially equivalent to conditioning on a smaller number of peaks; a valid test could be based on such a culled series, although a study of its sensitivity to alternative models would be difficult. Nevertheless, when the culling looks beyond adjacent stages to nearest minima [as was done in (*9*)], the simple randomization test will be biased toward periodic alternatives.

12. One extreme form of an autoregressive process was suggested in an earlier critique of this test by A. Hoffman [*Nature (London)* **315**, 659 (1985)] and by A. Hoffman and J. Ghiold [*Geol. Mag.* **122**, 1 (1985)]. In particular, Hoffman and Ghiold considered a random walk model, which is an autoregressive process with $\theta = 1.0$. Such a model implies a long system memory and has not been widely accepted.
13. Because the variance of the sine of a random angle is six times that of U_i, the ratio of the standard deviation of the periodic signal to that of the random noise is 0.98θ, and hence θ may be conveniently thought of as the signal-to-noise ratio here, where we use this term to refer to the ratio of the respective standard deviations.
14. D. M. Raup, *Science* **231**, 1528 (1986); based on P. W. Signor III and J. H. Lipps [in *Geological Implications of Impacts of Large Asteroids and Comets on the Earth, Conference on Large Body Impacts and Terrestrial Evolution*, L. T. Silver and P. H. Schultz, Eds. (Geological Society of America Special Papers, no. 190, Boulder, CO, 1982), pp. 291–296]. The manner in which misrecorded extinctions generate a moving average process of the type we consider is most easily seen where the stratigraphic stages are of equal duration. In that case, if in each stage a fraction $\theta/(1 + \theta)$ of that stage's extinctions are misrecorded as occurring in the previous stage and the remaining fraction $1/(1 + \theta)$ are correctly recorded, then the series of recorded extinctions (and hence the rates) will be proportional to a "moving average" of the type we consider, with weight θ on the previous stage and weight 1 on the current stage. The same will be true for series of unequal stages if the fraction misrecorded is rescaled by the ratio of the successive stage lengths.
15. Thus the effect found here is not related to the "wrapping effect" noticed by T. M. Lutz [*Nature (London)* **317**, 404 (1985)] in a critique of the application of this test to magnetic reversal data. That effect, while real, is quite small here, as indeed it was in the magnetic reversal case. D. M. Raup (*ibid.*, p. 384) has noted that the extinction data do not exhibit the type of long-term variation that was responsible for the major effect at the basis of the convincing criticism Lutz made of the application of this test to the reversal data.
16. The sensitivity of the nonparametric test to patterns in the duration of stages helps explain why it tends to support different conclusions from those reached by analyses like that of J. A. Kitchell and D. Pena [*Science* **226**, 689 (1984)], which treat the observed rates as if they are equally spaced.
17. J. J. Sepkoski, Jr., *Lect. Notes Earth Sci.* **8**, 47 (1986).
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Atmospheric Trends in Methylchloroform and the Global Average for the Hydroxyl Radical

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Frequent atmospheric measurements of the anthropogenic compound methylchloroform that were made between 1978 and 1985 indicate that this species is continuing to increase significantly around the world. Reaction with the major atmospheric oxidant, the hydroxyl radical (OH), is the principal sink for this species. The observed mean trends for methylchloroform are 4.8, 5.4, 6.4, and 6.9 percent per year at Aldrigole (Ireland) and Cape Meares (Oregon), Ragged Point (Barbados), Point Matatula (American Samoa), and Cape Grim (Tasmania), respectively, from July 1978 to June 1985. These measured trends, combined with knowledge of industrial emissions, were used in an optimal estimation inversion scheme to deduce a globally averaged methylchloroform atmospheric lifetime of 6.3 (+1.2, −0.9) years (1σ uncertainty) and a globally averaged tropospheric hydroxyl radical concentration of $(7.7 \pm 1.4) \times 10^5$ radicals per cubic centimeter (1σ uncertainty). These 7 years of gas chromatographic measurements, which comprise about 60,000 individual calibrated real-time air analyses, provide the most accurate estimates yet of the trends and lifetime of methylchloroform and of the global average for tropospheric hydroxyl radical levels. Accurate determination of hydroxyl radical levels is crucial to understanding global atmospheric chemical cycles and trends in the levels of trace gases such as methane.

METHYLCHLOROFORM IS A LONG-lived atmospheric species whose only known sources are anthropogenic. It is widely used in industry as a solvent for degreasing and in other applications; its global production and use accelerated significantly in the mid-1970s as it replaced the increasingly regulated solvent trichloroethylene (*1*). Its concentration has rapidly increased worldwide (*1–3*). This increase is of considerable concern because methylchloroform is a significant stratospheric source of atomic chlorine and chlorine monoxide (*4*) that can catalytically destroy stratospheric ozone (*5*), and because it is one of the greenhouse gases that may contribute to future climate change (*6*).

The principal recognized atmospheric sink for methylchloroform (CH_3CCl_3) is the reaction (*7, 8*)

$$CH_3CCl_3 + OH \rightarrow CH_2CCl_3 + H_2O \quad (1)$$

The global rate of loss of CH_3CCl_3, which can be deduced from its known industrial emissions and observed global trends, can be used to deduce accurately an appropriately weighted globally averaged tropospheric concentration for the hydroxyl radical (OH) (*1–3, 8*). Knowledge of precise OH concentrations is crucial because OH is widely recognized as the major gas-phase oxidant in clean tropospheric air. Thus it plays a central role in tropospheric chemistry, including chemical destruction of a wide range of species of anthropogenic and natural origin that are important radiatively or chemically or both (for example, CO, CH_4, NO_x, and SO_2) (*9*).

Since 1978 we have performed frequent (4 to 12 measurements per day) real-time gas chromatographic measurements of methylchloroform at stations throughout the world, first as part of the Atmospheric Lifetime Experiment (ALE) and (since late 1984) as part of the Global Atmospheric Gases Experiment (GAGE) (*1, 10*). The surface measurement stations are located at coastal sites remote from industrial and urban sources and are designed to measure accurately the tropospheric trends of trace gases whose lifetimes are long compared to global tropospheric mixing times (*11*). In this report we present and interpret ALE-GAGE data obtained over the 7-year period from July 1978 to June 1985 which, primarily because of the greater number of measurements, provide much more accurate determinations than previously possible (*1–3, 8*) of the global trend and atmospheric destruction time for methylchloroform and for the globally averaged OH concentration.

Monthly mean volume mixing ratios for methylchloroform were computed from the approximately 100 to 400 measurements made each month at each of the five ALE-

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GAGE stations (Table 1). The data are calibrated with a more accurate absolute standard than was used previously (*12*). Each station (or combination of stations in the case of Ireland and Oregon) is intended to be indicative of the air between the surface and a pressure of 500 mbar in the semihemisphere in which it lies. Objective techniques were used therefore to recognize periods (typically less than a few days in duration) of local air pollution (*1, 10, 13*). These time periods are not represented in the data reported here but have been archived (*14*) and used to deduce information on local sources (*15*).

Greater variability in methylchloroform levels is observed at Northern Hemisphere sites than at Southern Hemisphere sites even after removal of local pollution effects in the data. This variability is expected on theoretical grounds because of the presence of continental-scale methylchloroform source regions (North America, Europe, eastern Asia, and Japan) in the northern mid-latitudes that have no Southern Hemisphere analog (*16*). After removal of pollution effects, methylchloroform levels were still slightly greater at Adrigole than at Cape Meares, probably reflecting higher methylchloroform concentrations in Atlantic air compared to Pacific air, which is also expected theoretically (*16*). Although most of the variance in the monthly mean data is associated with real atmospheric variability, there are also instrumental contributions associated with detector signal processing and calibration tank changes (*1, 10*).

The long-term components of variability in the monthly-mean mixing ratios χ_i measured at station i can be described by an empirical model

$$\chi_i = a_i + b_i t + d_i t^2 + e_i t^3 + c_i \cos(2\pi t) + s_i \sin(2\pi t) \qquad (2)$$

in which t is time (in years) measured from the midpoint of the record (1 January 1982 unless otherwise noted). Maximum likelihood estimates of the coefficients in Eq. 2 and their uncertainties (Table 2) are computed with techniques described elsewhere (*17*). Approximating Eq. 2 by using zero-order and first-order Legendre polynomials, the mean concentration is $a_i + 4.08\, d_i$, and the mean linear trend is $b_i + 7.35\, e_i$ over the 7-year period of the observations. From the mean concentrations it is evident that a strong north-to-south gradient exists. Statistically significant negative values for d_i at the stations indicate that the trends decrease with time in a manner consistent with a slow approach to a steady state. Significant seasonal cycles (described by c_i and s_i) are evident in the Northern Hemisphere sites and in Tasmania but not at Samoa. These seasonal cycles differ from those observed for the Freons or chlorofluoromethanes (*17*). In particular, Adrigole and Cape Meares are out of phase for methylchloroform but in phase for the Freons; there is a significant cycle for the Freons at Point Matatula but not at Ragged Point (*17*). These differences must be due to differences in space and time in the emissions of methylchloroform and the Freons. The seasonal cycle of methylchloroform at Tasmania has been attributed to seasonal cycles either in OH (*3*) or in interhemispheric circulation (*1*).

Detailed information on annual production $P(t)$ and sales $S(t)$ of methylchloroform worldwide in year t are available from industry sources (*18*). Global emissions $E(t)$ are computed from these data with the formula

$$E(t) = (1 - a)fS(t) + afS(t-1)$$
$$= (1 - a - b + ab)fP(t) + (a + b - 2ab)fP(t-1) + abfP(t-2) \qquad (3)$$

Here a is the fraction of annual sales that enters the user's inventory, b is the fraction of annual production entering the producer's inventory, and f is the fraction of annual sales to the users that is released (the remainder is destroyed or incarcerated). By using assessments of a, b, and f and their (2σ) uncertainties, which were based on industry information (*19*), we computed $E(t)$ values with 2σ uncertainties (Table 3).

To deduce the chemical destruction rate of methylchloroform in the atmosphere from the observed concentrations and the above emissions, we used an optimal estimation inversion technique (*17, 20*). The technique includes the use of a two-dimensional model (eight tropospheric boxes, one upper atmospheric box) of the global atmosphere

Table 1. Monthly mean mixing ratios (χ) and standard deviations (σ) observed at ALE-GAGE sites over the period July 1978 to June 1985. Units are parts per trillion by volume. For Oregon (beginning September 1983) and Tasmania (beginning July 1981), ALE (HP 5840) and GAGE (HP 5880)

Year	Month	Ireland		Oregon		Barbados		Samoa		Tasmania	
		χ	σ	χ	σ	χ	σ	χ	σ	χ	σ
1978	7	112.1	4.6	0.0	0.0	99.6	5.8	71.1	2.9	68.8	3.4
1978	8	109.8	3.8	0.0	0.0	99.5	6.2	72.1	3.4	66.6	2.6
1978	9	105.8	3.9	0.0	0.0	94.2	8.2	72.4	2.9	68.5	2.9
1978	10	107.4	3.8	0.0	0.0	94.6	8.2	74.2	2.9	70.8	2.2
1978	11	107.7	3.3	0.0	0.0	92.7	7.1	74.6	4.2	74.9	1.1
1978	12	0.0	0.0	0.0	0.0	99.3	6.7	75.0	5.1	74.2	1.0
1979	1	111.4	4.6	0.0	0.0	100.2	7.4	78.0	3.3	73.1	1.2
1979	2	112.7	3.1	0.0	0.0	99.8	7.0	75.8	3.6	73.1	1.1
1979	3	112.2	5.0	0.0	0.0	100.9	6.9	76.6	3.0	75.1	1.6
1979	4	115.4	4.9	0.0	0.0	0.0	0.0	76.2	3.4	76.5	1.0
1979	5	117.2	4.6	0.0	0.0	101.7	3.3	77.9	2.0	76.6	1.4
1979	6	117.7	5.1	0.0	0.0	99.9	4.6	78.5	0.7	78.1	1.8
1979	7	115.1	5.6	0.0	0.0	102.8	6.6	79.7	1.1	77.3	1.4
1979	8	115.8	5.0	0.0	0.0	105.7	4.2	81.2	1.7	78.7	1.2
1979	9	116.9	5.1	0.0	0.0	99.0	7.4	81.3	1.9	79.8	1.3
1979	10	120.3	4.1	0.0	0.0	98.9	5.9	83.0	1.8	80.8	0.9
1979	11	119.7	5.8	0.0	0.0	102.8	5.8	85.1	1.7	81.5	1.1
1979	12	122.5	5.6	125.4	7.0	105.2	4.1	79.1	4.6	81.0	0.7
1980	1	121.8	6.4	127.7	4.8	107.8	5.0	84.0	2.4	80.6	0.9
1980	2	123.0	5.4	0.0	0.0	108.5	5.2	86.2	2.6	81.0	1.1
1980	3	126.6	5.7	123.9	1.9	112.5	3.8	86.7	2.6	82.4	1.1
1980	4	130.1	6.0	126.4	2.4	110.1	3.1	87.1	3.1	82.0	1.3
1980	5	132.1	5.9	126.3	1.8	111.0	3.8	88.2	1.8	85.9	1.8
1980	6	130.6	6.6	124.1	2.4	113.8	3.4	89.2	1.2	86.8	1.8
1980	7	130.7	5.0	120.8	2.9	112.9	4.6	90.5	0.8	87.6	1.4
1980	8	127.0	4.7	121.5	2.4	111.3	3.4	91.6	1.0	88.7	1.1
1980	9	124.8	4.2	125.4	6.2	109.6	6.6	92.1	1.6	89.9	0.8
1980	10	127.4	4.4	132.1	6.6	109.9	6.3	92.5	1.0	90.8	1.0
1980	11	129.0	3.8	130.1	5.4	114.9	4.6	94.2	1.8	90.6	1.4
1980	12	129.2	4.0	128.2	4.6	115.4	6.2	96.1	3.0	89.4	0.6
1981	1	128.5	5.8	129.4	4.2	114.8	4.4	96.7	3.2	89.4	0.7
1981	2	129.4	4.2	133.0	7.8	116.8	4.2	0.0	0.0	89.7	0.7
1981	3	130.2	4.9	128.6	2.9	112.6	3.8	97.8	1.6	91.2	1.0
1981	4	131.9	3.3	128.9	2.2	117.4	5.3	96.2	1.9	92.1	0.7
1981	5	135.0	4.0	129.8	2.9	119.1	3.6	95.9	2.3	92.8	1.0
1981	6	135.3	4.7	130.6	2.2	117.5	3.4	97.4	1.5	93.4	1.1
1981	7	131.4	6.3	126.4	3.5	120.4	3.7	97.4	1.8	93.2	1.0
1981	8	131.9	5.1	126.2	3.0	116.4	7.2	99.4	1.0	0.0	0.0
1981	9	134.2	6.5	128.9	2.8	115.9	6.2	100.2	1.8	93.7	1.9
1981	10	134.2	5.4	131.0	3.1	116.6	5.4	97.8	1.4	96.2	3.2
1981	11	134.7	5.4	134.3	2.4	116.3	4.8	97.9	1.7	96.5	1.3
1981	12	137.2	5.4	135.8	2.5	115.4	4.2	98.8	2.2	97.2	2.0

with horizontal surfaces at 1000, 500, 200, and 0 mbar and tropospheric vertical surfaces at latitudes 30°N, 0°, and 30°S. Mean advective and eddy diffusive transports in the model are specified from meteorological observations and an optimal fit to global data for the Freons fluorotrichloromethane and dichlorodifluoromethane (*17*). The above methylchloroform emissions are input into the four lower tropospheric boxes in the model. The chemical lifetime for methylchloroform in the upper atmospheric box (6 years) is specified from detailed calculations in a global three-dimensional circulation model (*16*). The lifetime τ_i in the *i*th tropospheric box is given by

$$\tau_i^{-1} = k_i A[\mathrm{OH}]_i^* \qquad (4)$$

where k_i is the temperature-dependent rate constant for reaction 1 in box *i*, $[\mathrm{OH}]_i^*$ is a theoretical estimate of the OH concentration in box *i* (*21*), and *A* is an unknown dimensionless coefficient by which the theoretical estimates are to be multiplied to provide an optimal fit between the model and observed methylchloroform concentrations and trends (*1*). There is also sufficient information in the observations to permit an estimate of the factor α by which our current absolute concentrations should be multiplied to provide the best fit to the emission and station data. Because the two-dimensional model is not capable of accurately simulating oscillations associated with the measurement technique (for example, periodic renewal of on-site calibration gases) or natural meteorological oscillations on interannual, seasonal, and shorter term time scales, the 12-month running mean model predictions are used. The model is then augmented by two empirical models that are designed to describe the spectrum of the differences between the observations and the two-dimensional model predictions [that is, the residuals that for methylchloroform have a mean standard deviation of 2.4 parts per trillion by volume (pptv)]. Lower frequencies in this spectrum of residuals were fit with a first-order auto-regressive model common to all sites with a correlation of 0.5 after 1 month; higher frequencies were modeled by assuming that the spectra at each site were the same as those found in the residuals between the observations and the empirical model (Eq. 2). Because both the Adrigole and Cape Meares stations lie in the region from 30° to 90°N, the concentrations observed at these sites were combined into a single time series in which they overlap in time by adding 0.493 times the Adrigole concentrations to 0.507 times the Cape Meares concentrations (this slightly unequal weighting avoids producing spurious trends because of the different mean concentrations and observational time periods at the two sites).

monthly data were combined by weighting equally ALE and GAGE monthly means to determine χ, and ALE and GAGE individual measurements to determine σ. An absolute calibration factor of 0.8 is included.

Year	Month	Ireland		Oregon		Barbados		Samoa		Tasmania	
		χ	σ	χ	σ	χ	σ	χ	σ	χ	σ
1982	1	132.4	5.8	134.6	1.4	120.3	3.1	99.4	2.4	96.7	1.6
1982	2	133.8	4.9	135.3	2.9	120.5	3.0	101.8	2.7	96.6	1.5
1982	3	138.9	6.6	136.4	2.3	120.1	3.0	100.0	1.0	97.0	1.4
1982	4	140.9	5.1	139.6	2.1	126.0	3.3	0.0	0.0	98.3	1.6
1982	5	138.5	5.2	139.0	1.8	123.8	3.8	0.0	0.0	100.1	0.9
1982	6	138.8	3.7	136.9	2.2	124.1	3.0	101.3	1.4	101.4	0.7
1982	7	138.3	5.5	134.4	2.5	125.6	2.8	100.9	1.6	102.2	0.9
1982	8	134.5	4.6	131.0	2.8	125.0	3.8	102.2	1.7	103.1	0.9
1982	9	135.5	5.6	130.6	3.9	121.3	4.9	102.1	1.3	103.3	0.5
1982	10	139.8	5.0	134.5	2.6	119.3	5.2	102.1	1.0	103.9	0.7
1982	11	142.8	4.2	135.9	2.3	123.1	4.5	101.4	0.9	103.8	0.7
1982	12	141.4	5.2	138.9	2.2	130.1	3.6	100.9	1.0	103.0	0.5
1983	1	138.2	4.6	137.4	3.6	128.9	3.8	100.2	0.9	102.4	0.5
1983	2	140.5	4.3	137.5	2.0	127.4	3.8	101.8	1.2	102.7	0.9
1983	3	141.8	3.4	141.6	3.4	125.4	3.0	102.9	1.1	103.2	0.7
1983	4	145.1	4.1	143.1	3.8	130.4	3.0	103.4	1.2	103.7	0.9
1983	5	150.2	5.5	141.7	2.3	129.0	2.2	104.6	1.2	104.8	0.8
1983	6	146.4	6.2	141.4	2.2	128.4	3.7	105.9	1.0	105.4	0.7
1983	7	142.4	3.0	139.4	1.8	130.3	5.2	106.6	1.0	106.6	0.9
1983	8	142.3	3.3	137.1	3.2	129.7	6.0	106.8	1.0	107.2	0.9
1983	9	139.3	3.7	138.1	3.4	127.0	4.2	108.2	1.0	107.0	0.7
1983	10	141.8	4.6	141.6	2.4	124.7	4.2	107.6	1.0	107.3	0.5
1983	11	146.2	4.9	143.5	2.1	125.4	5.2	106.6	1.3	107.1	0.6
1983	12	147.1	4.6	147.0	3.2	132.1	4.1	109.1	1.8	106.3	0.7
1984	1	0.0	0.0	143.0	0.5	132.6	2.5	111.6	2.4	105.6	0.6
1984	2	0.0	0.0	147.3	2.7	132.3	3.4	112.6	2.5	105.4	0.6
1984	3	0.0	0.0	147.2	2.5	135.5	3.1	114.5	5.4	106.0	0.7
1984	4	0.0	0.0	149.3	1.2	131.6	2.3	111.9	3.6	106.5	0.8
1984	5	0.0	0.0	150.4	1.6	135.8	3.0	109.0	1.4	107.2	1.0
1984	6	0.0	0.0	150.4	1.7	136.5	3.4	110.0	0.9	108.4	1.0
1984	7	0.0	0.0	147.3	2.9	137.7	4.9	111.0	1.4	109.4	1.0
1984	8	0.0	0.0	143.4	2.5	139.6	3.8	112.2	1.0	110.5	1.2
1984	9	0.0	0.0	144.8	3.1	135.4	4.9	113.2	1.6	110.8	0.6
1984	10	0.0	0.0	149.8	2.1	134.2	3.8	112.6	1.4	112.2	1.9
1984	11	0.0	0.0	152.0	2.4	132.0	7.0	113.5	2.4	111.8	1.6
1984	12	0.0	0.0	154.1	2.2	139.6	3.4	115.6	3.0	112.1	1.6
1985	1	0.0	0.0	158.4	5.2	140.5	4.3	116.5	5.6	112.3	1.4
1985	2	0.0	0.0	153.0	1.9	140.8	5.7	117.2	2.3	112.0	1.1
1985	3	0.0	0.0	155.4	1.7	142.6	3.2	116.4	2.9	112.8	1.4
1985	4	0.0	0.0	155.8	2.3	140.1	3.1	115.8	1.9	114.6	1.3
1985	5	0.0	0.0	155.7	1.0	144.0	3.1	116.7	2.9	115.6	1.2
1985	6	0.0	0.0	155.8	1.6	137.4	2.5	116.5	1.8	116.2	1.2

The optimal estimation scheme we used (*17, 20*) was designed to minimize the squares of the deviations between the logarithms of the observed (χ) and model-calculated (χ_c) mixing ratios at time *t* (months)

$$\ln \chi(t) - \ln \chi_c(t) = -\ln \alpha - [A(t) - A(t - \Delta t)] \left\{ \frac{\partial \ln \chi_c(t - \Delta t)}{\partial A} + \frac{d}{dt} \left[\frac{\partial \ln \chi_c(t - \Delta t)}{\partial A} \right] \Delta t \right\} \qquad (5)$$

by continuously updating the values of α, *A*, and thus $\partial \ln \chi_c/\partial A$ in the model. Because *A* and the inverse atmospheric lifetime $1/\tau$ of methylchloroform are equivalent variables (*1*), *A* in Eq. 5 can also be replaced by $1/\tau$.

Estimates of $1/\tau$ (or *A*) can be obtained with each station data set alone or all station data sets simultaneously (Table 4). The estimate of lifetime obtained by using all station data and including emission trend uncertainty (Table 3) is 6.9 (+1.2, −0.9) years (1σ). The estimate for α is 1.09, which is in satisfactory agreement with our absolute calibration uncertainty of ±10% (1σ). Relative to the lifetime estimates for 3 years of data (*1*), there is substantially closer agreement between the individual site lifetime estimates because of the much better definition of long-term variability in methylchloroform with 7 years of data. Moreover, all the individual site lifetime estimates are shorter in this report because of increases of 5 to 10% in the estimates of global sales between 1979 and 1983 (*18*). This sensitivity of the lifetime estimates to the emissions during this period was emphasized in our report (*1*), which noted that hypothetical changes of up to 8% in the emissions could reduce the estimated lifetime deduced from 3 years of data on trends in methylchloroform from 10 to 6.5 years.

Table 2. Optimally determined coefficients (with 1σ uncertainties) in empirical model (Eq. 2) fit to data in Table 1. The mean fractional trends for the 7-year time intervals are given by $(b_i + 7.35\ e_i)/(a_i + 4.08\ d_i)$.

Site	a_i (pptv)	b_i (pptv year^{-1})	d_i (pptv year^{-2})	e_i (pptv year^{-3})	c_i (pptv)	s_i (pptv)
Adrigole, Ireland*	135.6 ± 0.6	5.1 ± 0.8	0.0 ± 0.3	0.1 ± 0.3	1.3 ± 0.7	−1.4 ± 0.7
Cape Meares, Oregon*	132.9 ± 0.5	4.8 ± 0.8	0.2 ± 0.4	0.2 ± 0.4	−1.0 ± 0.6	−2.6 ± 0.7
Adrigole and Cape Meares†	134.3 ± 0.4	5.1 ± 0.3	−0.2 ± 0.1	0.17 ± 0.04	0.2 ± 0.5	−1.8 ± 0.5
Ragged Point, Barbados†	120.0 ± 0.4	6.1 ± 0.3	−0.2 ± 0.1	0.04 ± 0.04	1.2 ± 0.4	−1.4 ± 0.4
Point Matatula, American Samoa†	99.0 ± 0.6	5.1 ± 0.5	−0.4 ± 0.1	0.16 ± 0.06	−0.2 ± 0.5	0.1 ± 0.5
Cape Grim, Tasmania†	97.0 ± 0.3	6.0 ± 0.3	−0.5 ± 0.1	0.07 ± 0.03	0.2 ± 0.3	1.0 ± 0.3

*From December 1979 through December 1983. †From July 1978 through June 1985.

Table 3. Global emissions $E(t)$ computed with Eq. 3 and industry data (*18, 19*). Units are 10^9 g/year and uncertainties are 2σ. Also shown are modified emissions computed by adding or subtracting the quantity 4.353 times t (where t is time in years measured from 1 July 1980) for the years 1976 to 1985, which represents the maximum and minimum trends in emissions in the period from 1976 to 1985 consistent with the 2σ uncertainties.

Year	Emission	Uncertainty	Emissions: Maximum trend	Emissions: Minimum trend
1951	0.09	0.01	0.09	0.09
1952	0.18	0.01	0.18	0.18
1953	0.88	0.09	0.88	0.88
1954	0.58	0.23	2.58	2.58
1955	7.47	0.67	7.47	7.47
1956	12.55	0.95	12.55	12.55
1957	18.83	1.37	18.83	18.83
1958	20.40	1.35	20.40	20.40
1959	29.11	2.11	29.11	29.11
1960	35.23	2.39	35.23	35.23
1961	37.36	2.46	37.36	37.36
1962	54.22	3.95	54.22	54.22
1963	54.62	3.58	54.62	54.62
1964	57.45	4.54	57.45	57.45
1965	75.37	5.08	75.37	75.37
1966	105.14	7.39	105.14	105.14
1967	133.21	8.92	133.21	133.21
1968	147.07	9.38	147.07	147.07
1969	156.42	9.90	156.42	156.42
1970	168.74	10.73	168.74	168.74
1971	178.54	11.29	178.54	178.54
1972	242.12	16.89	242.12	242.12
1973	319.00	21.76	319.00	319.00
1974	360.98	23.18	360.98	360.98
1975	352.58	22.04	352.58	352.58
1976	419.31	19.59	399.72	438.98
1977	455.50	21.24	440.27	470.74
1978	476.21	22.17	465.33	487.10
1979	540.59	25.39	534.06	547.12
1980	544.91	25.28	542.73	547.08
1981	538.68	24.97	540.85	536.50
1982	510.91	23.65	517.44	504.38
1983	515.97	23.97	526.85	505.09
1984	550.03	37.71	565.26	534.79
1985	581.22	39.84	600.81	561.63

The above method for determining τ makes maximum use of the fractional trends in the concentration at each site that are more accurately measured than the total atmospheric content (which requires knowledge of absolute calibration). An alternative method for determining τ that involves matching model and observed contents (*1, 17, 20*) yields $\tau = 6.0$ (+1.1, −0.8) years (1σ) based on the 7 years of data and includes emission uncertainties. The decrease in the τ estimate by this method from that obtained from 3 years of data (*1*) is almost entirely due to the revision of absolute calibration for methylchloroform (*12*). The calculated atmospheric content was 2400×10^9 g on 1 January 1982, which is the midpoint of the 7-year data period; this result is sensitive to our specified time of 4 years for mixing between the upper tropospheric boxes and the stratospheric box in our model.

A third method for determining τ compares observed and model-calculated latitudinal gradients. If we take into account the uncertainty in the observed latitudinal gradient that results from uncertainties in the 30° to 90°N average concentration (exemplified by the difference between Adrigole and Cape Meares a_i values) and in the concentrations at the other three stations (Table 2), we calculate that $\tau = 6.0$ (+1.4, −1.0) years (1σ). Uncertainties in the latitudinal distribution of emissions are not included here but are not expected to be a significant source of error.

By combining all three of the above ways of analyzing the data, the best estimate of $1/\tau$ is 0.159 ± 0.026 year^{-1} (1σ); that is, the atmospheric lifetime of methylchloroform is 6.3 (+1.2, −0.9) years (1σ). If we assume that 6.3 years is the precise methylchloroform lifetime, an alternative inversion problem can be solved in which the emissions $E(t)$ are the unknowns rather than $1/\tau$ (*17*). In this way, for the seven successive 12-month intervals beginning July 1978, we predict emissions (in units of 10^9 g/year) of 497 ± 41, 553 ± 24, 509 ± 20, 519 ± 42, 520 ± 50, 574 ± 61, and 583 ± 26. These generally compare well with emissions for these intervals deduced from industry data (Table 3).

Our best estimate for $1/\tau = 0.159 \pm 0.026$ year^{-1} (or, equivalently, $A = 0.661 \pm 0.121$) corresponds to a globally averaged tropospheric OH concentration of $(7.7 \pm 1.4) \times 10^5$ radicals cm^{-3} (1σ uncertainties). This estimate is much more accurate than that derived from the much smaller data sets previously available (*1–3, 8*). Since methylchloroform concentrations are proportional to total air density and since the rate of reaction 1 increases with air temperature, this average OH concentration must be interpreted as an appropriate density- and temperature-weighted average. On the basis

Table 4. Lifetime estimates for methylchloroform derived from trends in 7 years of ALE-GAGE data at each site and for all sites combined. Uncertainties are 1σ and, in contrast to uncertainties given in Prinn *et al.* *(1)*, include allowance for potential biases of the time series inferred from the variance of the individual site lifetime estimates. Also given are lifetimes derived from global atmospheric content and from latitudinal gradients.

Case	Reciprocal lifetime (year^{-1})	Lifetime (years)	Weight given to site in optimal estimation of lifetime
Adrigole, Ireland and Cape Meares, Oregon	0.162 ± 0.016	6.2 (+0.7, −0.6)	0.26
Ragged Point, Barbados	0.156 ± 0.016	6.4 (+0.7, −0.6)	0.26
Point Matatula, Samoa	0.138 ± 0.017	7.2 (+1.1, −0.7)	0.22
Cape Grim, Tasmania	0.131 ± 0.016	7.6 (+1.1, −0.8)	0.26
All sites from trend	0.145 ± 0.008	6.9 (+0.4, −0.4)	
All sites from trend (with emission trend uncertainty included)	0.145 ± 0.021	6.9 (+1.2, −0.9)	
Global atmospheric content (with emission uncertainty included)	0.167 ± 0.025	6.0 (+1.1, −0.8)	
Latitudinal gradient	0.167 ± 0.031	6.0 (+1.4, −1.0)	

Table 5. Optimally determined tropospheric OH concentrations (units are 10^5 radicals per cubic centimeter and uncertainties are 1σ). Global average tropospheric OH concentration is $(7.7 \pm 1.4) \times 10^5$ radicals per cubic centimeter.

Pressure (mbar)	OH concentration			
	90° to 30°N	30°N to 0°	0° to 30°S	30° to 90°S
200 to 500	4.8 ± 0.9	9.9 ± 1.8	10.4 ± 1.9	6.0 ± 1.1
500 to 1000	4.9 ± 0.9	10.4 ± 1.9	9.8 ± 1.8	5.4 ± 1.0

of the spatial pattern in the theoretical OH concentration $[\mathrm{OH}]_i^*$ we can also compute the average OH concentration in each box (which equals $A[\mathrm{OH}]_i^*$) (Table 5).

The sensitivity of these results to the assumed theoretical spatial distribution of OH may be evaluated by repeating the calculations with a tropospherically uniform distribution of OH (that is, OH is reduced in the tropics and increased in higher latitudes relative to the theoretical values). A comparison of the two-dimensional model results for nonuniform and uniform distributions shows a decrease in the model Northern Hemisphere mid-latitude methylchloroform concentrations by 2.3% because of the substantially increased OH levels there. The increase in the model tropical lower troposphere is less (only 0.4%) because of the reduction in the OH concentrations there. There is thus a small overall decrease in globally averaged model methylchloroform concentrations of 1.4% for the case of uniform OH concentrations. The sensitivity of the globally averaged lifetime estimates to the distribution of OH within the troposphere is negligible (a decrease in the estimated lifetime τ of only 0.1 year is obtained with uniform OH) except for the lifetime that would be inferred from the latitudinal distribution of methylchloroform, which would decrease by approximately 0.3 year).

Methane is observed to be increasing throughout the world and its global tropospheric distribution has been measured *(22)*. The major tropospheric sink for methane is reaction with the hydroxyl radical with a rate constant similar to that for methylchloroform *(23)*. Therefore, the average hydroxyl radical concentrations deduced from methylchloroform (Table 5) have been used together with observed atmospheric temperatures and the global distribution and rate data for methane *(22, 23)* to calculate an average tropospheric lifetime for methane of 9.6 (+2.2, −1.5) years (1σ). The uncertainty in this lifetime does not include uncertainty in the rate constants.

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10. ALE is described by R. Prinn *et al.* [*J. Geophys. Res.* **88**, 8353 (1983)] and in five reports that immediately follow. GAGE is a follow-on to ALE in which the ALE HP 5840 instruments (Hewlett-Packard) (4 measurements per day) were first run together with and then replaced by HP 5880 instruments (12 measurements per day). Agreement between ALE and GAGE instruments for methylchloroform was excellent during the overlap period.
11. The stations are located at Adrigole, Ireland (52°N, 10°W), Cape Meares, Oregon (45°N, 124°W), Ragged Point, Barbados (13°N, 59°W), Point Matatula, American Samoa (14°S, 171°W), and Cape Grim, Tasmania (41°S, 145°E). The Cape Meares station was opened in January 1980 and the Adrigole station was closed in December 1983. All of the other stations opened in July 1978.
12. Our new calibration, which is based on A. Khalil and R. Rasmussen [*Chemosphere* **13**, 789 (1984)], is specifically 0.80 ± 0.08 (1σ) times our old calibration standard, which was based on R. Rasmussen and J. Lovelock [*J. Geophys. Res.* **88**, 8369 (1983)]. This means that the so-called ALE-GAGE calibration factor for methylchloroform is 0.80 ± 0.08 in the present report compared to 1.0 ± 0.15 in our previous report *(1)*. In *(1)* we noted that multiplying our old calibration standard by 0.82 yielded a better fit to observations and a lifetime estimate of 6.5 years [similar conclusions were made in *(2)* and *(3)*].
13. The techniques involved identifying large, highly coherent short-term increases in several anthropogenic halocarbons and detection of the anthropogenic species trichloroethylene and perchloroethylene, which have atmospheric lifetimes of only a few days *(1, 10)*. Episodes of pollution are fairly common at Adrigole (about one-third of the time) and, although much rarer, are becoming more common at the other sites. Autocovariances computed by using the complete data record at Adrigole indicate that these techniques are indeed effective in identifying polluted air at this site (M. Prather, personal communication).
14. A tape that contains every calibrated measurement taken from 1978 to 1985 including the polluted periods can be obtained from F. Alyea, Georgia Institute of Technology, Atlanta, GA 30332.
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18. Global production data are from W. Neely and J. Plonka [*Environ. Sci. Technol.* **12**, 317 (1978)] for 1951 through 1976, and P. Midgley [in *Atmospheric Ozone 1985* (World Meteorological Organization, Geneva, 1985), p. 72], for 1976 through 1983. Global and semihemispheric sales data are from Prinn *et al.* *(1)* for 1977 through 1981, and P. Midgley (ICI Americas, Inc., letter, 18 April 1986) for 1979 to 1985. Uncertainty (2σ) in these production and sales data is ±5%. The percentages sold in each semihemisphere (90° to 30°N, 30°N to 0°, 0° to 30°S, and 30° to 90°S) are 96.67, 1.36, 0.47, and 1.50 in 1977; 96.38, 1.41, 0.55, and 1.66 in 1978; 95.70, 1.6, 0.9, and 1.8 in 1979; 95.5, 1.8, 0.9, and 1.8 in 1980; 95.1, 2.0, 1.0, and 1.9 in 1981; 94.7, 2.2, 1.1, and 2.0 in 1982; 94.50, 2.5, 1.1, and 1.9 in

1983; 94.4, 2.8, 1.1, and 1.7 in 1984; and 94.4, 2.9, 1.1, and 1.6 in 1985. We assumed the percentages before 1977 varied linearly from their 1951 values (100, 0, 0, and 0) to their 1977 values.

19. Specifically, we assumed that $a = 1/24 \pm 1/24$ after 1964 and $0 \pm 1/24$ before 1964, $b = 1/12 \pm 1/12$, and $f = 0.94 \pm 0.02$, based on industry evaluations (*1*). Uncertainties are 2σ.
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21. Values for $[\mathrm{OH}]_i^*$ and k_i are given in Prinn *et al.* (*1*) and are based, respectively, on the theoretical model of J. Logan *et al.* [*J. Geophys. Res.* **86**, 7210 (1981)] and the kinetic studies of K. Jeong and F. Kaufman [*Geophys. Res. Lett.* **6**, 757 (1979)] and others. Theoretical OH concentrations are a sensitive function of ultraviolet irradiance and O_3, H_2O, CO, NO, and NO_2 concentrations.
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A DNA Segment Encoding Two Genes Very Tightly Linked to Huntington's Disease

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The discovery of D4S10, an anonymous DNA marker genetically linked to Huntington's disease (HD), introduced the capacity for limited presymptomatic diagnosis in this late-onset neurodegenerative disorder and raised the hope of cloning and characterizing the defect based on its chromosomal location. Progress on both fronts has been limited by the absence of additional DNA markers closer to the HD gene. An anonymous DNA locus, D4S43, has now been found that shows extremely tight linkage to *HD*. Like the disease gene, D4S43 is located in the most distal region of the chromosome 4 short arm, flanked by D4S10 and the telomere. In three extended HD kindreds, D4S43 displays no recombination with HD, placing it within 0 to 1.5 centimorgans of the genetic defect. Expansion of the D4S43 region to include 108 kilobases of cloned DNA has allowed identification of eight restriction fragment length polymorphisms and at least two independent coding segments. In the absence of crossovers, these genes must be considered candidates for the site of the HD defect, although the D4S43 restriction fragment length polymorphisms do not display linkage disequilibrium with the disease gene.

HUNTINGTON'S DISEASE (HD), A neurodegenerative disorder of mid-life onset, is caused by a highly penetrant dominant defect that causes specific neuronal loss, leading to progressive motor disturbance, psychological manifestations, and intellectual deterioration (*1*). No treatment is effective in halting or delaying the inexorable progression of HD, which results in complete disability, and ultimately death, typically 15 to 20 years after onset.

The biochemical basis for the cell death in HD is not understood. Recent efforts to elucidate the nature of the genetic defect have concentrated on the chromosomal position of the HD gene, located 4 centimorgans (cM) from the anonymous DNA marker D4S10 in the terminal cytogenetic band of the chromosome 4 short arm (*2*). The recombination rate implies a physical distance of several million base pairs between the two loci, a strong deterrent to the application of chromosome walking strategies for cloning the HD gene. Furthermore, this genetic separation, together with the absence of a marker flanking the disease locus, have limited the accuracy which can be achieved in presymptomatic diagnosis of this disorder.

D4S10 has been physically mapped to 4p16.3, the terminal cytogenetic subband, which comprises about 3% of the cytogenetic length of chromosome 4 (*3*). Multipoint linkage analysis with additional proximal DNA markers has established that the HD gene is located closer to the telomere than D4S10, which limits the potential for isolating probes closer to or flanking the HD gene (*2*). By physically mapping more than 200 randomly chosen chromosome 4 probes, we have identified a single locus, D4S43, that has the potential for being closer to, or flanking the HD defect (*2, 3*).

The D4S43 locus was initially defined by the anonymous DNA probe C4H, which is a 3.0-kb single-copy Hind III fragment derived from a chromosome 4–specific library (*2, 3*). C4H detects two relatively infrequent restriction fragment length polymorphisms (RFLPs) in Bcl I– or Msp I–digested DNA (Table 1) which were uninformative for linkage in most HD kindreds, including the extended Venezuela HD pedigree critical to the discovery of the D4S10 marker (*2*). However, these RFLPs were segregating in a portion of the Venezuela family used as a "reference" pedigree for determining the linkage relationships of DNA markers (*4*). D4S43 was linked to D4S10 with a maximum logarithm of the odds (lod) score of $\hat{z} = 31.97$ at a recombination fraction $\hat{\theta} = 0.04$ (Table 2), but showed very loose linkage to *RAF2*, a proximal marker located in 4p16.1. Multipoint analysis (*5*) of the three loci revealed that a position of D4S43 distal to D4S10 was favored by more than $10^5{:}1$ relative to a location between the other two markers, or proximal to *RAF2*. D4S43 therefore maps at the same approximate genetic distance from D4S10 as *HD*, in the terminal segment of the short arm of chromosome 4 bordered by D4S10 and the telomere (*2*).

To find more informative RFLPs at the D4S43 locus, we isolated a cosmid clone, C9A, which contains the C4H segment. Figure 1 includes a restriction map of C9A, with the locations of three single-copy fragments C4H, HB1.4, and H2.0. The integrity of the C9A cosmid was tested by mapping each of these fragments to the same terminal region of 4p by means of a somatic cell hybrid panel (*3*). This analysis revealed that HB1.4 detected significant homology in rodent DNAs, suggesting that it contained a conserved coding sequence. Consequently we probed a human liver complementary DNA (cDNA) library to obtain LCD, a cDNA clone encoded within a 13-kb stretch of the D4S43 region (Fig. 1).

Three additional infrequent RFLPs were identified with H2.0 or portions of LCD, but these only modestly increased the general utility of the locus (Table 1). However,

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