gen cycling. The inconveniently short half-life of ^{13}N requires that field samples be returned to the cyclotron and has discouraged investigators from conducting ^{13}N radiotracer experiments. We are presently proceeding with plans to apply this ^{13}N technique to denitrification studies in anaerobic sediment and anoxic bottom water of Castle Lake, California. In order to determine actual in situ rates, we intend to carry out future experiments on undisturbed sediment cores and water samples without mixing or ^{13}N outgassing until sample incubation is complete.

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Atmospheric Carbon Tetrachloride: Another Man-Made Pollutant

Abstract. *On the basis of an analysis of historic worldwide emissions and removal mechanisms for carbon tetrachloride, a possible precursor for stratospheric ozone destruction, it has been demonstrated that the present atmospheric loading and distribution of carbon tetrachloride is primarily attributable to man-made emissions and no natural sources need be invoked to explain its presence in the atmosphere.*

In recent years, the release of chlorofluorocarbons into the atmosphere has received attention because of potential damage to the stratospheric O_3 layer (*1*). The commonly used refrigerants and aerosol propellants F-11 (CCl_3F) and F-12 (CCl_2F_2) are estimated to be present in the atmosphere in amounts approximately equal to their probable cumulative emissions (*1–5*). These observations have tended to confirm the anthropogenic nature of F-11 and F-12 and their tropospheric stability.

An equally important (and ubiquitous) compound present in the ambient air at concentrations similar to those of F-11 and F-12 is CCl_4 (*4–7*). Because of the extreme inertness of this compound in the troposphere, it has been proposed that CCl_4—like F-11 and F-12—may be a likely precursor of stratospheric O_3 destruction (*7*). Although the sources of F-11 and F-12 are known to be exclusively anthropogenic, the atmospheric budget of CCl_4 has been a subject of considerable uncertainty.

Lovelock and his co-workers (*2, 4*) suggested that CCl_4 must have a natural source. Their suggestions were based on two observations: (i) the current emissions of CCl_4 seem unlikely to account for the present atmospheric loading of CCl_4; and (ii) the global distribution of CCl_4 is more uniform than that of F-11. This report demonstrates, by an analysis of worldwide production-emission relationships of CCl_4, its possible secondary anthropogenic synthesis, and its atmospheric sinks, that the present biospheric loading and distribution of CCl_4 is consistent with cumulative anthropogenic emissions.

Curves 1, 2, and 3 (Fig. 1) show the production data for CCl_4 for the United States, Japan, and Western Europe, respectively. Data on U.S. production were available for blocks of time between 1914 and the present from a number of different sources (*8, 9*). The Japanese yearly production data were available from 1967 to 1973 (*10*); these data were found to be linear on a logarithmic scale, and the relationship has been extrapolated to 1940 to obtain curve 2 (Fig. 1). The production of CCl_4 in Western Europe was negligible before 1950 and did not reach the 1000–metric ton mark until 1954 (*11*). An estimate for the production of CCl_4 in Western Europe was available for the year 1973 (*12*). The total Western Europe production for other years was estimated at three times the value for the French or the United Kingdom production figures, which were available (*9, 11*).

The pattern of industrial CCl_4 usage has undergone significant changes over the last four decades. Before 1950, the major world market for CCl_4 was in the United States, where it was primarily used dispersively as an industrial solvent, dry-cleaning agent, fire extinguisher, grain fumigant, and in other miscellaneous applications. Since 1950, the world production of CCl_4 has kept pace with the production of chlorofluorocarbons, for which it is the principal reactant (*11, 13*). Figure 1 also shows the various types of dispersive uses of CCl_4 in the United States (*8, 9, 14*). Although the U.S. production of CCl_4 increased nearly tenfold between 1940 and 1972, the dispersive fraction declined from 84 to 7 percent of the total production (*14*). This decline is principally attributable to the recognition of the acute and chronic toxicity of CCl_4 and the substitution of less toxic solvents, such as perchloroethylene and 1,1,1-trichloroethane.

In Japan and Western Europe, however, no significant amount of CCl_4 was used before 1950. In Europe, chloroethylenes were more popular than CCl_4 for degreasing and dry cleaning, although CCl_4 was used as a spotting agent and a fire extinguisher. In Japan, the CCl_4 fraction used dispersively declined from 15 percent in 1967 to 9.6 percent in 1973 (*10*), a trend somewhat similar to that in the United States. The dispersive fraction for other years was obtained by a linear interpolation between the 1967 and 1973 fractions. Extensive data for European dispersive usage were not available and were assumed to be the same as those for Japan, since the industry developed along parallel lines in both Japan and Western Europe after World War II, with the same technology used in both localities.

All the dispersively used CCl_4 is eventually emitted to the atmosphere, except for a small fraction that may be used during fire extinguishing, deposited in landfills as residues in containers, or discharged to fresh or salt water by the disposal of solvents in sewer systems. These latter phases—land and water disposal—are probably intermediary to eventual loss to the atmosphere (*14*). In addition, relatively significant losses to the atmosphere take place during CCl_4 manufacture and its handling for chlorofluorocarbon production. These losses were uniformly taken to be 1.5 percent in 1973 and were linearly increased to 5 percent in 1910. This loss rate is generally consistent with those suggested in the literature (*15, 16*) and our own experience with the production of other intermediates.

Curves 5, 6, and 7 (Fig. 1) show total emissions as a function of time from the United States, Japan, and Western Europe, respectively. These emissions include dispersive losses, production losses during CCl_4 manufacture, and handling losses during chlorofluorocarbon manufacture. Curve 5 (Fig. 1) shows that the total emissions in the United States actually declined after 1945 and have essentially remained unchanged since the late 1950's, with the emissions from increased CCl_4 production compensating for reduced dispersive usage. No such maxima were observed in either Japan or Western Europe, where CCl_4 emissions have been slowly increasing since 1950.

Figure 2 (curve 1) shows the cumulative U.S. emissions of CCl_4 to the atmosphere (an emission factor of 0.75 was used for the fire extinguisher category); the total integrated emissions from the United States alone amount to about 1.9 million metric tons by 1973, with the dispersive-use losses accounting for more than 85 percent of the total emission. The cumulative emissions for Japan and Western Europe are also plotted in Fig. 2 (curves 2 and 3, respectively) but together add up to only about 22 percent of the U.S. emissions. We have estimated that emissions of CCl_4 in the rest of the world (Eastern Europe, Australia, South America, Africa, and Asia) are about 10 percent of those in the United States, Western Europe, and Japan. Curve 4 (Fig. 2) shows our best estimate of the total worldwide CCl_4 emissions, adding up to an integrated value of about 2.5 million metric tons, or about 1.3 times the cumulative U.S. emissions.

The atmospheric concentration of CCl_4 in nonurban areas is in the range of 70 to 100 parts per trillion (ppt) (10^{-12} volume per volume) (*2–4*). Our own measurements in rural locations taken in 1975 have been in the range of 110 to 115 ppt (*5*) as compared to a uniform CCl_4 concentration of 80 to 90 ppt reported by Hanst *et al.* (*17*). However, if one considers only truly remote locations, the true geophysical background in 1973 is probably in the range of 70 to 80 ppt. For the purposes of the present discussion, we

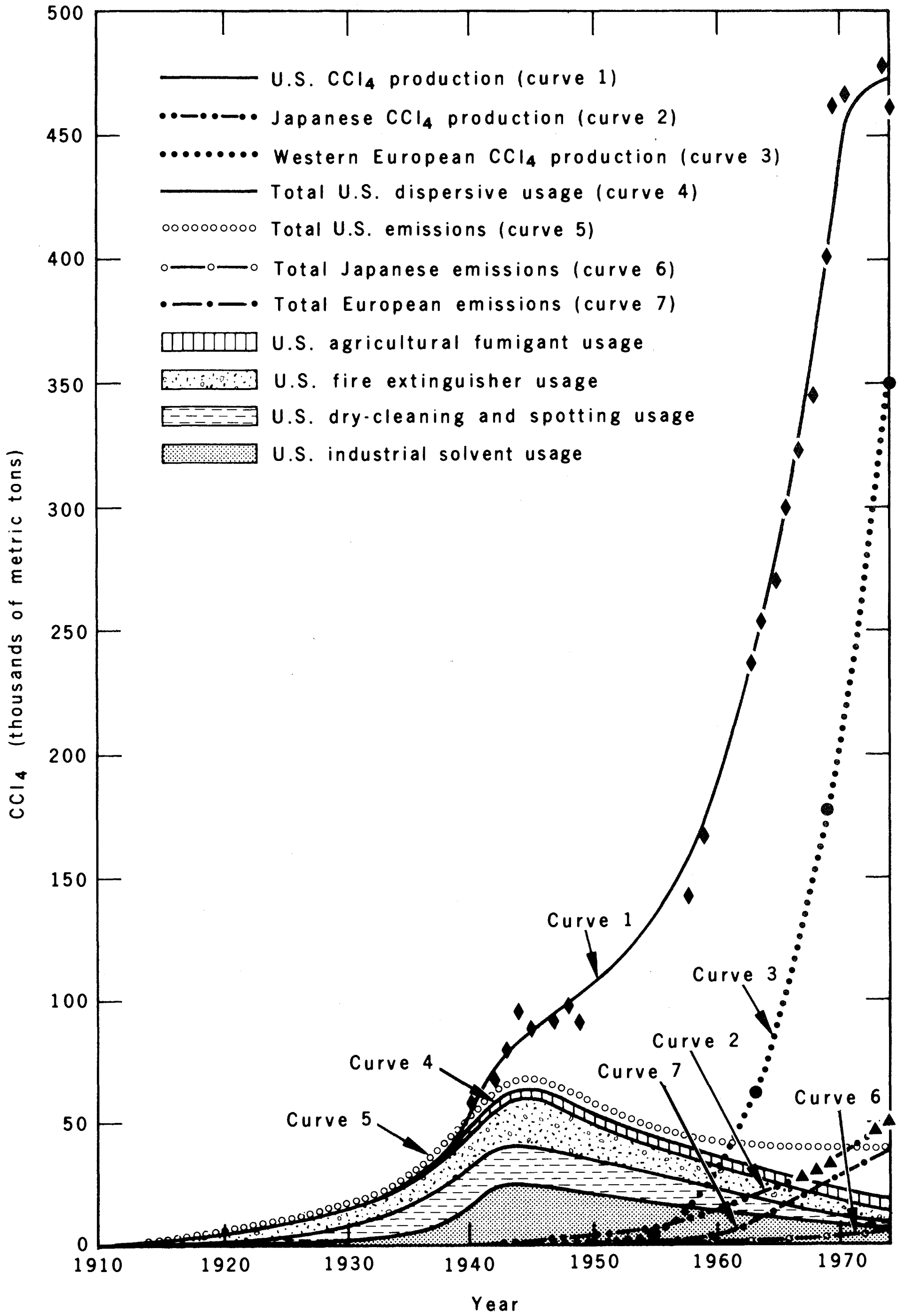

Fig. 1. Production and emission trends for CCl_4.

will consider a background CCl_4 concentration of 71.2 ppt as reported by Lovelock *et al.* (*2*) based on measurements in and over the Atlantic Ocean. This concentration corresponds to an atmospheric CCl_4 loading of 1.9 million metric tons.

Thus, our conservative estimates of worldwide cumulative emissions up to 1973 exceed the 1973 atmospheric loading by about 0.6 million metric tons, and the existence of one or more removal mechanisms is thereby indicated. The three possible sinks are tropospheric degradation, diffusion into the ocean and hydrolysis, and stratospheric transport and photolysis. Because CCl_4 is essentially inert in the troposphere and its lifetime in the troposphere has been estimated to be in excess of 330 years (*13*), the troposphere can be regarded as an insignificant sink. The ocean is also insignificant as a sink: CCl_4 is almost infinitely stable in an aqueous environment with a reported half-life (attributable to hydrolysis) of 7×10^4 years, a figure that is unaffected by *p*H (*13, 14, 18*). On the basis of data presented by Lovelock *et al.* (*2*) and McConnell *et al.* (*19*), we estimate that CCl_4 in solution in the ocean or sorbed to lipids is less than 2 to 3 percent of the biospheric loading. The e^{-1} depth of CCl_4 in the ocean has been reported to be about 50 m, as compared with 130 m for F-11. The preferential solubility of CCl_4 in lipids (octanol : water partition 500 : 1) and marine sediments, rather than hydrolysis, is probably responsible for this phenomenon.

The stratosphere is by far the most important sink for CCl_4. Molina and Rowland (*7*) have suggested an atmospheric lifetime for CCl_4 of 30 to 50 years. However, recent results from the Bureau of Standards (*20*) indicate that the stratosphere photolytic reactions are slower than the estimate of Molina and Rowland because of the reduced stratospheric temperatures. A more realistic estimate of the CCl_4 lifetime (turnover rate) is probably in the range of 60 to 100 years (*16*). Figure 2 shows the amount lost to the stratosphere on the basis of an average atmospheric lifetime of CCl_4 of 75 years and a quasi-steady-state loading (1.33 percent loss rate per year). Curve 5 (Fig. 2) shows the net calculated worldwide profile of CCl_4 cumulative atmospheric loading, resulting solely from emissions from anthropogenic sources with concurrent removal by transport to the stratosphere and photolysis.

It is clear from Fig. 2 (curve 5) that the cumulative buildup of CCl_4 from anthropogenic sources up to 1973 of about 1.9 million metric tons is approximately equal to the 1973 measured atmospheric loading of CCl_4. Furthermore, examination of the atmospheric accumulation rate of CCl_4 (curve 5) and that of F-11 (curve 6) reveals that 65 percent of the total CCl_4 released to the atmosphere was emitted before 1960 whereas 96 percent of the F-11 was released after 1965. This additional time available to CCl_4 for global dispersion and its slow release to the atmosphere explains the relative global uniformity of CCl_4 (as compared with F-11) observed by Lovelock *et al.* (*2*).

An important secondary anthropogenic source of CCl_4 has been suggested by Singh *et al.* (*21*). On the basis of preliminary smog chamber studies, these authors suggest that as much as 8 percent of all the C_2Cl_4 emitted to the troposphere may be eventually converted to CCl_4. The mechanisms of this process are unclear but might entail heterogeneous decomposition of trichloroacetyl chloride, a product of C_2Cl_4 photooxidation. From the cumulative worldwide C_2Cl_4 production estimates and an emission factor of 0.75, this source of CCl_4 is estimated at 0.7 million metric tons or about 26 ppt if uniformly mixed in the air. Of this, about 6 ppt will be lost to the stratosphere. In 1974, for example, this source alone could account for 1.5 ppt of added CCl_4, as opposed to about 3.4 ppt resulting from direct CCl_4 emissions. Total losses to the stratosphere would be about 1 ppt per year. We have not included this source in our calculations in Fig. 2, since further research is required to establish unequivocally whether such heterogeneous re-

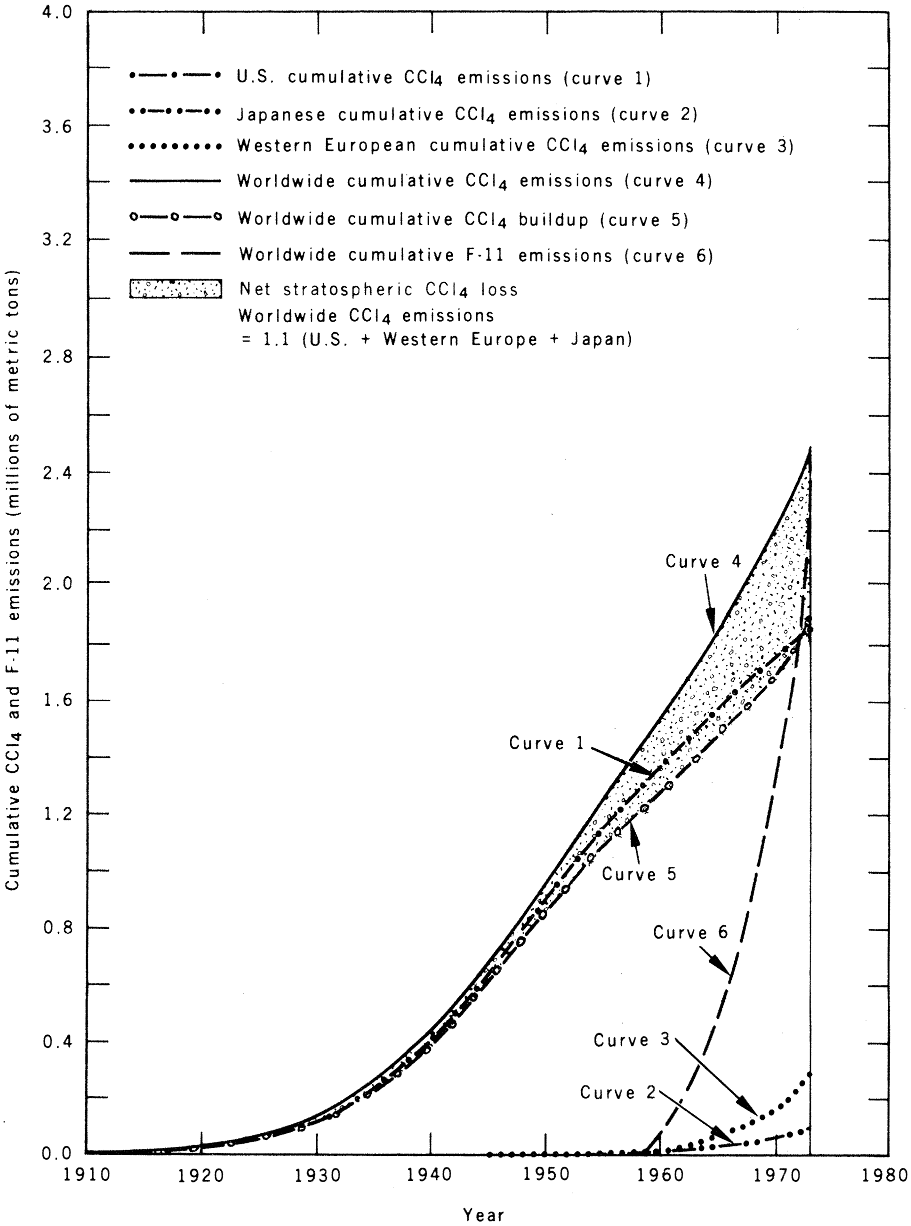

Fig. 2. Cumulative CCl_4 and F-11 emissions.

actions do or do not occur in the atmosphere.

In summary, on the basis of a conservative analysis of emissions data, the anthropogenic sources of atmospheric CCl$_4$ appear consistent with the present biospheric loading. However, there is considerable uncertainty about CCl$_4$ background concentrations, as well as the production-emission data and the atmospheric lifetimes of halocarbons. Therefore, although one cannot exclude the existence of small natural sources, it is clear that atmospheric CCl$_4$ is predominantly anthropogenic. According to our calculations, we would also predict that, at its current rate of emissions, CCl$_4$ atmospheric loading will increase at the rate of about 2.4 ppt per year in the troposphere. This rate suggests a uniform CCl$_4$ concentration of about 76 ppt for the year 1975. This value is in fair agreement with the 1975 Northern Hemisphere CCl$_4$ concentration of 80 to 90 ppt reported by Hanst *et al.* (*17*), recognizing that a CCl$_4$ hemispheric gradient of about 10 to 15 ppt probably exists (*2*).

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Carbon-Nitrogen Cycling Through Microbial Formamide Metabolism

Abstract. *A microbially mediated carbon-nitrogen cycle involving a newly isolated facultatively methylotrophic pseudomonad is described. The new isolate utilizes formamide as its sole carbon, nitrogen, and energy source. Other organisms involved in the proposed cycle are cyanogenic plants; phytopathogenic fungi, which convert cyanogenic glycosides to formamide; and nitrifying microorganisms. This cycle may be quantitatively important in view of the large variety of cyanogenic plants known to exist.*

The cycling of carbon and nitrogen in the environment has been widely investigated, but with the exception of urea and *N*-methylated amines, cycling involving microbial growth on nitrogen containing one-carbon compounds has not been demonstrated.

We have isolated a bacterium which is capable of growth on formamide (HCONH$_2$) as the sole carbon, nitrogen, and energy source, producing CO$_2$ and NH$_3$ from formamide during the course of growth. This organism, which has been designated *Pseudomonas SL-4*, was isolated from a lesion on the leaf of a cyanogenic plant, *Sorghum*, which was infected with the pathogenic fungus *Gloeocercospora sorghi*. This fungus has been shown to convert the cyanide present in *Sorghum* to formamide, possibly as a means of cyanide resistance (*1*).

Pseudomonas SL-4 is a gram-negative pink-pigmented rod which is catalase-positive, oxidase-positive, and motile by a single polar flagellum. It is capable of rapid growth (heavy turbidity after 24 hours) on a variety of one-carbon compounds, such as formamide, formate, methanol, and methylamine.

Pseudomonas SL-4 represents one component of a proposed carbon-nitrogen cycle (Fig. 1) which also involves *Sorghum* and the plant-pathogenic fungus *G. sorghi*. The CO$_2$ produced by *P. SL-4* during the metabolism of formamide is available for utilization by plants in photosynthesis. Incorporation of CO$_2$ into cell material by cyanogenic plants such as *Sorghum* yields cyanide in the form of cyanogenic glycosides (*2*). Conversion of cyanide to formamide by the enzyme formamide hydro-lyase in *G. sorghi* (*1*) converts carbon and nitrogen into a form metabolizable by *P. SL-4*. In

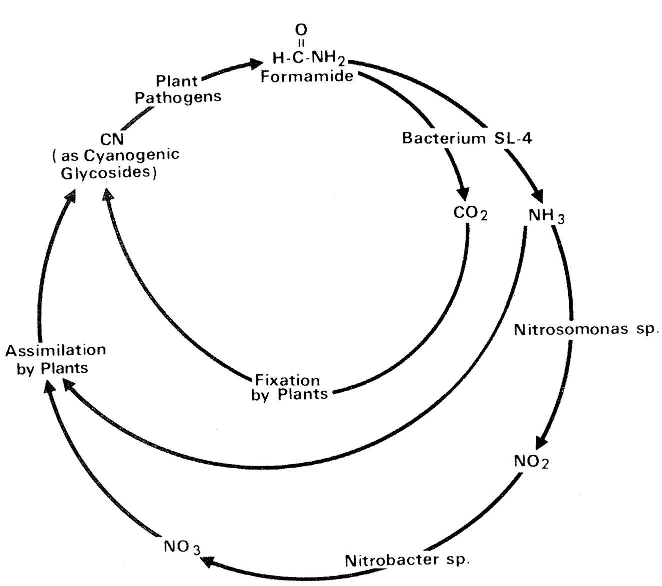

Fig. 1. Carbon-nitrogen cycling through formamide.