volts. Since this is less than the 10⁸-volt potential that is estimated to be developed by an average storm, the maintenance of a vortex-stabilized discharge appears to be within the storm's voltagecurrent capability, granting the prior existence of a vortex.

Now consider the power output of a continuous current discharge situated inside a tornado. From the preceding discussion it is seen that if a thunderstorm were to supply a continuous current of the order of 1 amp through an arc stabilized in a tornado vortex, in which the voltage is only 5×10^7 volts, the power thus released by heating in the vortex would be at most of the order of 5×10^4 kw. This, approximately half of the estimated 10⁵ kw being developed by the storm, would probably be unimportant compared with the 4×10^6 kw that would be required to produce a tornado with a radius of 50 m and a speed of 10^2 m/sec (4). Thus, although an ordinary electrical storm would be capable of supplying the continuous current and cloudto-ground voltage required to maintain a vortex-stabilized arc inside a tornado, the power output of the discharge would be negligible compared to the aerodynamic power dissipated by the tornado.

Although an ordinary thunderstorm could not maintain a vortex-stabilized discharge with a power output comparable to that of a tornado, it is possible that a giant electrical storm could. These extraordinary storms rise to an altitude of 20 km, twice that of ordinary storms, and have comparably greater horizontal dimensions (11). The lightning stroke rates reach values as high as 20 per second in contrast to rates of under 20 per minute characteristic of ordinary storms. Assuming a charge transfer of 5 coulombs per stroke, it can be estimated that currents as high as 10² amp might be available in the giant storm. Even assuming the extraordinary continuous current of 10² amp, we find from Fig. 6 that the heating in a 5-km-long arc would still be only 10⁶ kw, somewhat less than the 4 \times 10⁶ kw estimated to be required for a modest tornado.

Conclusions. Even though extrapolations of the results of our laboratory experiments indicate that either an ordinary or a giant electrical storm might be capable of maintaining a vortex-stabilized arc, the arc would not be of tornadic power. This is so because the impedance of the plasma associated with a steady discharge is so low that even the highest conceivable steady-state currents would produce insufficient heating to maintain even an average tornado. Therefore, although continuous current discharges may occur in tornado vortices, the energy supplied by this type of discharge would be at most 25 percent and probably a much smaller percentage of the energy budget of the tornado. Thus it would not constitute a major power source. Even if our extrapolations are correct, however, the possibility is not precluded that significant electrical heating could occur as the result of other kinds of electrical processes, such as a high-impedance glow discharge or an arc maintained by intermittent heavy current surges.

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References and Notes

- B. Vonnegut, C. B. Moore, C. K. Harris, J. Me-terol. 17, 468 (1960); E. Wilkins, J. Geophys. Res. 69, 2435 (1964); O. H. Vaughan, Jr., and B. Vonnegut, Bull. Am. Meteorol. Soc. 57, 1220
- 2. R T. Ryan and B. Vonnegut, Science 168, 1349 (1970)
- O. Schonherr, *Elektrotech. Z.* 30, No. 16 (1909).
 B. Vonnegut, J. Geophys. Res. 65, 203 (1960). 3
- B. vonnegut, J. Geophys. Res. 65, 203 (1960).
 S. A. Colgate, Science 157, 1431 (1967).
 R. P. Davies-Jones and J. H. Golden, J. Geophys. Res. 80, 1614 (1975);
 S. A. Colgate, *ibid.*, p. 4556;
 R. P. Davies-Jones and J. H. Golden, *ibid.*, p. 4550;
 B. Davies-Jones and J. H. Golden, *ibid.*, p. 4550; R. 6. 4559; R. P. I ibid., p. 4561. Davies-Jones and J. H. Golden,
- C. Suits, Phys. Rev. 55, 561 (1939). J. D. Cobine, Gaseous Conductors (Dover, New
- S. D. Colme, Gassas Conductors (Dover, New York, 1958), p. 335.
 H. Maecker, Ed., Ionization Phenomena in Gases (North-Holland, Amsterdam, 1961).
 M. Uman, Lightning (McGraw-Hill, New York, 1969), p. 264.
- Boy, p. 264.
 B. Vonnegut and C. B. Moore, in *Recent Advances in Atmospheric Electricity*, L. G. Smith, Ed. (Pergamon, New York, 1959), p. 399.
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Methyl Chloroform: Impact on Stratospheric Ozone

Abstract. Regulations to limit the use of trichloroethylene as a degreasing solvent have led to an increased use of the more photochemically inert solvent methyl chloroform as a substitute. Model calculations show that about 15 percent of the methyl chloroform released into the atmosphere will reach the stratosphere. Time scenarios based on past production figures and reasonable projections for future release rates lead to a steady-state ozone depletion due to this solvent about 20 percent as large as those resulting from the continuous release of chlorofluoromethanes at 1973 rates.

Urban air pollution has been a matter of considerable concern for some time, and regulations have been enforced to limit the emissions of harmful substances (1). More recently, concern has also been expressed over possible depletion of stratospheric O₃ resulting from the release of certain halocarbons (2, 3), and steps are now under way to limit their release rates. The criteria for classifying substances as potentially harmful to the stratosphere and troposphere are not the same and are, in fact, more likely to be opposed.

The Environmental Protection Agency (EPA) has classified as "restricted" solvents those that they define to be photochemically reactive, that is, those that are readily attacked, for example, by O_3 and HO; the EPA has designated as "safe" solvents those that are not readily oxidized (1). One such restricted solvent is CHClCCl₂ (trichloroethylene), used largely for metal degreasing (4). In 1970, 16 states adopted legislation to restrict the use of this solvent; on 8 July 1976, the EPA announced that 28 states had been advised that they will be required to adopt more stringent controls over photochemical oxidants, including trichloroethylene (5). In 1970 the U.S. production of this solvent was 2.8×10^5 metric tons, but by 1976 it had decreased to less than half this amount (4, 6). The world production capacity of this solvent in 1976 was 9.8×10^5 tons, but only 54 percent of this total was utilized (7). Part of this diminished use resulted from the regulations which forced a changeover from this solvent mainly to CH₃CCl₃ (1,1,1-trichloroethane or methyl chloroform), which EPA has classified as a safe substance.

In 1970 the U.S. production of methyl chloroform was 1.7×10^5 tons, and by 1976 it had increased to 3.0×10^5 tons (8, 9). Worldwide capacity in 1976 was $5.3\,\times\,10^{5}$ tons with 90 percent utilization (7). Additional capacity figures have been announced: Europe, 9×10^4 tons for the last quarter of 1976; United States, 2.2×10^5 tons for 1978; and Japan, 7.3×10^4 tons for 1979 (10). Thus, by 1979 the world production capacity of this compound will be 9.1×10^5 tons.

The EPA classified methyl chloroform as safe because it is relatively inert in the troposphere as compared with trichloroethylene. The rate constant for the attack of methyl chloroform by HO radi-

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Table 1. Production of methyl chloroform in millions of pounds per year (1 pound = 0.453 kg).

Year															Refer
1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1982	ence
							Unite	d States							
243	270	299	324	366	375	440	537	590	442	578					(6, 8)
										665					(9)
							533								(32)
							555								(33)
												1092			(10)
							W	orld							
345										.961	1291		1555	1876	(7)
							900								(34)
							925								(33)
					640										(8)
											1026	1440	1584		(7, 10)
							1060								(35)

cals (11) is about 100 times slower than that for trichloroethylene. Our calculations show that the tropospheric lifetime of methyl chloroform is about 8 years, whereas that for trichloroethylene is a few days (12). About 15 percent of the methyl chloroform will be transported into the stratosphere where it is rapidly photolyzed to yield Cl and ClO, which can catalytically destroy O_3 (13). We may compare the projected 1979 rate of emission of methyl chloroform, $9 \times$ 10⁵ tons, with the current release rates of F-11 (CFCl₃) and F-12 (CF₂Cl₂), about 7.2×10^5 tons (3). The chlorofluoromethanes (CFM's) are even more inert to HO attack than methyl chloroform, so that most of CFM's released will reach the stratosphere. It thus seems worthwhile to assess the effect on the O_3 layer of the increasing utilization of methyl chloroform, based on realistic projections for future release of this substance.

We have made computer simulations of the impact on stratospheric O3 of releases of methyl chloroform compared with that of F-11 and F-12. We have used actual release rates for the CFM's (3)through 1973, and several scenarios are projected for future releases (13). The release rates for methyl chloroform (Table 1) are based on past and projected production to 1982. Several scenarios are projected for release rates beyond that date. Calculations were done with a socalled one-dimensional model (14) in which the transport is parameterized by a vertical eddy diffusion coefficient, K_z , which is assumed to be a function of altitude only (15).

One check on the model is a comparison between calculated and measured atmospheric burdens of methyl chloroform. Lovelock and his co-workers (16, 17) obtained values for the mixing ratio of 65 ± 17 parts per 10^{12} by volume (pptv) in the Northern Hemisphere and 24 ± 3 pptv in the Southern Hemisphere for 1974 to give a global average 13 JANUARY 1978 of 40 ± 10 pptv (18). The global average calculated from the production figures in Table 1 and the model is 73 pptv for 1974. Rasmussen (19) obtained average values of 106 ± 10 pptv in the Northern Hemisphere and 72 ± 7 pptv in the Southern Hemisphere in late 1976 for a global average of 89 \pm 9 pptv. Singh (20) reported an average value for the Northern Hemisphere of 100 ± 10 pptv for 1976, which is within 5 percent of the value obtained by Rasmussen for the same period. Our calculations for 1976 give 90 pptv for the global average. Thus the calculations are within the range of the measurements.

Another test for the model is a comparison between calculated and measured hemispheric ratios. With our model it is not possible to directly calculate this ratio. However, we have used the chemical time constant $\tau_c = 8$ years (21) from our model and the interhemispheric transport time constant τ_1 for a simple box model in an attempt to obtain the ratios of the methyl chloroform burdens in the Northern Hemisphere, C_N , and the Southern Hemisphere, C_S . Assuming an exponentially increasing release rate of the compound in the Northern Hemisphere based on Table 1, we obtain a time constant $\tau_R = 8$ years (22). The expression relating the above quantities is

$$\frac{C_{\rm N}}{C_{\rm S}} = 1 + \frac{\tau_{\rm I}}{\tau_{\rm c}} + \frac{\tau_{\rm I}}{\tau_{\rm R}} \tag{1}$$

Using Rasmussen's data (19) for the interhemispheric ratio, we obtain $\tau_{I} \approx 1.8$ years. If we model measurements of F-11 in a similar way, we obtain $\tau_{I} \approx 2$ years (23). If the interhemispheric ratio of methyl chloroform is 2 as suggested



Fig. 1. Depletion of O₃ for various scenarios involving continuous release of CFM's. (Curve A) Depletion of O₃ due to F-11 and F-12 alone. Actual release rates are as in (3) until 1973 with continued release at the 1973 rate after that date. Steady-state reduction (labeled in parentheses with an arrow) = 6.6percent. (Curve B) Depletion of O₃ due to F-11, F-12, and methyl chloroform release rates as per the schedule of Table 1 until 1982, then increasing at 7 percent per year until a value of 3×10^9 pounds is reached in 1990, and then kept constant at that value beyond 1990. The 7 percent increase between 1982 and 1990 can be compared to an average of a 10 percent increase between 1966 and 1976 and is based on an estimate for an increase in the world gross national product between 1982 and 1990 (7). Steady-state reduction = 7.8 percent. (Curve C) Depletion of O₃ due to F-11 and F-12 alone. Actual release rates as in (3) until 1973, with continuous release after 1973 at half the 1973 rate. This scenario might occur if only the United States banned all uses of CFM's or if there were worldwide agreements to reduce the emissions by this factor, for example, by regulating against aerosol uses. Steady-state

reduction = 3.3 percent. (Curve D) Depletion of O_3 due to F-11, F-12, and methyl chloroform; F-11 and F-12 releases are as for curve C and methyl chloroform releases are as per curve B, that is, regulations for the reduction of CFM's by a factor of 2, with no restrictions on methyl chloroform. Steady-state reduction = 4.6 percent.

by the data of Lovelock et al. (18), then Eq. 1 yields $\tau_{I} \cong 4$ years. Other independent estimates of τ_1 range from 8 months (24) to 4 years (25). The values of $\tau_{\rm I}$ derived from Rasmussen's data for methyl chloroform and the F-11 data are in reasonable agreement and suggest $\tau_{\rm I} \cong 1.5$ to 2 years for constituents emitted at high northern latitudes (26). Thus a lifetime for methyl chloroform of $\tau_c = 8$ years is in agreement with the global inventory and the interhemispheric ratio based on recent data (19, 20). The global average data obtained from Lovelock's measurements (18) suggest $\tau_c \approx 4$ years but yield a $\tau_{I} \cong 4$ years which seems to be on the high side of the estimates. For this reason and because the two more recent independent measurements of methyl chloroform (Rasmussen and Singh) seem to be more consistent, we tend to favor $\tau_1 \cong 1.5$ to 2 years and $\tau_{\rm c} \cong 8$ years.

In order for our model to give a value of $\tau_{\rm I}$ as short as 1 year we would have to use a larger value for the rate of the reaction of HO with methyl chloroform, the major loss process in our model, or some effective sink such as removal by seawater, not included in our model. The uncertainty in the rate constant for the reaction between HO and methyl chloroform (11) is probably not large enough to produce such a reduction in τ_c . The alternative is an increase in the mixing ratio of HO over the value used in the model (27).

Values for τ_c of 1 to 1.4 years have been suggested in the National Academy of Sciences (NAS) report (3). However, such values would result in a calculated global mixing ratio in 1976 of 20 pptv, in disagreement with the measurements unless there was some additional source of methyl chloroform in the Northern Hemisphere. Natural sources plus release rates from the Eastern European countries (28) would need to be about five times larger than the values given in Table 1 in order to maintain the observed global atmospheric burden.

The results of our calculations for the time scenarios of O₃ depletion are shown in Figs. 1 and 2. Curve A in Fig. 1, showing O_3 depletion (ΔO_3) due to the release of CFM's alone at a constant (1973) level, can be used to scale our results to those that might be obtained from other models. For example, the steady-state ΔO_3 value of 6.6 percent can be compared with the 7.5 percent given in the NAS report (3). These disagreements are due largely to differences in the choice of eddy diffusion coefficients and in the rate constants (29). Curve B gives the ΔO_3 value obtained if the release schedule of



Fig. 2. Depletion of O₃ for various scenarios involving termination of CFM release in 1978. (Curve E) Depletion of O3 due to F-11 and F-12 alone. Actual release rates until 1973, constant release at the 1973 rate from 1973 to 1978, and zero release after 1978. (Curve F) Depletion of O₃ due to F-11, F-12, and methyl chloroform; F-11 and F-12 release rates are as in curve E, and the release rate for methyl chloroform is as in Fig. 1, curves B and D. Steady-state reduction = 1.3 percent. (Curve G) Depletion of O_3 due to F-11, F-12, and methyl chloroform; F-11 and F-12 release rates are as in curves E and F; methyl chloroform release is as in curve F until 1990 and zero release after 1990.

methyl chloroform (Table 1) is added to the CFM scenario used to obtain curve A; the steady-state ΔO_3 value increases to 7.8 percent, that is, increases by a factor of 1.2. Curve C shows that a decrease in the steady release rates of CFM's to half the 1973 values (for example, as a result of selective regulations) would decrease the steady-state ΔO_3 value to 3.3 percent. The corresponding value with inclusion of the methyl chloroform release schedule is 4.6 percent, an increase by a factor of 1.4 (curve D).

The response time of ΔO_3 to changes in release rates is guite different in the case of CFM's as compared to methyl chloroform (Fig. 2). A total ban on CFM (curve E in Fig. 2) release in 1978 results in a peak depletion of 0.7 percent, which occurs 14 years later and ΔO_3 recovery to the 1978 levels by about the year 2025. Curve F is similar to curve B in Fig. 1 except that the CFM release is zero from 1978 on. Curve F shows a peak ΔO_3 value of 1.8 percent occurring in 2010 and a steady-state reduction due to methyl chloroform of 1.3 percent. The effect of a total ban on this compound in 1990 following a total ban on CFM's in 1978 is shown as curve G; the peak ΔO_3 value of 1.4 percent occurs in 1995. Since methyl chloroform has a relatively short residence time in the atmosphere, it would make little contribution to ΔO_3 25 years after its ban (30). The absolute values in the time scenario curves will, of course, depend on the choice of eddy diffusion coefficients (29).

The relative sluggishness of ΔO_3 to bans on CFM's imposed at various times is due to the fact that the major sink is located above 30 km, which means that the CFM's are drained from the atmosphere from the top down, a relatively slow process. On the other hand, if the release of methyl chloroform is stopped, the response of ΔO_3 is much more rapid since a strong tropospheric sink exists and the CFM's are drained from the atmosphere from the bottom up. The products from the reactions of methyl chloroform are released at all altitudes. The maximum production of CIX in the stratosphere from this compound occurs several kilometers lower than it does for the CFM's and therefore closer to the tropospheric sink. For this reason, methyl chloroform molecules are not as efficient in effecting O₃ destruction as the CFM's (31). For example, curve F shows a steady-state value of ΔO_3 of 1.3 percent due to methyl chloroform alone, on the basis of the release rates given. If similar release rates of CFM's were used (no methyl chloroform), then $\Delta O_3 = 2$ percent.

Nevertheless, reasonable projections for the release schedules of methyl chloroform lead to steady-state ΔO_3 values about 20 percent as large as those resulting from the continuous release of F-11 and F-12 at the 1973 rates. We would suggest that regulations governing the release of chemical compounds for environmental reasons should not be based on consideration of only one region of the biosphere.

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References and Notes

- 1. For a general review of air pollution regulations and their implementation, see M. Feldstein, J. Air Pollut. Control Assoc. 24, 469 (1974).
- 2. M. J. Molina and F. S. Rowland, Nature (Lon-
- don) 249, 810 (1974). "Halocarbons: Effects on stratospheric ozone" (National Academy of Sciences, Washington, 3.
- D.C., 1976). 4. For a summary of regulations and data concerning trichloroethylene, see J. L. Blackford, in *Chemical Economics Handbook* (Stanford Research Institute, Menlo Park, Calif., 1975), p. 697.3031A.
- 5. Environmental News (Environmental Protection
- Agency, Washington, D.C., 8 July 1976). U.S. International Trade Commission Reports, "Synthetic organic chemicals," Series C/P-76-8, (Government Printing Office, Washington, D.C. 20. Outches 1976). 6. 20 October 1976)
- D.C., 20 October 1976).
 7. Unpublished data from Detrex Chemical Industries, Inc. (1976).
 8. J. L. Blackford, in *Chemical Economics Handbook* (Stanford Research Institute, Menlo Park, Calif., 1972), p. 697.3031A.
 9. Based on 7 months of data from (6).
 10. *Chem. Mark. Rep.* 211, 9 (1977); *Chem. Week* 119, 32 (1976).
 11. There have been ecoural measurements to data
- 11. There have been several measurements to date of the rate of reaction of methyl chloroform with

HO. Cox et al. (17) give 2.8 × 10⁻¹⁴ cm³ sec⁻¹;
C. J. Howard and K. M. Evenson [J. Chem. Phys. 64, 4303 (1976)] give 1.5 × 10⁻¹⁴ cm³ sec⁻¹. Values obtained by D. Davis and R. T. Watson and by J. S. Chang, C. Steen, and F. Kaufman [Appendix A in (3)] are 1.6 × 10⁻¹⁴ and 2.2 × 10⁻¹⁴ cm³ sec⁻¹, respectively. We have adopted the temperature-dependent rate of 8 × 10⁻¹³ exp(-1200/T) cm³ sec⁻¹.
12. The reaction between trichloroethylene and HO is ~ 2 × 10⁻¹² cm³ sec⁻¹ [see, for example, table A. 1 in Appendix A of (3)].

- is ~ 2 × 10⁻¹² cm³ sec⁻¹ [see, for example, table A.1 in Appendix A of (3)].
 13. P. J. Crutzen, I. S. A. Isaksen, and J. McAfee (J. Geophys. Res., in press) have calculated that about 12 percent of the methyl chloroform released will reach the stratosphere. They have also calculated the loss of O₃ due to methyl chloroform production increasing at the present rate
- In the model we used the implicit finite dif-14. for the induct we used the implicit infite dif-ference technique with conservation conditions applied to each family of atmospheric com-ponents, a technique similar to that described by R. P. Turco and R. C. Whitten [J. Geophys. Res. 79, 3179 (1974)]. The families are as fol-Res. (9, 51/9 (19/4)]. The families are as follows: $O_x = O_3$, NO_2 , and O_1 , $NO_x = N$, NO_1 , NO_2 , NO_3 , N_2O_5 , and HNO_3 ; $HO_x = H$, HO_1 , and HO_2 ; CIX = CI, CIO, HCI, and $CIONO_2$. The concentrations of CFCl₃, CF2₂, and CH_3CCl_5 were also allowed to vary with time CH₃CCl₃ were also allowed to vary with time and altitude, as were the concentrations of CH₃Cl, CO, N₂O, CH₄, and H₂O₂. Each constit-uent was allowed to vary subject to the follow-ing boundary conditions. The mixing ratios of O₂, H₂, CO₂, and H₂O were kept fixed. Constant flux boundary conditions were assumed for O_x, ClX, and NO_x. The surface mixing ratios of N₂O, CH₄, CO, and CH₃Cl were kept constant at typical tropospheric values. Quasi steady-state was assumed for determining the mixing was assumed for determining the mixing s of short-lived species, for example, NO, state ratios o H, and HO. The reaction rate data were taken largely from the compilation of recommended values by the National Bureau of Standards [R. values by the National Bureau of Standards [R. F. Hampson and D. Garvin, "Chemical, kinetic and photochemical data for modelling atmo-spheric chemistry" (Technical Note 866, Na-tional Bureau of Standards, Gaithersburg, Md., 1975)] and from the report of the National Acad-emy of Sciences (3); a value of 5×10^{-11} cm³ sec⁻¹ was adopted for the uncertain rate con-stant for HO + HO₂ \rightarrow H₂O + O₂. Cross sec-tions for photolysis were taken from J. C. McConnell and M. B. McElroy [J. Atmos. Sci. 30, 1465 (1973)] and from (3) excent for methyl McConnell and M. B. McElroy [J. Atmos. Sci. 30, 1465 (1973)] and from (3) except for methyl chloroform; the data for this compound were kindly supplied by Dr. F. S. Rowland (personal communication). Values of the solar flux as a function of wavelength were taken from (3). The photodissociation rate coefficient J was approxi-mated by a 24-hour average at 30°N for equinox. This approximation tends to exaggerate the ClONO₂ concentration and minimizes O₃ losses. The results presented here were obtained with
- 15. The results presented here were obtained with the eddy diffusion profile developed by D. M. Hunten [*Proc. Natl. Acad. Sci. U.S.A.* **72**, 4711
- 16. J. E. Lovelock, Nature (London) 252, 292
- J. E. LOVEICK, Marke (1974).
 R. A. Cox, R. G. Dervent, A. E. J. Eggleton, J. E. Lovelock, Atmos. Environ. 10, 305 (1976).
 We calculated the average value, assuming that traditional variation and the second se methyl chloroform has a latitudinal variation similar to that for F-11 as reported by J. E. Lovelock, R. J. Maggs, and R. J. Wade [*Nature* (*London*) 241, 194 (1973)]. This calculation gives a value of 2.0 for the interhemispheric ratio. This can be compared with a value of 2.7 ob-tained by taking the measurement of methyl chloroform referred to in the text for 51.7°N and 34°S as being representative of the Northern
- and Southern hemispheres, respectively. R. A. Rasmussen, personal communication. H. B. Singh, *Geophys. Res. Lett.* 4, 101 (1977).
- 21. Here $\tau_c =$ the total amount in the atmosphere in the steady state divided by the input flux.
- the steady state divided by the input nux. 22. The time constant for release (τ_R) is defined by the expression: release rate = $A \exp(t/\tau_R)$, where t is time and A is a constant. 23. We have used the F-11 measurements of Love-lock et al. (18). A similar value for τ_1 has been obtained by F. S. Rowland (personal communi-cation).
- 24. Using low-altitude meridional wind fields dis-24. Using low-altitude meridional wind fields discussed by E. R. Reiter [in Atmospheric Transport Processes, Part 1, Energy Transfers and Transformations (Atomic Energy Commission, Washington, D.C., 1969), p. 14], we obtain an estimate for τ₁ of 8 months.
 25. A. Walton, M. Eergin, and D. D. Harkness [J. Geophys. Res. 75, 3089 (1970)] found that τ₁ = 4 years is in agreement with data on ¹⁴C in the troposphere.

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- 26. Y. L. Yung, M. B. McElroy, S. C. Wofsy [Geophys. Res. Lett. 2, 397 (1975)] obtained $\tau_c \approx 3$ years, implying $\tau_1 \approx 1$ year. However, the global inventory calculated on this basis would be too small by a factor of about 2.
- 27. The tropospheric HO values that we have ob-The tropospheric HO values that we have ob-tained are $\approx 5 \times 10^5$ cm⁻³. Ground values are lower than those given by some other models [S. C. Wofsy, Annu. Rev. Earth Planet. Sci. 4, 441 (1976)] but are in reasonable agreement at other altitudes. However, they are not in dis-agreement with HO values suggested by P. Warneck [*Tellus* 26, 39 (1974)], who investigated the effects of heterogeneous reactions oc on the surfaces of particles terminating $HO-HO_2$ cycles. W. Seiler and U. Schmidt [in *Pro-ceedings of the International Conference on the* Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Pos-sible Anthropogenic Perturbations, N. J. Derco and E. J. Truhlar, Eds. (Atmospheric Environ-ment Services, Downsview, Ontario, Canada, 1974), p. 192], on the basis of interhemispheric CO mixing ratios, suggested that low to inter-mediate HO densities should obtain. In view of the fact that the HO densities we calculate ar average densities, they are not in conflict with measurements such as those of D. Perner, D. H. Ehhalt, H. W. Pätz, V. Platt, E. R. Roth, and A. Volz [*Geophys. Res. Lett.* **3**, 466 (1976)] ob-tained at Julich (51°N, 6°E).
- S. Rowland, personal communication.
 The steady-state value of ΔO₃ that we obtain, using the profile of eddy diffusion coefficients of D. H. Ehhalt, L. E. Heidt, R. H. Lueb, and E. A. Martell [J. Atmos. Sci. 32, 163 (1975)], is 9.6 ercent.
- Obviously, if the values of HO that we have 30. used do not obtain and are adjusted, then the ΔO_3 values calculated must be modified. Similarly, the conclusions may be modified by a change in the rate constant for the reaction of
- 31.
- change in the rate constant for the reaction of HO with methyl chloroform.
 R. J. Cicerone, R. S. Stolarski, S. Walters, Sci-ence 185, 1165 (1974).
 Chem. Mark. Rep. 205, 9 (1974).
 A. D. Little, Inc., Preliminary Economic Impact Assessment of Possible Regulatory Action to Control Atmospheric Emissions of Selected Hy-drocarbons (Publ. PB-247-115, National Techni-cal Information Service. Springfield, Va. 1975).
- cal Information Service, Springfield, Va., 1975). A. D. Little, Inc., Report on the Problem of Halogenated Air Pollutants and Stratospheric Ozone (Publ. PB-247-699, National Technical Information Service, Springfield, Va., 1975).
 C. R. Pearson and G. McConnell, Proc. R. Soc. London Sect. B 189, 305 (1975).
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Phytolith Analysis of Archeological Soils:

Evidence for Maize Cultivation in Formative Ecuador

Abstract. Soil samples from the archeological sites of Real Alto and OGCh-20, Santa Elena Peninsula, Ecuador, show the presence of cross-shaped silica bodies identifiable as maize (Zea mays L.) phytoliths by size comparison with known wild grass and maize phytoliths. These results support arguments for the cultivation of maize at 2450 B.C. in coastal Ecuador.

In attempting to reconstruct the subsistence systems of prehistoric peoples, archeologists have come to rely on techniques such as soil flotation and pollen analysis to recover the remains of utilized wild plants and cultigens. The recovery of phytoliths, silica bodies present in the epidermal cells of some plant groups, is a technique less known to American archeologists. It has been used in Europe, the Middle East, and Japan to indicate the presence of cultivated grasses in sites with poor botanical preservation (1). During the University of Illinois excavations of the Valdivia culture (3000-1500 B.C.) site Real Alto and the Machalilla (1500-1000 B.C.) site OGCh-20 in the Santa Elena Peninsula, Ecuador, soil samples were taken for phytolith analysis to test for the presence of maize (Zea mays L.) at these sites (2). Preliminary efforts to distinguish maize phytoliths from phytoliths present in the native grasses of the peninsula have given positive results. Cross-shaped phytoliths distinguishable as maize have been found in ten archeological soil samples.

As plants grow and take up water from the soil, they absorb dissolved minerals, including silica. Silica is deposited in the epidermal cells of the leaves, both across the veins and between them. In many taxa, distinctively shaped bodies are formed when the silica completely fills a cell (3, 4). In the grasses, phytolith types can be associated with distinctive tribes or genera and distinguished from herbaceous or tree phytoliths. Identification of the parent plant from phytoliths deposited in the soil is possible, particularly when quantitative data on the frequency of occurrence of the types are available (5). Agronomists and soil scientists have used the occurrence of phytoliths deposited in soils as the result of plant decay or burning to determine the composition of an area's flora in previous epochs. Areas of grassland vegetation can be distinguished from those of woodland on this basis (6).

Leaves of maize and ten genera of wild grasses occurring in coastal Ecuador were used as comparative materials in this study. During the 1975 rainy season on the Santa Elena Peninsula, I collected native grasses and identified them to genus. I selected from this collection the genera Aristida, Bouteluoa, Cenchrus, Chloris, Dactyloctenium, Eleusine, Eragrostis, Panicum, and Ischaemum for this study. Tripsacum grown in Illinois was also included. These genera were selected to include a variety of phytolith types, including the cross-shaped type which characterizes maize (4). The

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