Reports

Soil: A Natural Sink for Carbon Monoxide

Abstract. A potting soil mixture depleted carbon monoxide in a test atmosphere from a concentration of 120 parts per million to near zero within 3 hours. Maximum activity occurred at 30° C. Steam sterilization of the soil, the addition of antibiotics or 10 percent (by weight) saline solution, and anaerobic conditions all prevented carbon monoxide uptake. Sterilized soil inoculated with nonsterile soil acquired activity with time. Samples of various natural soils differed in their ability to remove carbon monoxide from the air. Acidic soils with a high content of organic matter were generally the most active. The soil's ability to remove carbon monoxide from the atmosphere is ascribed to the activity of soil microorganisms.

The ambient concentration of carbon monoxide in the earth's atmosphere is estimated to be 0.04 to 0.90 part per million (ppm) (1). To this apparently resident mass man is adding 200 million metric tons annually on a global basis (1), and more than 87 million tons in the United States alone (2). Numerous natural sources, most notably the world's oceans (3), contribute additional CO to the atmosphere. On the basis of these estimates, the ambient concentration of CO could be expected to double within 4 to 5 years if it were not for its relatively short residence time in the atmosphere. This time has been estimated at 2.7 to 4 years (1, 4), on the basis of a consideration of production rates and ambient concentrations. More recently, Weinstock (5), using radiocarbondating methods, obtained a lower estimate of 0.1 year. Hence, CO apparently is not accumulating in the earth's atmosphere since ambient concentrations are remaining essentially constant.

These results strongly suggest that a natural sink (or sinks) removes CO from the atmosphere soon after it is liberated. Jaffe (2) has discussed some possible sinks, including various elements of the biosphere and atmospheric oxidation of CO to CO_2 . Most of these, if at all significant, can be only very minor sinks (atmospheric reactions, hemoglobin) or have since been shown to be sources (seawater) of, rather than sinks for, CO. As suggested by Jaffe, however, evidence indicates that the soil, or certain soil constituents, may be a major sink. Anaerobic methane bacteria, Methanosarcina barkerii and Methanobacterium formicum, are known to oxidize CO 18 JUNE 1971

to CO_2 in the absence of H_2 or to reduce CO directly to methane in the presence of H_2 (6). Likewise, Bacillus oligocarbophilus (7) and Clostridium welchii (8) can metabolize CO in pure culture, and cell-free extracts of Desulfovibrio desulfuricans oxidize CO to CO_2 enzymatically in the presence of sulfite (9). Carbon monoxide has been shown to disappear readily from the subterranean atmosphere of a coal mine (10). The existence of a natural sink, however, has not been clearly demonstrated, and we believed that a specific and more definitive study was needed. We report here the initial results from a direct investigation of the possible role of the soil as a natural sink for atmospheric CO.

Various soils were exposed to test atmospheres within closed containers



Fig 1. Reduction in the amount of CO in a test atmosphere over 2.8 kg of potting soil with time.

holding known amounts of CO in air, and CO concentrations were determined periodically by means of gas chromatographic techniques described by Porter and Volman (11). Depending on the needs of the experiment, the test systems were housed in large fiber glass chambers (120.5-liter capacity), labyrinthine plexiglass chambers (10-liter capacity), or various glass flasks (up to 2 liters capacity). Preliminary experiments were conducted with a greenhouse potting mixture consisting of a sandy loam (95 percent) and peat moss (5 percent). Later tests were conducted with samples of soil collected in California, Florida, and Hawaii. In tests with the 10-liter plastic atmospheric chambers (PAC) 2 liters of air-dried soil were brought to 10 to 20 percent moisture and maintained at that level during an incubation period of 14 days at room temperature prior to testing. This soil volume occupied approximately onetenth (1 liter) of the actual air space within the PAC. Test atmospheres contained 80 to 130 ppm of CO in air at the beginning of the tests. In anaerobic tests we used a CO-in-N₂ mixture following repeated purging of the test system with N_2 and incubation under N_2 for 5 days at room temperature.

Most of the soils tested showed a surprising capability to remove CO from the test atmospheres. During preliminary experiments, nonsterile potting soil was observed to reduce the total amount of CO in a PAC atmosphere from 1443 to 47 μ g within 3 hours (Fig. 1). Sterilization of the soil by autoclaving (1.02 atm, 20 minutes, 121°C) completely eliminated this activity. As a matter of fact, the amount of CO over steam-sterilized soil increased by 8 percent during a 4-hour test period, possibly the result of the breakdown of organic matter during autoclaving. This effect was observable as long as 7 days after autoclaving, even though the soil was left exposed to biologically clean air on a clean bench during that period.

The inhibition of CO removal by autoclaving indicated that the removal mechanism was mediated either by the biological activity of the soil or by some adsorptive physical soil property that was labile to steam heat. Nonsterile potting soil was therefore tested for activity under a variety of controlled conditions in an attempt to characterize the mechanism further. We determined the effects of temperature on uptake

Table 1. Rate of CO removal over 100 g of potting soil at different temperatures.

Temper- ature (°C)	CO uptake rate* (mg/hr per square meter of soil)	Test period duration (hr)		
10	0.30	24		
15	0.38	6		
20	1.25	5		
25	2.38	3		
30	3.46	2		
35	2.44	2.3		
40	1.89	4		
45	1.17	4.5		
50	0.20	19		

* Average rate at the end of the test period.

rates by using 100 g of air-dried soil plus 16 ml of sterile distilled water in 500-ml filter flasks in a constant-temperature water bath. Samples of the atmosphere above the soil were analyzed periodically to monitor the CO concentration until depletion was essentially complete, in order to determine CO uptake rates. Results, expressed as CO uptake in milligrams per hour per square meter of soil surface, are given in Table 1. Maximum activity occurred at 30°C, with uptake rates falling sharply on either side of this peak. At 25°, 30°, and 35°C rates rose during the first hour of testing and declined thereafter. At 20° and 45°C rates declined steadily during the period of treatment. At 10°, 15°, and 50°C rates were essentially constant throughout the test period. Of additional interest was the differential evolution of CO from autoclaved soil at different temperatures in the dark. At 20°C approximately 3.5 mg of CO

per hour per kilogram of soil was evolved; at 40°C 36 mg of CO per hour per kilogram of soil and at 55°C 136 mg of CO per hour per kilogram of soil was evolved. At 40°C, CO evolution in the light was approximately 30 percent greater than in the dark. No CO evolution was observed at any temperature by nonautoclaved soil.

Treatment of potting soil at 30°C with 10 percent (by weight) NaCl solution (50 ml per 200 g of soil) completely prevented CO uptake. Incubation at 20°C under 100 percent N₂ for 5 days also completely inhibited CO uptake under anaerobic conditions (100 ppm CO with the balance N_2) at 30°C. Treatment of the soil with 500 ppm of cycloheximide, streptomycin, or erythromycin (50 ml per 200 g of soil) did not appreciably affect the rate of CO depletion. Activity was eliminated, however, by alternate drenching and air-drying the soil over a 6-day period with a mixture containing 1000 ppm of cycloheximide, 510 ppm of streptomycin, and 870 ppm of erythromycin in 1.5 percent (by volume) ethanol. A control sample treated with deionized water remained active.

When autoclaved potting soil was inoculated with nonsterile soil, a gradual increase in activity with time was observed. Autoclaved soil (2.8 kg) was inoculated by sprinkling 1 g of nonsterile soil over the surface. Uptake rates were determined daily during 2hour test periods over the next 5 weeks. Between tests the soil in the PAC was exposed to biologically clean air. Re-

Table 2. Rate of removal of CO from test atmospheres at 25°C by various soils.

Location of soil*	Vegeta- tion	pН	Sand: silt:clay (%)	Organic matter (%)	CO up- take† (mg/hr per square meter of soil)
Eureka-Arcata	Coast redwoods	5.7	53:34:13	25.1	16.99
H. Cowell State Park	Oak	5.3	73:12:15	11.2	15.92
H. Cowell State Park	Coast redwoods	5.7	57:26:17	13.6	14.39
Lake Arrowhead‡	Ponderosa pine	6.2	65:24:11	17.4	13.89
Redding	Grass-legume pasture	5.1	53:32:15	21.0	11.94
Riverside‡	Grapefruit§	6.6	75:14:11	4.3	11.48
Yosemite Valley	Grass meadow	5.05	49:42:9	20.6	10.52
Kauai, Hawaii	Forest	4.74	58:18:24	22.8	9.90
San Bernardino Freeway‡	None	7.2	55:30:15	2.2	6.89
Mojave Desert	Chaparral	7.9	79:6:15	2.4	6.46
Woodland	Oak stubble§	6.6	33:32:35	2.1	6.23
Riverside (desert)‡	Chaparral	7.35	85:4:11	1.0	4.31
Yosemite wall	White fir	5.1	65:18:17	5.7	3.48
Corcoran	Cotton (fallow)§	7.1	57:22:21	2.8	3.48
Hanford	Almond§	6.95	53:26:21	3.5	2.82
Boynton Beach, Florida	Weeds (fallow)§	6.0	86:0:14	1.4	2.65
Oahu, Hawaii		4.93	40:26:34	15.3	2.16

* All soils were collected in California unless otherwise noted. † Average rate at the end of the test period; two to three determinations. ‡ Locations where high levels of air pollution occur as a result of the combustion of fossil fuels and photochemical smog. § Land under cultivation or with recent history of cultivation.



Fig. 2. Increasing capability of 2.8 kg of autoclaved potting soil to remove CO from a test atmosphere with time after inoculation with 1 g of nonsterile soil.

sults are shown in Fig. 2. A gradual increase in the rate of CO removal occurred with time. On the 36th day after inoculation, the uptake rate was 4.1 mg of CO per hour per square meter of soil, which was equivalent to the rate observed for nonsterile soil. Sterile, noninoculated controls did not develop the capacity to take up CO during the 36-day test period. Temperatures between tests varied between 25° and 31° C, which may account for some of the irregularity in loci noticeable in Fig. 2.

The results of tests with potting soil indicated that the phenomenon of CO uptake was due to a biological rather than a physical mechanism. Temperature effects coincided with those expected if biological action were involved. The effects of treatment with 10 percent saline and antibiotics support the same contention. The soil biosphere, most probably certain elements of the soil microflora, must therefore be responsible. The gradual increase in activity with time in inoculated soil would appear to coincide with the expected gradual buildup of microorganisms from the inoculum. Moreover, the failure of the mechanism under anaerobic conditions indicates that, at least in this soil, aerobic microorganisms alone are responsible.

The activity of different soils, collected from various ecological situations of climate, soil, and vegetation types, and various ambient concentrations of air pollutants, is shown in Table 2. As a general rule, soils with a higher content of organic matter were the most active. The variety and quantity of the soil microflora would be expected to vary in proportion to the amount of organic matter present. Glaring exceptions to the rule were the soils from the grapefruit orchard near Riverside (low organic matter, high activity) and from Oahu (high organic matter, low activity). The Oahu soil was the red, porous, granular volcanic soil characteristic of that island. The fact that the Riverside soil was under cultivation may have been a factor in its higher activity. With the exception of the Riverside soil, however, cultivated soils were not appreciably active. As a general rule, the more acidic soils were the most active. The Riverside orchard soil (high pH, high activity) and the Oahu soil (low pH_{1} , low activity) were also exceptions to this rule. The soil from the Yosemite wall taken under white fir also defied this classification. No relation was apparent in this listing between soil activity and the prevalence of air pollution conditions.

On the basis of measurements listed in Table 2, an estimate of the total capacity of soil to remove CO from the atmosphere can be attempted. The average activity of the soils tested was 8.44 mg of CO per hour per square meter of soil, equivalent to 191.1 metric tons per year per square mile. If we assume that this value is representative of the average capacity of soils in the temperate zone, the capacity of the total soil surface of the continental United States [2,977,128 square miles $(7,792,533 \text{ km}^2)$] is estimated to be 569 million metric tons per year, which is 6.5 times the annual estimated production of CO attributed to the United States and almost three times the estimated worldwide production due to man's activities. The soil, therefore, must now be considered as a major natural sink for CO that is released into the atmosphere by natural emitters or by the burning of fossil fuels.

ROBERT E. INMAN

ROYAL B. INGERSOLL ELAINE A. LEVY

Stanford Research Institute-Irvine, Irvine, California 92664

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Net Kinetic Energy in Littoral Transport

Abstract. Studies of coastal erosion and coastal management can be put on a firm physical basis only after methods have been developed for closely estimating the energy expended in actual unidirectional net littoral transport of sediment. Such measures have now been obtained for six coastal drift cells. The results, for a 68-year period, vary from a minimum of 0.6×10^4 ergs (very low energy) to a maximum of 340×10^4 ergs (moderately high energy) per cell.

There have been two ways of approximating the energy level of the surf zone: (i) by making a precise computation for actual total energy delivered to the coast, regardless of whether it produces any net changes or not (and most of it typically does not); and (ii) by estimating the energy from some convenient observation such as ramp slope (1) or breaker height (2). Neither method has been completely satisfactory (from the standpoint of the student of coastal processes); yet, if we are to deal effectively with problems of coastal erosion, it is important that we know the energy involved. A third method is now available.

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Stapor (3) showed that the coast of the Gulf of Mexico southwest of Tallahassee, Florida (low to moderate energy), can be divided into essentially independent cells, separated by inlets or by large shoals which act as transverse bars (4). Stapor isolated six such cells in a distance of about 125 km and studied them, using a technique which involved a numerical comparison of measured water depths from selected nautical charts, which he checked carefully for accuracy; a seventh and an eighth cell, in the same array, could not be treated on the charts available.

Stapor's data, for each cell, included the mass of sand moved (volume measure), the distance moved, and the time interval covered. The distance and time terms can be set in a ratio to provide a velocity; the volume term can be converted into a mass (inasmuch as the sand is essentially pure quartz). Kinetic energy, as a measure of work, can be expressed as:

K.E. $= mv^2/2$

where m is the mass and v is the velocity. This formula gives a minimum estimate of the work done, inasmuch as the shuffling of individual grains back and forth, important in absorbing wave energy, is not included; that is, this formula provides an estimate of net unidirectional work.

The results of the calculation, for six cells from east to west, are as follows (for a 68-year period ending about 1940): cell 1, northeastern Dog Island: 0.6×10^4 ergs; 0.3×10^{-5} erg/sec; cell 2, southwestern Dog Island: 7.1×10^4 ergs, 3.3×10^{-5} erg/sec; cell 3, northeastern St. George Island: 5.4×10^4 ergs, 2.5×10^{-5} erg/ sec; cell 4, Cape St. George (St. George Island): 9.4×10^4 ergs, $4.4 \times$ 10^{-5} erg/sec; cell 5, Cape San Blas: 9.9×10^4 ergs, 4.6×10^{-5} erg/sec; and cell 6, St. Joseph peninsula: 340 $\times 10^4$ ergs, 170×10^{-5} erg/sec. Individual cells are between 5 and 25 km in length.

In general, the energy level increases toward the west (that is, from cell 1 to cell 6). Furthermore, westward-moving and northwestward-moving drift systems (cells 2, 4, and 6) represent more energetic conditions than eastward-moving and northeastward-moving drift systems (cells 1, 3, and 5). Both of these results are consonant with the easterly prevailing winds in the region and the resulting westward overall drift.

I would estimate that this kinetic energy is perhaps roughly 10 percent of the available bidirectional littoral energy, and a much smaller fraction of the total wave energy delivered to points along this coast. For purposes of comparison, measured wave heights within cell 5 (5) are about 13 cm, on the average; and estimated wave heights, based on repeated field observations, are markedly larger to the northwest (cell 6) and somewhat smaller toward the northeast (cells 1, 2, 3, and 4) toward the "zero" energy coast southeast of Tallahassee.

WILLIAM F. TANNER Geology Department, Florida State University, Tallahassee 32306