of extraterrestrial origin (*9*). Wüstite may be produced in industrial processes, but the manganese nodules studied are believed to be several million years old (*10*), which precludes the possibility of contamination by industrial particles.

On the basis of these criteria, the evidence suggests that both Group I and Group II particles are extraterrestrial in origin. The absence of elements other than Fe, Ni, and Co indicates that Group I particles are apparently ablation products of iron meteorites or of the metallic fraction of stony meteorites. The Si, Mg, Al, and Ca detected in Group II particles suggest that these particles are ablation products of stony meteorites. These elements are among the most common elements in stony meteorites, but they are essentially absent in iron meteorites (*11*). The presence of a metallic nucleus in the Group II particles is not inconsistent with an origin from stony meteorites, which contain significant quantities of metallic nickel-iron.

The presence of significant amounts of titanium and manganese in Group III particles is highly suggestive of a terrestrial origin (*5*). The ellipsoidal shape of these particles indicates that they were once molten droplets. The similarity of the chemical analysis to the analysis of magnetic spheroids derived from recent volcanic eruptions (*12*) and the proximity of these samples to the Hawaiian Islands suggests a volcanic origin.

Two particles have characteristics common to more than one category; they have internal structures similar to those of Groups I and II but chemical compositions similar to Group III particles. It is possible that they are Group I particles that have undergone intense weathering.

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15. I thank Drs. Michael B. Duke and Daniel Appleman (U.S. Geological Survey), Dr. Frederic Siegel (George Washington University), and Dr. Robin Brett (National Aeronautics and Space Administration) for their valuable assistance.

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The Ocean: A Natural Source of Carbon Monoxide

Abstract. *The surface waters of the western Atlantic are supersaturated with respect to the partial pressure of carbon monoxide in the atmosphere. Under these conditions, the net transport of carbon monoxide across the air-sea interface must be from the sea into the atmosphere. Thus, the ocean appears to act as a source of carbon monoxide. The ocean may be the largest known natural source of this gas, contributing possibly as much as 5 percent of the amount generated by burning of fuels by man.*

It is generally agreed that the largest single source of carbon monoxide in the atmosphere is the burning of fuel by man, which at the present time is estimated to produce approximately 2×10^{14} g (200 million tons) per year of this toxic pollutant (*1*). Several natural sources of carbon monoxide have also been reported (*2*); however, no estimate of output of these sources is available. Despite a continually increasing rate of input into the atmosphere, the background amount of carbon monoxide in the marine atmosphere far removed from sources of pollution appears to be remaining at approximately 0.1 ppm (*1, 3*). Efficient mechanisms of removal must therefore exist, but the nature of these processes is not clear (*2*). In order to determine the possible role of the oceans as a sink for this pollutant, we undertook an investigation of the distribution of carbon monoxide between the atmosphere and surface waters. Preliminary results indicated that the surface waters are supersaturated in carbon monoxide with respect to the partial pressure of this gas in the atmosphere (*3*). Additional data we now present confirm these findings, and it now appears that rather than acting as a sink the ocean may indeed be the largest natural source of carbon monoxide now known.

During a recent oceanographic cruise in the Atlantic, two 24-hour stations were occupied at which both air and surface water samples were taken at 2-hour intervals. All samples were collected and analyzed within 1 hour of collection by methods previously described (*3*). The stations were at 13°13.9′N, 59°07′W (approximately 64 km east of Barbados), and 10°38′N, 60°05′W (about 112 km east of Trinidad), respectively. At both locations, the prevailing easterly trade winds minimize the possibility of contamination from man-made sources of pollution. The biological characteristics of the water at the two stations, however, differ significantly; the water in the vicinity of the first station is much lower in overall productivity than that at the second station (*4*).

Two characteristics of the data (Fig. 1) are evident: (i) the relatively constant concentration of CO in the atmosphere at both locations, and (ii) a marked diurnal effect with respect to concentration of CO in the surface waters. The average atmospheric concentrations of 0.14 ppm and 0.09 ppm at stations 1 and 2, respectively, agree with values previously reported for clean marine air of 0.05 ppm (*1*), and 0.08 ppm (*3*). They are also in agreement with an average value of 0.09 ppm (*5*) for Arctic air. The surface water concentrations of CO showed a greater diurnal effect at station 2, which may possibly be related to the high biological productivity of these waters as compared to station 1. The concentrations of dissolved CO between 10^{-4} and 10^{-5} ml/liter agree with values reported for western Atlantic waters (*3*), and also with unpublished values of from 1 to 3×10^{-5} ml/liter found by us in the vicinity of the Chesapeake Light Tower, some 24 km from the entrance to Chesapeake Bay. The observed decrease in dissolved CO during the late afternoon and early evening hours appears to be accompanied by a slight but significant increase in atmospheric CO. That the correlation is not more clearly evident is likely due to very rapid mixing in the atmosphere, since the wind velocities during all sampling operations were between 10 and 15 knots.

A state of nonequilibrium between

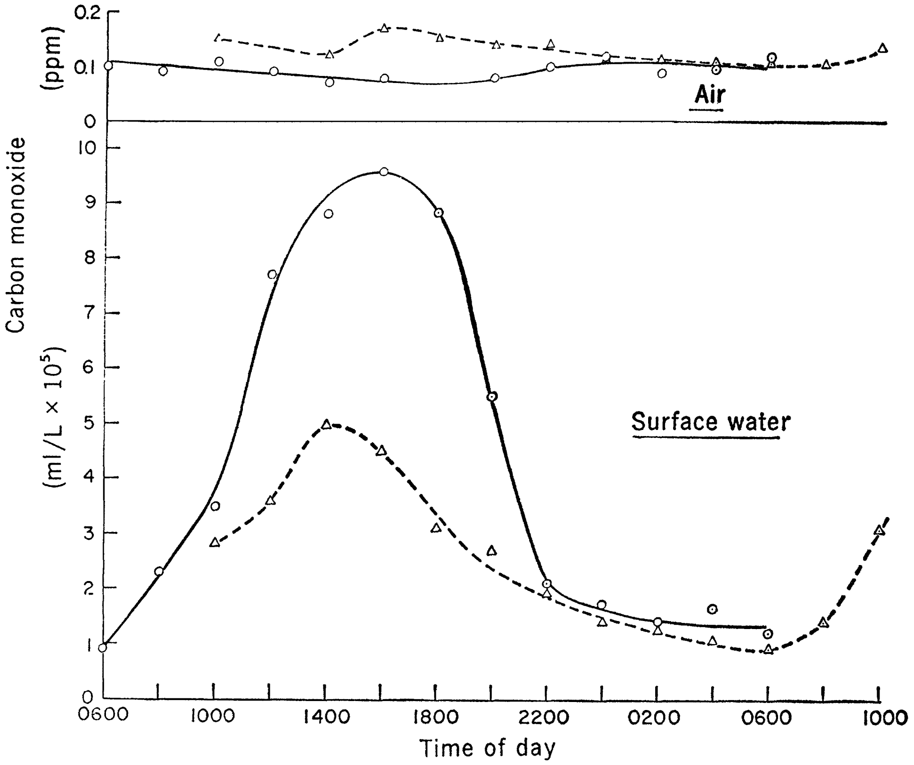

Fig. 1. Concentration of carbon monoxide in surface waters and in the atmosphere. (Triangles) Station 1, 13°13.9′N, 59°07′W; 18 to 19 April 1969. (Circles) Station 2, 10°38′N, 60°05′W; 21 to 22 April 1969.

atmospheric and dissolved CO has been reported based on a comparison of the measured concentrations of dissolved CO with those calculated on the assumption that the atmosphere was the only source of CO (*3*). This is confirmed by the data we now present (Fig. 2). The ratio, R_{CO} of measured to calculated dissolved CO concentrations, in which the calculated values are obtained by multiplying the measured partial pressures of CO in the atmosphere by the solubility coefficients for CO in seawater as given by Douglas (*6*), is a measure of departure from equilibrium. Since the value of R_{CO} at equilibrium would be unity, it is apparent that the distribution of CO between atmosphere and surface waters is indeed far from equilibrium, and that the water is in general supersaturated with respect to the partial pressure of CO in the atmosphere. This is true even during the night, when R_{CO} drops to its minimum value of about 5.

The source of the excess carbon monoxide found in the seawater is not known. The mechanism of production may be biological in nature; marine algae (*7*), the Portuguese man-of-war (*8*), and some siphonophores (*9*) have been reported to produce carbon monoxide. Biological production would explain the higher peak concentrations found at station 2, in waters of higher productivity. It is also possible that photochemical decomposition of organic matter near the surface is responsible. For example, we observed that weather conditions at station 1 during the sampling operations were generally cloudy and overcast, as contrasted to bright and sunny weather which prevailed at station 2. Further observations are needed to clarify this point.

The supersaturation of the surface waters with respect to the atmospheric partial pressures of CO indicates that the net transport of carbon monoxide across the air-sea interface should be from the water into the atmosphere. Although the absolute concentrations of dissolved CO are low, on a worldwide basis the amount of CO produced could be considerable. If the average concentration of CO in the surface waters of the world ocean is approximately 10^{-5} ml/liter, and if it is assumed that the upper 2 m of water could release the major portion of its CO to the atmosphere in 24 hours (the values of R_{CO} even during the night would still result in a net transport of gas into the atmosphere), then in 1 year the ocean could contribute approximately 9×10^{12} g of CO to the atmosphere, based on a surface area of 3.61×10^{8} km² for the world ocean. This amount represents about 5 percent of the estimated carbon monoxide produced by

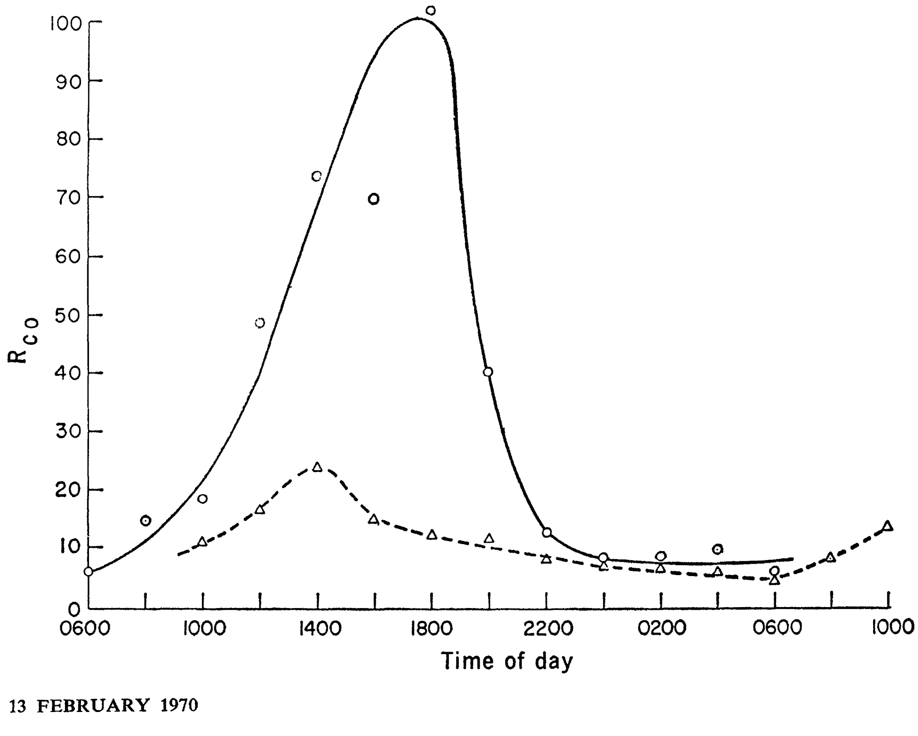

Fig. 2. Variations during a 24-hour period in the ratio R_{CO} of measured to calculated carbon monoxide concentrations in surface waters. Calculated concentrations based on equilibrium distribution of CO between sea and atmosphere, assuming atmosphere to be sole source of CO. (Triangles) Station 1, 13°13.9′N, 59°07′W; 18 to 19 April 1969. (Circles) Station 2, 10°38′N, 60°05′W; 21 to 22 April 1969.

man, which makes the ocean by far the largest natural source of carbon monoxide known, if one assumes a worldwide production of carbon monoxide in the upper layers of the ocean similar to that found in the western Atlantic.

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Airborne Lead and Carbon Monoxide at 45th Street, New York City

Abstract. *Daily business-day traffic determines the diurnal lead concentration as well as diurnal carbon monoxide concentration. Daily averages of 7.5 micrograms per cubic meter for lead and 13 parts per million of carbon monoxide were found for the 10-week period of the study. Correlations were demonstrated for lead and traffic and lead and carbon monoxide.*

The Department of Air Resources of the City of New York has initiated a program to monitor the lead content of the city's air. This effort is part of a larger monitoring program that includes the analyses of 12 metals collected at 38 sampling sites (New York City's Aerometric Network).

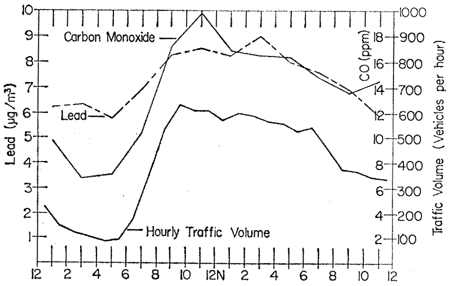

Fig. 1. Two-hour average lead concentrations in grams per cubic meter, carbon monoxide in parts per million, and hourly average traffic in vehicles per hour at East 45th Street, New York City.

This report includes lead concentrations at 6 m above street level at 110 East 45th Street and lead concentrations at two other elevated sampling sites in Manhattan—the Central Park Arsenal Building (Fifth Avenue and 64th Street) and at 240 Second Avenue. The sampling probes at the Central Park Arsenal Building and at 240 Second Avenue were located at an approximate height of 14 and 30 m, respectively. The 45th Street data represent the lead levels collected during a 10-week period from 12 January to 22 March 1969. Additionally, carbon monoxide readings are included for the same 10-week period for the 45th Street site. The lead was monitored by a sequential tape sampler. Two-hour spots were collected at 0.007 m^3/min with Whatman No. 4 tape. The carbon monoxide was measured with nondispersive infrared analyzer. The concentrations of lead and carbon monoxide are reported in micrograms per cubic meter and parts per million, respectively.

A previous study (*1*) at the 45th Street site showed this section of the city to be high in traffic volume and carbon monoxide pollution.

Equipment capable of collecting 2-hour sequential lead samples and continually monitoring for carbon monoxide concentrations was already present at 45th Street as part of a continuing effort by this department. The sampling probe for lead was located at approximately 6 m above street level and 2.6 m in from the curb. The carbon monoxide sampling probe was located approximately 6 m above street level and 3 m in from the curb. Lead samples were collected from the air over 2-hour periods, 24 hours per day, 7 days per week. The carbon monoxide concentrations were continuously monitored, 24 hours per day, 7 days per week. The average 2-hour concentrations of lead and carbon monoxide for the 10-week period between the hours of 8:00 a.m. and 6:00 p.m. were 9.3 $\mu g/m^3$ and 18 ppm, respectively. The carbon monoxide results are compatible with the previously reported results for 45th Street where the earlier investigators reported that the average hourly concentrations exceeded 15 ppm from 9:00 a.m. to 7:00 p.m. The carbon monoxide in both studies exceeded New York State's proposed standards.

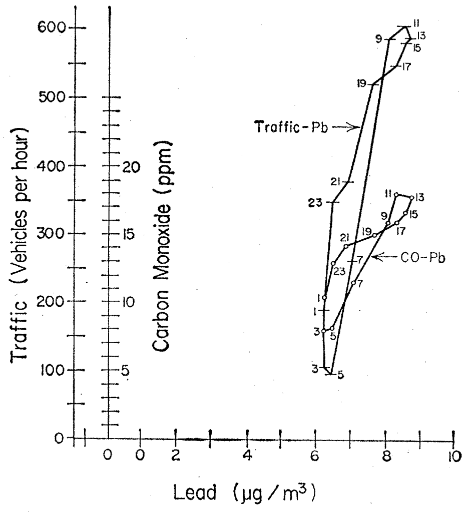

Fig. 2. Lead concentrations, traffic volume and lead concentrations, and carbon monoxide concentration curves at East 45th Street, New York City.

The means of the daily averages were 7.5 $\mu g/m^3$ for lead and 13 ppm of carbon monoxide for the 10-week period of the study. Similar results were reported (*2*) in another New York City study (on Broadway between 34th and 35th Streets). Here the authors reported an annual average for lead of 7.9 $\mu g/m^3$.

The frequency distribution for lead concentrations in the 2-hour samples (812 samples in milligrams per cubic meter), grouped in class intervals of 0 to 4.4, 4.5 to 8.4, 8.5 to 12.4, 12.5 to 16.4, and 16.5 to 20.4, was 32, 35, 16, 9, and 4 percent, respectively. During this same period, eight 2-hour readings were reported between 20.5 and

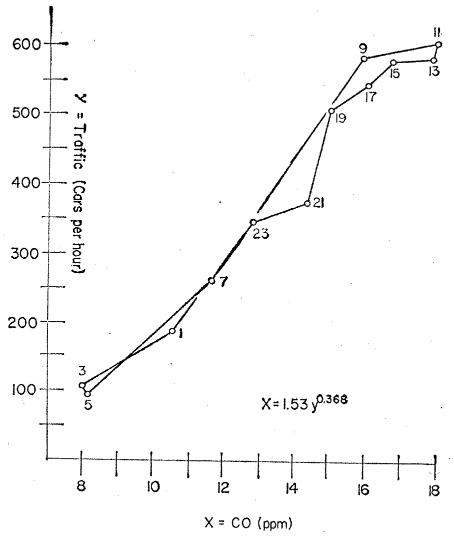

Fig. 3. Carbon monoxide concentration and traffic volume curves at East 45th Street, New York City.