Soil's potential as a sink for atmospheric carbon monoxide

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ABSTRACT

The CO uptake capacity of soils was studied in the field in order to refine previous estimates of the potential of soil as a CO sink. Soils representative of most of the major vegetative regions of North America as well as roadside soils and soils under cultivation were exposed *in situ* to atmospheres containing initial concentrations of ca. 100 ppm CO in the air. The CO uptake capacities of the soils ranged from 7.6 to 115 mg CO/h/m^2, with the tropical soils showing the greatest activity and the desert soils the least. Soils under cultivation were consistently less active than the same soils nearby under natural vegetation. Laboratory investigations indicate that the differences were probably not due to agricultural chemicals but rather to a lack of organic matter in the tilled soils. Roadside soils were consistently higher in CO uptake capacity than similar soils in remote regions. Laboratory studies support the idea that this increased rate was due to the constant exposure of roadside soils to high levels of CO. Data for the field studies was corrected for the influence of environmental variables based on laboratory studies and the potential capacity of the soils of the conterminous United States was estimated to be an uptake of 505 million tons of CO per year. This capacity, more than twice the estimated anthropogenic CO in the U.S. annually, indicates that potentially soil is a major sink for atmospheric CO.

1. Introduction

For some years now, carbon monoxide (CO) has been linked to various biological mechanisms that were believed to influence its concentration and residence time in the atmosphere. As far back as 1926, Wehmer reported that garden soil could remove the CO found in illuminating gas. In the 1930s, Jones & Scott (1939) reported that certain bacteria in sealed coal mines were capable of removing CO from the mine atmosphere. Anaerobic methane bacteria found in soil are known to oxidize CO to CO_2 in the absence of H_2, or to reduce CO directly to methane in the presence of H_2 (Kluyver & Schueller, 1947). Cell-free extracts of *Desulfovibrio desulfuricans* oxidize CO to CO_2 in the presence of sulfite (Yagi, 1958) Kistner (1954) has shown that the bacterium *Hydrogenomonas carboxydovorans* oxidizes CO through an adaptive enzyme system.

Last year we reported that soils exposed to test atmospheres of 100 ppm CO in air could reduce the CO concentration to near zero in 2 to 3 hours (Inman et al., 1971). This activity was shown to be biological in nature. A number of fungal species isolated from the soil were shown to have the capacity to remove CO from atmospheres above them when they were grown in pure culture. Based on these laboratory studies of the CO uptake rates of several soils collected in California, an average potential CO uptake rate for the total land mass of the United States was calculated to be 8.44 mg CO/h/m^2. Based on the assumption that this value was representative, the total capacity of the soils of the United States was calculated to be 569 million tons of CO annually. This estimate, which is 6.5 times the calculated annual production of CO in the United States, was based on such limited data and broad assumptions that a further study was initiated to refine the estimate. A field study of the CO uptake rates of North American soils and a laboratory study of the influence of environmental variables were conducted. This paper reports some of the findings of this study.

2. Procedures

Test sites were selected throughout North America so that soils in most of the major

vegetative regions would be sampled. Sites were limited to areas accessible to a mobile laboratory and where reliable weather information was available. Testing was done in the field at each site by covering a square meter of undisturbed soil and covering vegetation with a gas tight chamber. The sides of the chamber base were sealed to the soil surface during testing by burying them to a depth of 15 cm and then compacting soil around the outside edge. This technique provides a good seal as studies using mixtures of methane and carbon monoxide showed no reduction in methane levels in the chamber during the removal of carbon monoxide. A concentration of 100 ppm CO was established in the chamber by injecting pure CO, and the disappearance of CO in the chamber was continuously monitored for 2 to 3 hours using an infrared gas analyzer (Beckman Model 315B).

Experiments on the influence of environmental variables were conducted in the laboratory using 50 g soil samples sealed in 250 ml flasks. CO analysis was performed by gas chromatography, using techniques previously described.

A potting soil mixture consisting of loam, sand, leaf mold, peat moss and steer manure (25:25:16.6:16.6:16.6) was used as the base test soil in all experiments except those involving organic matter variables. Also, soil samples taken at various continental test sites were used in the laboratory to study effects of temperature variables on CO uptake rates.

Effects of soil moisture on CO uptake activity were determined in studies using 50 g of the base soil mixture contained in 250-ml filter flasks. Starting with air-dried soil, sufficient water was added to the respective samples in duplicate to establish a series of soil moisture levels. Soils so amended were incubated at 30°C for 24 hours prior to testing at 30°C.

Since it was suspected that agricultural chemicals applied to soils under cultivation might be influencing the CO uptake rates of these soils, several chemicals representative of different classes of agricultural pesticide usage were selected for study: Triox, a herbicide, Diazinon and Isotox as insecticides and Benlate and another fungicide. Effects of amending the base soil with these selected agricultural chemicals on CO uptake rates were studies in 250-ml filter flasks. One-kilogram samples of potting soil were treated with 100 ml of one of the following:

Triox:
- (1.86 %) 2-methoxy-4,6-bis(isopropyl amino *s*-triazine)
- (<1 %) parachlorophenol and other chlorinated phenols (11 ml/100 ml)

Benlate:
- (50 %) benomyl(methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate (0.2 g/100 ml)

Isotox:
- (5 %) gamma benzene hexachloride
- (10 %) *p,o*-dimethyl dithiophosphate of diethyl mercaptosuccinate
- (5 %) dichloro diphenyl trichloroethane
- (3 %) 2,4,5-tetrachlorodiphenyl sulphone
- (20 %) aromatic petroleum solvent (0.4 ml/100 ml)

Diazinon:
- (25 %) 0,0-diethyl-0-(2-isopropyl-4-methyl-6-pyrimidinyl
- (57 %) aromatic petroleum solvent (0.26 ml/100 ml)

Fungicide:
- (25 %) pentachloronitrobenzene
- (25 %) N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide
- (10 %) zinc ethylene bisdithiocarbamate (0.37 g/ml)

Organic matter amendments of a base soil consisting of loam and sand (50:50) were studied for possible effects on CO uptake. Two-kg samples each of base soil were amended (8 % and 25 % by weight) with commercial preparations of peat moss, steer manure, and leaf mold and maintained in Plastic Atmospheric Chambers PAC's (described previously) Inman et al., 1971) at 10 % soil moisture level during the course of the tests. Uptake activity by the various soils was monitored over a period of 9 weeks at 25°C. During the intervals between tests, the soils were maintained at 25°C in an incubator, with the PAC lids placed askew over the soils to provide for aeration. Tests were conducted by sealing the lids in place, flushing the PAC's for 5 minutes with the test atmosphere containing initially 100 ppm CO, then sealing the PACs and monitoring CO concentrations over a 2- to 4-hour test period.

The effects of constant exposure of soil to various levels of CO on the rate of CO uptake by soil was studied using 175-g samples of the base soil in 1 000-ml filter flasks. Duplicate flasks were continually flushed (100 ml/min) with a

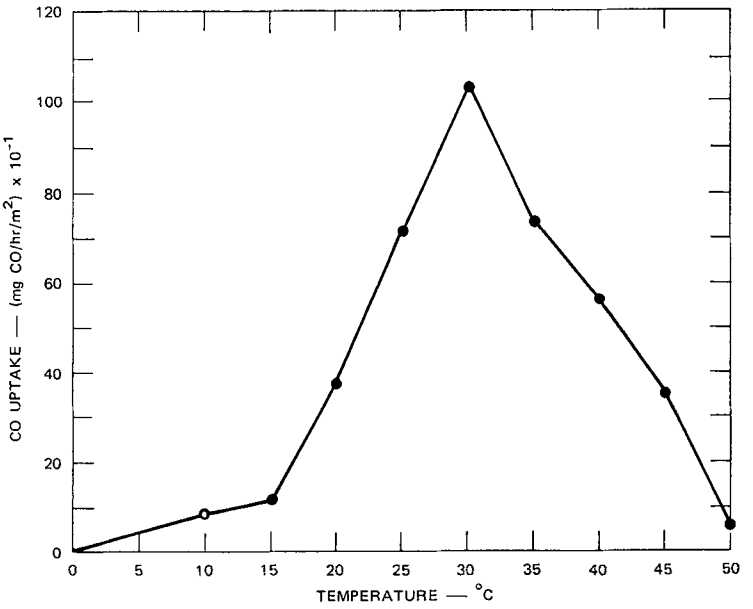

Fig. 1. Effect of temperature on the CO uptake rate of potting soil.

test atmosphere containing 0, 5, 28, or 100 ppm CO. The gas stream was bubbled through a water column prior to entry into the flasks to prevent excessive drying of the soil during the flushing process. Soils were maintained at their original moisture content (ca. 10 %) by daily weighings, and were held at 25°C throughout the test period, which lasted for 45 days. Uptake capabilities of the test soils exposed to different CO levels were determined every 2 to 3 days via the usual procedure as described above, and changes in uptake capabilities were plotted over time.

3. Results

The CO uptake rate of soils measured in the field showed a great deal of variation with values ranging from 7.5 to 109 mg/h/m^2. These values were then corrected for seasonal temperature fluctuations. These corrections were made by comparing the field rate to the laboratory rate shown in Fig. 1. The following equation was used to make the corrections.

$$C = R\frac{\text{rmt}}{\text{rft}}\frac{m}{12}$$

where C is the corrected value, R is the observed field value, rmt is the rate of uptake on Fig. 1 for the average yearly temperature for the test site, rft is the rate of uptake on Fig. 2 of the temperature during the actual field test, and m is the number of months during the year when the temperature at the test site averages above 0°C.

This correction is an approximation based on fluctuations of the test temperature above and below the average temperature for the site, since each site could be visited only once and the temperature during testing was limited to whatever it happened to be at the time of testing. Although the surface temperature of the soil in many areas warms to above freezing during the day in months in which the average monthly temperature is below freezing and therefore some CO uptake may occur, there are also nights in months in which the average temperature is above freezing but the soil temperature may be 0°C or below. These two would tend to balance each other out.

No corrections were made for differences in soil moisture content. Laboratory studies (Table 1) indicated that over a wide range of average soil moisture contents, the rate of CO uptake by the soils is not significantly different.

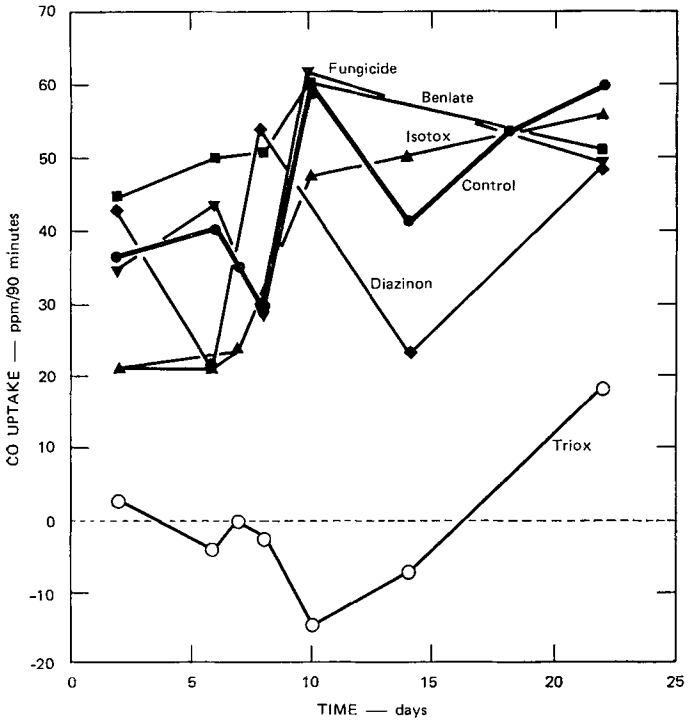

Fig. 2. Influence of agricultural chemicals on CO uptake by soil.

Wherever possible, field test sites were chosen at locations where two tests could be made for comparison—one on the soil under natural vegetation and the other on the same soil under cultivation. The results of this testing program are shown in Table 2. In all cases, the cultivated soils were significantly less active than the corresponding soils under natural vegetation.

Table 1. *Effect of soil moisture on the uptake of carbon monoxide by potting soil exposed to 100 ppm CO at 25°C*

Soil moisture (%)	CO uptake (mg/h/m²)[a]
5	6.44
10	7.01
16	7.08
19	7.00
22	7.04
28	6.64

[a] Average of 3 replicates.

The average uptake rates for the natural and cultivated soils were 11.7 and 2.6, respectively.

It was suspected that the lack of organic matter in the agricultural soil might be the reason for the lower activity of that soil. Hence, a study on the influence of organic matter in soil was conducted. The results of this study (Table 3) show that both the amount and type of organic matter in a soil influence the CO uptake rate of a soil. Soils containing leaf mold or steer manure had higher CO uptake rates than soils containing peat moss. These rates are low compared to rates found in some of the active natural soils.

It was also suspected that the treatment of agricultural fields with chemicals such as herbicides and fungicides might be the reason for the lower CO uptake. Therefore, a laboratory study (Fig. 2) was done on that parameter. All the compounds were applied in their recommended dosages. Only Triox, a vegetation-killer containing pentachlorophenol and prometone, was effective in reducing the soil CO uptake capacity, and after a period of three weeks it appeared

Table 2. *Comparison of the CO uptake capacity of soils under cultivation and soils under natural vegetation*

Test site	Soils under natural vegetation		Soils under cultivation	
	Vegetation type	Rate[a]	Type	Rate[a]
Grouard, Alb.	Boreal forest	4.2	Plowed field	1.1
Athens, Ohio	Mixed deciduous forest	21.3	Plowed field	3.4
Ft. McMurray, Alb.	Boreal forest	6.8	Plowed field	2.4
Chenango, N.Y.	Deciduous forest	26.2	Plowed field	1.8
Wichita Falls, Tex.	Grassland	11.9	Wheat stubble	7.5
Regina, Sask.	Grassland	2.7	Plowed field	1.6
Van Meter, Mo.	Oak-hickory forest	10.2	Newly planted milo field	2.9
Shrevesport, La.	Flood plain forest	26.3	Plowed field	4.3
Sabetha, Kans.	Grassland	3.6	Milo stubble	2.9
Grants Pass, Ore.	Coastal forest	14.1	Plowed field	2.2
Cincinnati, Ohio	Oak-hickory forest	21.3	Fallow field	3.4
Prairie View, Kans.	Bluestem prairie	2.3	Plowed field	1.2

[a] mgCo/h/m², corrected for annual average temperature at test sites.

that even the soil treated with Triox was resuming its capacity to take up CO. The temporary effect of Triox during the first two weeks after exposure which resulted in a net evolution of CO by the soil rather than uptake was probably due to a sterilization of the soil by Triox. Earlier studies on sterilizing potting soils with steam under pressure in an autoclave had shown that CO evolved from sterilized soils (Table 4). This phenomenon persisted for a number of weeks if the soil was maintained in a sterile condition. Also, it can be seen in Table 4 that CO evolution was very temperature dependent with rates approaching zero below 20°C and increasing greatly at temperatures above 30°C.

Table 3. *Effect of type and quantity of organic matter in a soil on its CO uptake capacity*

Organic treatment	Organic (%)	Average CO uptake (mg/h/m²) after 2 weeks	4 weeks	9 weeks
Leaf mold	0	9.03	7.47	14.50
	8	13.30	19.13	23.53
	25	27.94	30.22	28.01
Peat moss	0	10.74	9.46	20.97
	8	10.17	15.86	20.90
	25	13.65	12.23	15.71
Steer manure	0	8.03	8.53	20.69
	8	13.51	16.57	24.74
	25	21.09	21.47	25.03

Since soils alongside roads and, in particular, major highways are constantly exposed to high levels of CO, a study on the rates of CO uptake by these soils was conducted. Sites along a 15-mile section of a major highway (U.S. 101) near Menlo Park, California were selected in areas with different vegetative ground covers (Table 5) depicts the results of this study. In general, soils that were covered by a ground cover (e.g., ice plant, ivy, or grass) had higher CO uptake rates. All the soils had generally higher rates than soils would be expected to have at that latitude. To test the hypothesis that the constant exposure of these soils to CO was responsible for the high rates, a laboratory experiment was

Table 4. *CO evolution by autoclaved soil*

Incubation temperature (°C)	CO evolution rate (μg CO/kg soil/h)[a]
20	3.3
40	36
50	136

[a] Based on the average of three replicates.

Table 5. *Soil activity at sites alongside a 20-mile stretch of the Bayshore Freeway (US 101) preselected on the basis of representative vegetation or ground cover*

Test site	Vegetation	CO uptake (mg/h/m²)	Avg. temp.[a] (°F)	Soil pH	Soil moisture[b] (%)
Embarcadero Road interchange	Iceplant	64.5	65	7.6	19.6
San Antonio Road interchange	Iceplant	47.9	85	7.8	5.7
Mathilda Avenue interchange	Ivy	52.5	66	8.2	3.9
W. Bayshore Road[c]	Ivy	43.0	60	8.3	19.2
Frontage Road[c]	Grass	63.4	69	7.8	10.0
Dirt road[c]	Barley	32.7	81	7.6	2.5
San Tomas Expressway interchange	Grass	36.9	80	7.4	5.1
Trimble Road interchange	Grass	17.8	76	8.0	7.3
U.S. 85 interchange	Bare	22.6	95	7.7	6.1
Mathilda Avenue off-ramp	Bare	16.2	82	7.7	3.7
W. Bayshore Road[c]	Plowed	23.1	77	7.0	4.2
W. Bayshore Road[c]	Plowed	15.0	71	8.7	3.5

[a] Soil temperature inside test chamber.
[b] Percent moisture of surface soil.
[c] Site off freeway right-of-way, but within 100 ft of freeway.

performed in which soils were constantly exposed to various levels of CO and their CO uptake capacity was monitored for several weeks. As shown in Fig. 3, soils exposed to 100 and 28 ppm CO developed higher rates of CO uptake than did soils exposed to 5 ppm or to ambient air (control). The rate for the soil exposed to 5 ppm was only slightly higher than that for the control soil.

Tables 6 and 7 summarize the CO uptake potential of the soils of the conterminous United States and the world. The values of CO uptake for the various vegetative regions were averaged and corrected for temperature variations, then multiplied by the area of that region. The respective totals for the U.S. and the world potential uptake rates are 505 million and 14.3 billion tons annually. An inspection of

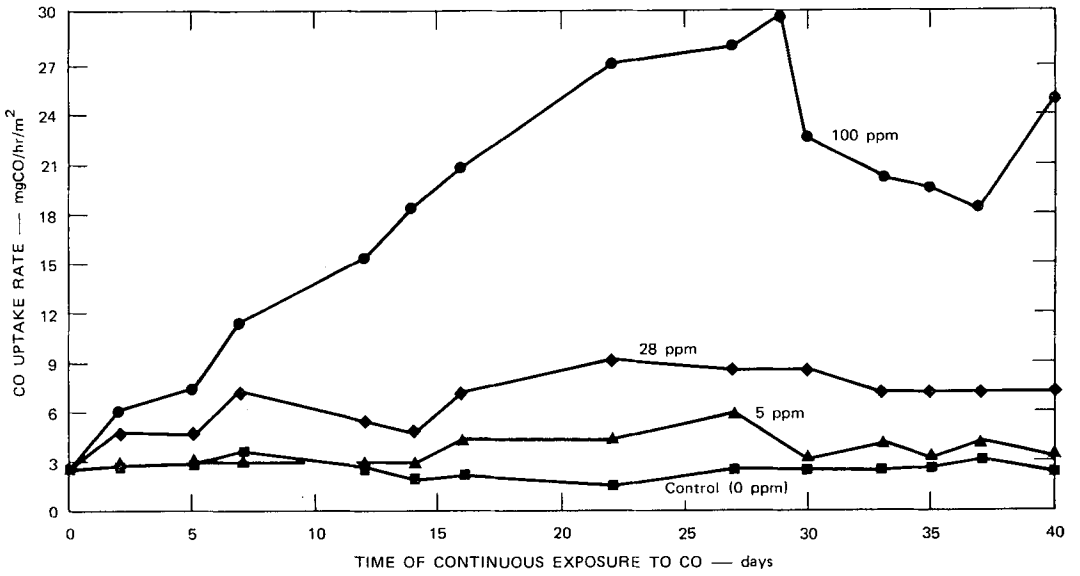

Fig. 3. Effect of continuous CO exposure on the CO uptake rate of soils.

Table 6. *Potential CO uptake rates of the soils of the conterminous united states*

Soil-vegetation type	Area[a] (mi²)	CO uptake[b] (tons/yr/mi²)	Total CO uptake (tons × 10⁶/yr)
Cropland	468 000[a]	86.0	40.25
Pasture	616 674[a]	179.3	110.57
Coastal forest	329 390[b]	200.7	83.93
Deciduous forest	339 485[b]	254.8	86.50
Montane forest	87 150[b]	242.0	21.10
Southern mixed forest	48 644[b]	86.5	4.21
Appalachian forest	265 519[b]	313.7	84.17
Southern flood plain forest	58 782[b]	595.0	34.95
Sagebrush steppe	264 867[b]	76.7	20.32
Sagebrush	145 047[b]	52.2	19.09
Desert scrub	220 723[b]		
Paved roads	28 100[c]	0	0
Covered area	26 500[d]	0	0
Lakes, rivers, etc.	78 267[d]	0	0
Total	2 977 128		505.12

[a] Areas based on figures found in: (*a*) Statistical Abstract of the United States, 1971, 92nd Ed., U.S. Department of Commerce, Washington, D.C.; (*b*) Map of U.S. Forests, U.S. Geological Survey; (*c*) 1969 Highway Statistics, U.S. Departments of Transportation, Washington, D.C.; (*d*) 1971 World Almanac, Newspaper Enterprise Assoc., Inc., New York, N.Y.
[b] Corrected for annual temperature variations.

these two tables indicates that, potentially, the forest regions of the United States could serve as major sinks due to the large proportion of the area they cover and, on a global basis, the tropical regions are potentially the largest sinks due to high year-round uptake rates.

4. Discussion

The potential rates of CO uptake by the soils of the United States and the world are estimated in this study to be 505 million and 14.3 billion tons per year, respectively. These rates are based on studies conducted at a uniform expo-

Table 7. *Potential CO uptake rates of the soils of the world*

Soil-vegetation type	Area (10⁶ mi²)[b]	Average CO uptake[a] (tons/yr/mi²) × 10	Total CO uptake (tons × 10⁶/yr)
Agricultural	4.60	86.0	395.4
Pasture	1.84	179.3	329.7
Tropical grassland	3.45	886.9	3 062.5
Temperate grassland	3.10	86.5	268.4
Steppe	3.45	76.7	264.5
Montane forest	4.66	175.7	817.8
Taiga forest	4.71	127.5	600.9
Mixed and broadleaf forest	1.32	254.8	410.0
Southern pine forest	0.29	505.8	145.2
Tropical deciduous forest	1.78	1 105.9	1 969.6
Tropical rain forest	6.55	805.6	5 277.5
Tundra	1.15	123.0	141.3
Desert	10.86	52.2	567.0
Covered by ice, water, roads, structures, etc.	9.20	0	0
Total	56.96		14 250.0

[a] Areas based on figures derived by integrating vegetation areas found in map types of natural vegetation in Readers Digest World Atlas (pp. 146 and 147) and the 1971 World Almanac.
[b] Corrected for annual temperature variations.

sure of 100 ppm CO and are thus an estimate of the potential of the soil if exposed to this high level of CO. Recent laboratory studies by Seiler (1972) indicate that the rate of CO uptake by soils exposed to an ambient level of CO (0.2 to 1.0 ppm) is one-tenth of the values obtained in this study. The actual CO uptake rates for the soils of the United States and the world are thus probably somewhere around 0.05 to 1.4 billion tons of CO annually—still a considerable fraction of the estimated annual 407 million tons of CO produced by man globally.

The higher CO uptake rates for the soils in tropical regions of Mexico are quite probably due to the higher microbial populations in these soils due to favorable climate and high amounts of organic matter in these soils. The rates of CO uptake in the tropical rain forests were somewhat lower than expected, probably due to the high moisture content of this soil, which may have limited diffusion of the gas. Also, the rates in the arctic tundra were somewhat higher than expected, indicating that the microbial populations in these soils increase during the summer months when this soil warms.

The uptake of CO by agricultural soils was, in all cases, much lower than the uptake rate for the same soil under natural vegetation. This was most probably due to a lack of organic matter in the surface layer of soils that are cultivated.

A study on the influence of agricultural chemicals, another suspected cause of the reduced activity in cultivated soils, indicates that these chemicals have only a minor effect, if any at all.

The study alongside the freeway in California indicates that the uptake rate is highly dependent on the ground cover over it. This is quite probably due to an increase in organic matter and friability of soils with luxuriant ground cover, thus leading to a more active microfloral population in the soil. Prolonged gassing studies conducted in the laboratory indicate that soils that are constantly exposed to CO concentrations above 5 ppm have relatively high CO uptake capacities. Soils alongside the freeway are constantly exposed to higher than ambient levels of CO, and this may explain why they appear to be slightly more active in CO uptake, on the average, than other soils tested. Since soils alongside freeways are exposed to CO at higher levels on a more or less continuous basis, the rate of uptake of CO by these soils is increased due to the higher starting levels of CO and also probably due to an induced higher uptake rate of the soil.

An interesting aspect of this study is the evolution of CO by soils treated with Triox during the first two weeks after treatment. This is consistent with findings of CO evolution from soils sterilized by autoclaving. Studies by Seiler & Junge (1970) have indicated that at very low levels of atmospheric CO (<0.2 ppm), an equilibrium is established over a soil where CO uptake equals CO evolution by the soil. Thus, while soils on a net basis are a large sink for CO, they also quite probably are a natural source for CO as well. Information on the character of this CO equilibrium would help to answer questions that arise when isotope determinations are used to calculate the sources of CO in the atmosphere and the residence time of CO in the atmosphere.

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REFERENCES

Inman, R. E., Ingersoll, R. B. & Levy, E. A. 1971. Soil: A natural sink for carbon monoxide. *Science 172*, 1229–1231.

Inman, R. E. & Ingersoll, R. B. 1971. Uptake of carbon monoxide by soil fungi. *J. Air Pollution Control Assoc. 21*, 646–647.

Jones, C. W. & Scott, G. 1939. Carbon monoxide in underground atmospheres. The role of bacteria in its elimination. *Ing. Eng. Chem. 31*, 775–778.

Kistner, A. 1954. Conditions determining the oxidation of carbon monoxide and of hydrogen by *Hydrogenomonas carboxydovorans*. *Proc. Koninkl. Ned. Akad. Wetenschap. 57*, 186–195.

Kluyver, A. J. & Schueller, Ch. G. T. P. 1947. On the fermentation of carbon monoxide by pure cultures of methane bacteria. *Arch. Biochem. 14*, 57–70.

Seiler, W. 1972. Carbon monoxide in the atmosphere. *Symposium on Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment*, St. Petersburg Beach, Fla.

Seiler, W. & Junge, C. 1970. Carbon monoxide in the atmosphere. *J. Geophys. Res. 75*, 2217–2226.

Wehmer, C. 1926. Biochemische Zersetzung des Kohlenoxyds. *Chem. Ber. 59*, 887–890.

Yagi, T. 1958. Enzymic oxidation of carbon monoxide. *Biochem. Biophys. Acta 30*, 194–195.

ПОЧВА КАК СТОК АТМОСФЕРНОЙ ОКИСИ УГЛЕРОДА

Для улучшения предыдущих оценок способности почвы служить стоком CO в полевых условиях изучалась способность почвы связывать CO. Почвы, характерные для большинства основных областей с растительностью Северной Америки, так же как и придорожные и культивируемые почвы, приводились in situ в контакт с воздухом, имевшим начальную концентрацию CO, равную 10^{-4}. Связывающие способности почвы были в пределах от 7,6 до 115 *мг* CO/час/$м^2$, причем тропические почвы проявили наибольшую активность, а почвы пустынь — наименьшую. Культивируемые почвы были постоянно менее активны, чем аналогичные почвы из близлежащих участков с естественной растительностью. Лабораторные исследования показывают, что различия были, вероятно, вызваны не химическими веществами, употребляемыми в сельском хозяйстве, но недостатком органических веществ в возделываемой почве. Придорожные почвы имели постоянно бóльшую активность в поглощении CO, чем аналогичные почвы с удаленных от дорог областей. Лабораторные исследования говорят в пользу идеи, что эта повышенная активность вызвана постоянным контактом придорожных почв с высокими уровнями концентрации CO. В данные полевых исследований были внесены поправки на влияние окружающих условий, оцененные на основе лабораторных опытов. Потенциальная способность почв территории Соединенных Штатов связывать CO была оценена величиной 505 миллионов тонн CO в год. Эта способность более чем вдвое превышает антропогенное производство CO в США за год и это указывает, что почва потенциально является основным стоком атмосферного CO.