

some of these results relative to other comparable published work (2). We have demonstrated that amino acids can be produced from a hydrocarbon substrate with only one carbon atom, CH_4 , whereas Sagan and Khare (2) have stated that the two-carbon substrate C_2H_6 is required for the production of amino acids. They have also suggested that the amino acids from such experiments are very likely not primarily made free but result from the hydrolysis of nitriles or polypeptides (2). Our conditions never resulted in the formation of observable amounts of polymer, nor were acid or basic hydrolysis conditions ever employed. Furthermore, we observed the production of amino acids in two experiments utilizing $\text{C}_2\text{H}_5\text{OH}$ as one of the substrates and, considering the nature of the experiments, it would appear that no nitrile-containing molecules could be generated. We detected no HCN or nitrile-containing molecule at the completion of any experiment either in the gas phase or in solution (water trap), using gas chromatographic-mass spectrometric analysis. In view of these facts, we believe that the major yield of amino acids is produced not from the hydrolysis of a polymer but directly by a unique mechanism or mechanisms not hitherto considered.

Note added in proof: An experiment similar to experiment VI was repeated and the products subjected to esterification and acylation to form *N*-trifluoroacetyl isopropyl esters. Gas chromatography-mass spectrometry analysis positively identified the protein amino acids glycine, alanine, valine, leucine, aspartic acid, and glutamic acid plus some other nonprotein amino acids. This constitutes the first verification of protein amino acids from such reactions.

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Global Trends in Total Atmospheric Ozone

Abstract. Analyses of the mean monthly global distributions of total ozone for the 13-year period from 1957 through 1970 reveal an upward trend of about 7.5 percent per decade in the Northern Hemisphere and about 2.5 percent per decade in the Southern Hemisphere. The increase seems to have started about March 1961 in the Northern Hemisphere and about September 1961 in the Southern Hemisphere. The cause of these trends is at present unknown.

Studies by Komhyr *et al.* (1) of the temporal changes in the amounts of total ozone at a number of individual stations have shown that there was an increase during the 1960's over many parts of the world. The average increase for ten North American stations was determined to be about 5 percent per decade. Calculations based on data from additional individual stations showing similar results have also recently been discussed in the literature (2). It is of considerable concern to determine whether or not these reported long-period ozone changes represent a worldwide trend.

Ozone is a minor constituent in the atmosphere, and its principal importance derives from the fact that, even in relatively small amounts, it absorbs solar ultraviolet radiation that would otherwise penetrate down to the earth's surface and have disastrous effects on the biosphere (3). In addition, this absorption of solar radiation is responsible for the warm region at the top of the stratosphere (at about 50 km) and thereby helps to determine the thermal structure of that part of the atmosphere. Since ozone is a relatively inert gas below about 25 km, it represents a good tracer substance for atmospheric motions and has been a subject for considerable research by meteorologists and aeronomers (4). Added interest in studies of atmospheric ozone stems from recent suggestions that exhaust products from high-flying aircraft might somehow affect the stratospheric ozone distribution and thus change the ultraviolet shielding property of the atmosphere, or inadvertently modify the earth's climate (5).

We have been involved in a program

of analysis of all of the available total ozone data and have prepared mean monthly maps of the total ozone distribution for each hemisphere covering the 13-year period from July 1957 to July 1970. From the individual monthly maps we have extracted grid point values (for each 10° of latitude and 20° of longitude) of total ozone. These values provide the basic data for the derived global ozone trends as described below.

The average total ozone measured from the earth's surface (that is, the total amount of ozone in a vertical column) is about 300 matm cm (6). Although some observations of total ozone were made as early as 1905, data sufficient to enable one to determine its global distribution only became available at the start of the International Geophysical Year (July 1957). At that time routine observations of total ozone were being made at about 50 stations. Since then an increasing number of stations have been involved in the international ozone-observing network, and, by 1970, total ozone data were at hand for at least part of the 13-year period from 150 stations, about 80 percent of them in the Northern Hemisphere (7) (see Fig. 1). The distribution of these stations, both geographically and with time, is somewhat uneven. For example, most of the stations in each hemisphere are located in mid-latitudes. Also, there are no data from the large ocean areas except for the observations from a few island stations.

The standard observing instrument used in the ozone network is the Dobson spectrophotometer (8), although observers at a few stations, notably in

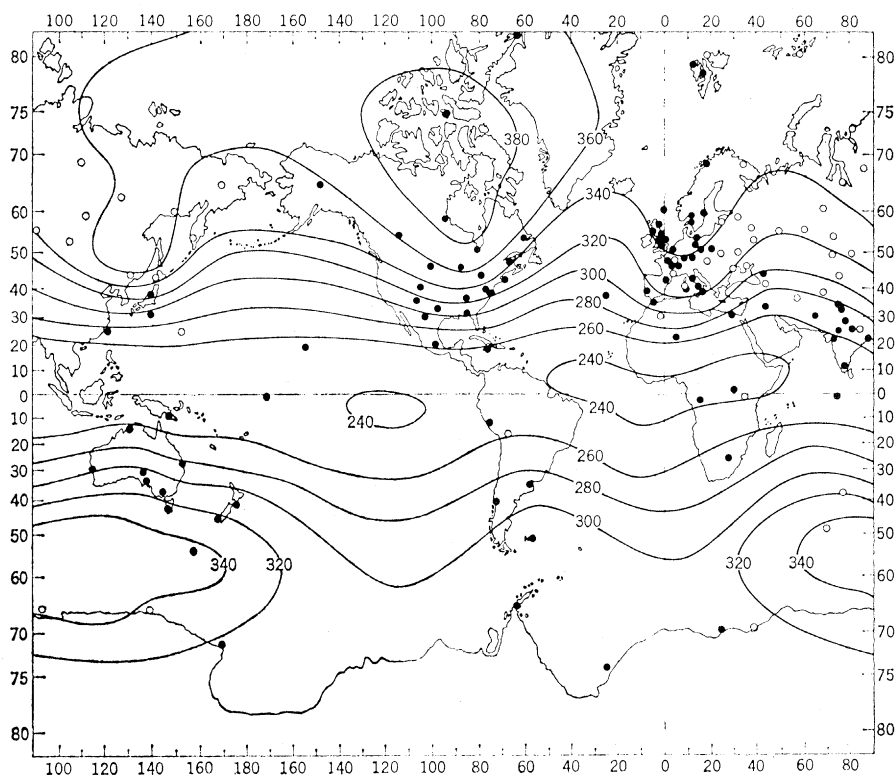


Fig. 1. The global distribution of average annual total ozone for the period from July 1957 through June 1970 (values are given in milliatmosphere centimeters); ●, Dobson spectrophotometer; ○, other measuring technique.

the Soviet Union, make use of an optical filter technique (9). A reasonably well-calibrated Dobson instrument can be expected to yield results within ± 1.5 percent of the total ozone amount. In general, the error, particularly for filter-type instruments, will be somewhat larger (9).

The annual distribution of total ozone over the globe averaged for the entire period (July 1957 through June 1970) is shown in Fig. 1. On the average, total ozone is a minimum at or near the equator and increases poleward to a maximum at 60° to 70° latitude in each hemisphere. In addition,

there are evident geographic variations more pronounced in the Northern than in the Southern Hemisphere (possibly a result of the disparity in the number of observing stations between the two hemispheres). The observed seasonal variation indicates a maximum in the spring and a minimum in the fall. Also, the seasonal range of total ozone is largest at subpolar latitudes and almost absent near the equator. Despite the nonuniform distribution of the reported observations and the standardization and calibration errors associated with the observing instruments, there is very good general agreement be-

tween total ozone variations derived from ground-based data and those recently derived from satellite observations (10).

Although ozone photochemistry can be used to explain the general vertical distribution (maximum concentration at about 25 km), photochemical calculations do not, by themselves, reproduce the observed day-to-day, seasonal or geographic variation of total ozone. Hemispheric differences in the amount and distribution of total ozone result, most probably, from the differences in stratospheric circulation patterns between the two hemispheres.

The latitude and longitude grid point data derived from our monthly global ozone maps were used to determine the global trend in total ozone for the period from 1957 through 1970 (Fig. 2). The values plotted in Fig. 2 are the hemispheric 3-month running means of the monthly departures of total ozone from the 13-year average for each month.

The computed trend and probable error for the 13-year change is $+7.8 \pm 2.4$ percent per decade for the Northern Hemisphere and $+2.4 \pm 1.9$ percent per decade for the Southern Hemisphere. Separate analyses for the trend at each latitude belt did not indicate strong differences with latitude in the Northern Hemisphere (although the trend was largest in the 40° to 60° latitude belt). At these latitudes in the Southern Hemisphere the trend was very small (and in some cases slightly negative). The overall positive (but nonsignificant) trend in the Southern Hemisphere is derived from a large apparent increase of total ozone in the south polar region, an area for which there are relatively few data.

Seasonal analysis of the 13-year change in total ozone indicated that the large increase in the Northern Hemisphere occurs during the months of December and January, the normal time for ozone buildup in the Northern Hemisphere. During these months the long-term trend in the Southern Hemisphere is negative. It would appear that these trends are, at least in part, associated with long-period inter-hemisphere exchange processes. Lag correlations calculated between the two hemispheric series were largest at about ± 6 months, but none was statistically significant.

As mentioned above, the distribution of stations reporting ozone observations during the 13-year period is non-uniform. We therefore compared the

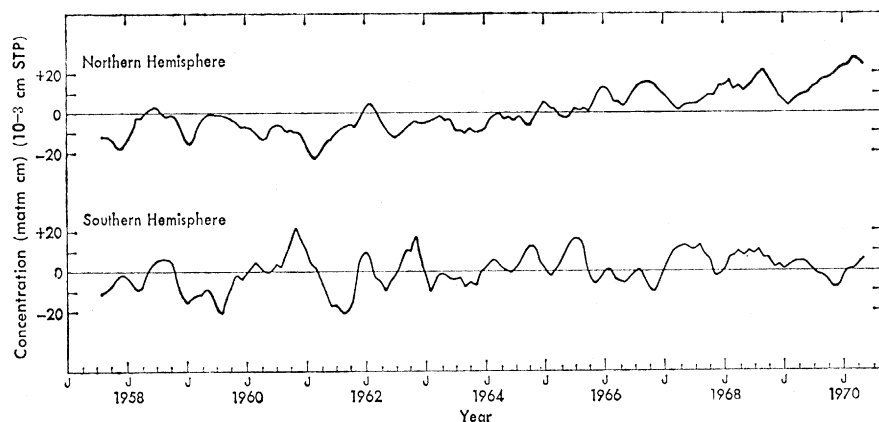


Fig. 2. Three-month running means of the total monthly ozone departures from the 13-year monthly average.

trends computed from the grid point data derived from the analyzed maps with the trends computed from all of the individual reporting stations suitably grouped and averaged over latitude. The results are essentially the same, although, as expected, the series based on the individual station data had larger short-period variations.

It is obvious that there is a change in slope of the trend lines (sometime in 1961) associated with the curves in Fig. 2. This change is particularly evident for the Northern Hemisphere curve. Each series was therefore divided into two subparts based on this apparent change, and separate regression lines were calculated with the following results and probable errors: for the Northern Hemisphere: August 1957 through March 1961, -4.7 ± 1.5 percent per decade; April 1961 through May 1970, $+11.3 \pm 2.3$ percent per decade; and for the Southern Hemisphere: August 1957 through September 1961, $+2.5 \pm 2.3$ percent per decade; October 1961 through May 1970, -1.1 ± 1.6 percent per decade.

It can be seen from these results that the upward trend in observed total ozone that occurred during the 1960's was primarily a Northern Hemisphere phenomenon and started in that hemisphere in the spring of 1961. Although these values might reflect, in part, systematic drifts in the calibration of the various instruments, there is no a priori reason why the calibration errors should be more pronounced in the Northern than in the Southern Hemisphere.

We have yet to establish whether these changes show a definitive worldwide pattern and to determine in what manner these trends are associated with changes in solar radiation, general stratospheric photochemistry, or fluctuation in the stratospheric circulation. The marked hemispheric difference in the trends, however, would seem to preclude any direct solar influence.

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Lead Aerosol Pollution in the High Sierra Overrides Natural Mechanisms Which Exclude Lead from a Food Chain

Abstract. *Most of the lead contained in sedge and voles (mountain meadow mice) within one of the most pristine, remote valleys in the United States is not natural but came from smelter fumes and gasoline exhausts. In a food chain, natural mechanisms do not allow lead to accompany the bulk of the nutritive metals as they proceed to higher trophic levels. This exclusion can be expressed quantitatively by a comparison of lead/calcium ratios at successive trophic levels. This ratio decreased by an overall factor of 200 in proceeding from rock, to soil moisture, to sedge, to vole. This factor would have been 1200 if lead aerosols had not collected on sedge leaves and circumvented the tendency by sedge to exclude lead from the nutritive metals it absorbed from soil moisture.*

We report here on our investigations of a common but unproved assumption, that natural concentrations of lead exist within plants and animals in open country; our conclusions are based on measurements of lead inputs and outputs for a natural ecosystem, on identification of the natural and industrial leads within the ecosystem, and on measurements of the distribution of lead within a food chain within the ecosystem. Our studies were carried out in Thompson Canyon which is located in the crest of the High Sierra in California and which lies within a single batholithic rock type (Cathedral Peak quartz monzonite) that was stripped clean by Wisconsin glaciation. The soils of the canyon were formed during post-Wisconsin weathering of local quartz monzonite. The input of lead-containing aerosols less than $1 \mu\text{m}$ in diameter collected by dry deposition on foliage, measured with a deposition instrument, was about 1 kg of lead entering the 14-km² watershed during the four summer months. The input of lead-containing aerosols coprecipitated in snow within 14 km² was estimated to be 12 kg of lead for the eight winter months. Rain contributes only 5 percent of the total water input and was not analyzed. About 97 percent of the aerosol lead entering Thompson Canyon is, on the basis of Pb/(K + Ca)

ratios, of industrial origin. The value of this ratio is 2.0 in Los Angeles air, 0.02 in Thompson Canyon snow, 0.01 in Thompson Canyon foliar dust, and 0.0005 in Thompson Canyon rocks. Mass balance estimates of the output of industrial lead aerosols from both the Los Angeles and San Francisco areas [based on the 5 metric ton/day emission from Los Angeles estimated by Huntzicker and Friedlander (1) and a 2 ton/day emission from San Francisco obtained by normalizing to the Los Angeles value on the basis of population ratios] suggest that the share of this emission available for deposition within Thompson Canyon from a uniform dispersal area 2000 km in diameter should be about 10 kg of lead per year, which is within the limits of the observed input of 13 kg of lead per year. We determined the output of lead from the canyon by streams by analyzing the lead content of stream waters and using water output data to obtain the total average yearly lead output, 0.2 kg of lead per year from 14 km². Stream runoffs and snow accumulations were monitored throughout the year by Hinkley (2).

The difference between lead input and lead output shows that, at present, about 98 percent of the industrial lead entering the valley as aerosols remains there. We believe that the strongly