with water during stage 1 that mud hurricanes, lahars, or sheetfloods may be the only phenomena observed. These may be only steam-blast eruptions like the 1976 eruptions of La Soufrière (*19*), which at times emitted lahars directly from the venting fissures (*20*).

In still other cases, a gradual increase in water/magma mixing ratios during stage 1 provides a change in eruptive characteristics with time. The Plinian deposits from the A.D. 79 eruption of Vesuvius (*1*) provide an excellent example of this type of progression. The dominantly magmatic initial pumice-fall phase went through an alternating transition into dry, hot base surges followed by dry, hot pyroclastic flows which reflected a progressive increase in the water/magma ratio in the chamber. By the late stages of the eruption, water greatly exceeded magma so that mud hurricanes, lahars, and steam explosions ended the cycle. The history of this eruption can be traced in Fig. 1 by considering a regular increase in the water/magma ratio during the 18 hours of activity. Low ratios (less than 1) during the Plinian phase increased to moderate levels (near 3) during the base-surge and pyroclastic-flow phases and to very high values (perhaps up to 30) during the final period of mud hurricanes and lahars.

Another documentation of this model is found in typical tuff cones, which are composed of a layer of explosion breccia, overlain by dry, hot base-surge deposits, in turn covered by cold wet-surge beds and lahars (*21*). This progression could likewise be interpreted as a result of increasing water/magma ratios from less than 3 to more than 3 as the vent widens during eruption (*22*).

Hydrovolcanic phenomena are common, and we believe that the use of our model will lead to a better understanding of the related deep processes, eruption phenomena, and surficial deposits.

MICHAEL F. SHERIDAN
KENNETH H. WOHLETZ
Department of Geology,
Arizona State University,
Tempe 85281

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11. Wet base surges are emplaced below the condensation temperature so that a film of water has condensed on the transported particles, often leading to the development of accretionary or ash-armored lapilli. Mud hurricanes are wet ash-laden blasts that travel at very high velocities and are capable of leaving thick deposits on vertical surfaces. Accretionary lapilli and bubble-filled ash layers (vesicular tuffs) are common products. Lahars are volcanic mudflows.
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Soil as a Sink for Atmospheric Carbon Monoxide

Abstract. *The rate of carbon monoxide oxidation by soil increased with increasing carbon monoxide concentration in the gas phase, in line with Michaelis-Menten kinetics. Rates of carbon monoxide oxidation were determined for 20 soils at 0°, 10°, 20°, and 30°C. The observed oxidation rates were used to calculate a global soil uptake rate of atmospheric carbon monoxide of* 4.1×10^{14} *grams per year, which is slightly less than the amount of carbon monoxide believed to be produced annually as a result of fossil fuel combustion.*

Much attention has been focused on the possible perturbation of the atmospheric CO cycle by anthropogenic CO emissions. Seiler (*1*) estimated that the amount of CO produced from fossil fuel combustion is 6.4×10^{14} g/year, a large value by comparison with the 7.4×10^{14} g of CO currently in the atmosphere (*2*). Crutzen *et al.* (*3*) suggested that biomass burning, which results largely from man's activities, produces more CO than fossil fuel combustion.

The effect of anthropogenic CO production of this magnitude on the atmospheric cycle depends to a great extent on the ability of removal mechanisms to maintain present atmospheric concentrations of CO (*1*, *4*). The main sinks for atmospheric CO are believed to be the reaction of tropospheric hydroxyl radicals with CO and the oxidation of CO by soil (*1*, *4*). Ingersoll *et al.* (*5*) estimated the global soil uptake of CO to be 1.4×10^{15} g/year. This value was derived from field studies of soils at 59 sites in North America that were exposed to 100 parts per million by volume (ppmv) of CO. Based on measurements of a few European soils in the laboratory, Seiler (*1*) estimated the global uptake of CO by soil to be 5.0×10^{14} g/year. We report here the effect of CO concentration on the rate of its destruction by soil, and we estimate the magnitude of CO uptake by soil on a global basis from uptake measurements on 20 soils.

We measured the effect of the CO concentration on the rate of its oxidation by a modification of the method of Pramer and Schmidt (*6*). Portions (5.0 g) of Williamson silt loam (*p*H 5.8, 2.6 percent organic matter, 22 percent moisture content) were placed in 25-ml Erlenmeyer flasks. The flasks were sealed with serum stoppers, and varying amounts of a ^{12}CO-^{14}CO mixture (9:1 ratio by volume) were added to the flasks by means of a gas-tight syringe. The flasks were incubated for 30 minutes at 23°C, after which the $^{14}CO_2$ formed from ^{14}CO was trapped and measured. We obtained the ^{12}CO-^{14}CO mixture by dehydrating H^{12}COONa and H^{14}COONa (New England Nuclear, specific activity of 52 mCi/mmole) with concentrated H_2SO_4 (*7*). Details of these methods and data showing that CO oxidation in soil results from microbial activity have been reported (*8*).

To study CO oxidation at different temperatures, samples of surface soils from sites in the eastern United States

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were cleared of loose debris and growing plants. Then a 24.1-cm length of polyvinyl chloride pipe (7.6 cm in diameter) was driven into the ground, and the soil core in the pipe was withdrawn together with the pipe. The ends of these columns of soil were sealed with polyethylene film, and the columns were brought to the laboratory. We reduced the length of the soil core to 13.4 cm by sliding the soil down inside the pipe and removing the soil from the bottom of the core. The remaining soil was pushed up to 6.7 cm from the top of the column by the use of polystyrene disks (7.6 cm in diameter) inserted in the bottom of the column. Four of these cores were taken at each site.

These soil columns were maintained at 0°, 10°, 20°, and 30°C for 3 days prior to the rate measurement at that temperature. For the assay, a polyvinyl chloride cap was placed at the top of the column to give an airtight seal. In the center of the cap was a septum, which permitted the injection of a ^{12}CO-^{14}CO mixture into the headspace above the soil. Suspended from this cap into the column was a small plastic cup in which was placed a piece of folded filter paper containing 0.3 ml of phenethylamine, a CO_2-trapping agent. After the column was sealed with a cap, 1.0 μl of ^{12}CO-^{14}CO (a final concentration of 3 ppmv or 6.2×10^5 disintegrations per minute) was injected into the headspace. The soil was then incubated for 10 minutes at the specified temperature, after which the cap of the column was removed and the filter paper was placed in a scintillation vial containing 11 ml of ACS scintillation cocktail (Amersham Corporation, Arlington, Illinois). The radioactivity of the $^{14}CO_2$ formed from ^{14}CO was counted in a scintillation counter (Beckman LS 7500). Each soil column was then incubated at a different temperature in a random order, after which testing at the new temperature was accomplished. This cycle was repeated for the entire temperature range studied.

Table 1. Soil characteristics and CO oxidation rates of several soils at four temperatures; N.D., not determined.

Soil*	Great soil group	CO oxidation rate (micrograms per square meter of soil per hour)			
		0°C	10°C	20°C	30°C
Spodosol 1 (*p*H 4.5, HF)	Unclassified	N.D.	400	480	410
Spodosol 2 (*p*H 3.7, MF)	Unclassified	N.D.	430	405	405
Histosol (*p*H 6.2, G)	Unclassified	120	160	270	290
Brookston silty clay loam 1 (*p*H 5.8, HF)	Argiaquoll	110	480	560	840
Brookston silty clay loam 2 (*p*H 5.5, C)	Argiaquoll	60	260	320	500
Canfield silt loam (*p*H 4.5, HF)	Fragiudalf	20	80	130	180
Wooster silt loam (*p*H 5.4, C)	Fragiudalf	3	30	60	90
Erie silt loam (*p*H 4.5, HF)	Fragiaquept	90	200	160	250
Williamson silt loam (*p*H 6.3, C)	Fragiochrept	30	74	160	210
Durham loamy sand (*p*H 4.8, C)	Hapludult	30	150	270	460
Wehadkee silt loam 1 (*p*H 4.0, HF)	Haplaquept	200	350	680	820
Congaree fine sandy loam (*p*H 4.5, HF)	Udifluvent	200	360	630	750
Enon fine sandy loam (*p*H 4.5, HF)	Hapludalf	170	280	520	630
Appling sandy loam (*p*H 4.7, CS)	Hapludult	230	460	630	850
Candler sand (*p*H 7.8, G)	Quartzipsamment	N.D.	300	430	450†
Holopaw sand 1 (*p*H 6.8, C)	Ochraqualf	N.D.	400	540	600†
Holopaw sand 2 (*p*H 6.4, HF)	Ochraqualf	N.D.	410	580	610†
Wehadkee silt loam 2 (*p*H 5.5, G)	Haplaquept	N.D.	60	120	120†
Buncombe loamy fine sand (*p*H 5.0, HF)	Udipsamment	N.D.	90	180	210†
Red Bay sandy loam (*p*H 6.4, C)	Paleudult	N.D.	210	360	390†

*Vegetative cover is indicated as follows: HF, hardwood forest; MF, mixed forest; G, grassland; C, cropland; and CS, conifer stand. †Incubation temperature was 28°C.

Williamson silt loam was exposed to various concentrations of ^{14}CO for 30 minutes, and the amount of $^{14}CO_2$ was determined. From the amount of $^{14}CO_2$ formed and the known ratio of ^{12}CO to ^{14}CO added, the amount of CO oxidized at each level of added CO was calculated. The results show that the rate of CO oxidation is markedly affected by its concentration (Fig. 1). This plot of the velocity of CO destruction as a function of its concentration is characteristic of Michaelis-Menten kinetics for enzyme reactions. An Eadie-Hofstee plot (*9*) of the data yielded a Michaelis constant of 44 ppmv of CO and a maximum rate of CO oxidation of 96 ng in 30 minutes per gram of soil. When the gas phase contained 5.0 and 1.0 ppmv of CO, the rates were only about 16 and 2 percent of the maximum rates, respectively, and far higher concentrations than are found in nature were required to achieve the greatest oxidation rates. When the CO concentration in the headspace was 100 ppmv, which is the CO concentration Ingersoll *et al.* (*5*) used in their field studies to estimate global rates of CO destruction, the rate of CO oxidation was 334 ng in 30 minutes per 5.0 g of soil, a value more than two orders of magnitude larger than the rate at 0.2 ppmv CO (approximately the atmospheric concentration). These data indicate that estimates of rates of global destruction of CO are probably seriously in error if the laboratory or field test is conducted on the basis of inappropriate gas concentrations.

The rates of CO oxidation at 0°, 10°, 20°, and 30°C by each soil are presented in Table 1. The rates at 20°C differed by an order of magnitude among the soils, from a low of 60 to a high of 680 μg per square meter of soil surface per hour. With the exception of the two spodosols, the rates of oxidation by all soils increased at higher temperatures.

The oxidation rates at 0°C were relatively high as compared to rates at higher temperatures, which may indicate the presence of preformed enzymes responsible for CO oxidation; such enzymes might continue to function at temperatures too low to permit appreciable microbial growth. Omitting the spodosols, the average of the quotient of the oxidation rate at 20°C divided by the rate at

10°C (Q_{10}) was 1.5 (standard deviation 0.2) for all the soils tested. The rates of CO oxidation in these soils showed no correlation, on the basis of linear regression analysis, with the content of organic matter, *p*H, moisture content, cation exchange capacity, or concentrations of plant nutrients.

The oxidation rates were used to estimate the global contribution of soils as a sink for CO. The soils were grouped according to their classification at the order level. The oxidation rates at 20°C for soils within each order were multiplied by estimates of the global surface area of the respective order to arrive at global figures for each soil type. The combined results for the estimated CO oxidation rates for all soils of the world, assuming a mean annual global temperature for the soil surface at 20°C, are presented in Table 2.

Table 2. World land surface areas at the order level and estimates for the annual amount of CO uptake by soil on a global basis.

Soil order	Land area* ($km^2 \times 10^6$)	CO removed (10^{13} g/year)†		
		Low	High	Average
Entisol	10.8	1.7	5.5	3.8
Inceptisol	11.5	1.2	6.3	2.8
Alfisol	17.1	0.9	8.7	5.4
Spodosol	5.6	2.0	2.4	2.2
Histosol	1.2	0.3	0.3‡	0.3
Mollisol	11.1	3.5	6.0	4.8
Ultisol	7.2	1.9	4.0	2.7
Aridisol	24.4	8.0	8.0	8.0
Vertisol	2.3	0.8	0.8	0.8
Oxisol	11.1	2.9	6.0	4.0
Mountain soils	25.6	5.7	5.7	5.7
Total	127.9	28.9	53.7	40.5

*Estimates of J. E. Witty, Soil Conservation Service, U.S. Department of Agriculture. †Low and high estimates are based on the lowest and highest CO oxidation rates, respectively, for a soil in that order. Average rates are the means of the rates of all tested soils belonging to that order. ‡Only one soil of that order tested.

Samples of aridisols, vertisols, oxisols, and mountain soils were not included in the tests. We estimated global uptake rates for aridisols and vertisols by multiplying their respective global surface areas by the average uptake rate at 20°C for all soils tested, 370 μg of CO per square meter of soil surface per hour. The estimate for the aridisol may be high because such soils have low microbial activity. Because the properties of oxisols and ultisols are similar, we assumed that the rate of CO oxidation was the same for these soil groups on an area basis. The oxidation rate for mountain soils was estimated as the average rate for all soils at 10°C (250 μg of CO oxidized per square meter of soil surface per hour) because of their lower average temperatures.

The value of 20°C assumed for the mean annual global soil temperature may appear to be high; but the surface 15-cm layer of soil, where much of the oxidation is probably occurring, is warmer than the air at every season of the year (*10*). Based on the average Q_{10} of 1.5, however, the estimate for the global rate of CO removal would be 25 percent less at a mean annual soil temperature of 15°C than at 20°C. The calculated rates may be underestimates because no mixing of the headspace occurred during incubation of the cores. Heichel (*11*) reported that the rate of CO removal in soil samples with no mixing of the headspace was 30 to 40 percent less than in samples with turbulent mixing of the air above the soil.

The average value for global CO destruction (4.1×10^{14} g/year) by soil is in remarkable agreement with the estimate of Seiler (*1*) of 5.0×10^{14} g/year. Seiler's estimate was made by multiplying the average uptake rate of a few soils at 15°C by the global land surface area. Ingersoll *et al.* (*5*), who proposed a global rate of 1.4×10^{15} g/year, determined the rates with a CO concentration of 100 ppmv above the soils, and the final estimate from these rates was reduced arbitrarily to 10 percent of the original value because of the high initial concentration of CO. However, our data indicate that the rate of oxidation at a CO concentration of 100 ppmv is higher by more than two orders of magnitude than the rate at ambient CO concentrations, so that the value of Ingersoll *et al.* (*5*) is probably an overestimate.

In view of our estimate that soils may destroy 4.1×10^{14} g of CO each year, the land surface appears to be of major significance in the global CO budget. This estimate of CO removal by soil is slightly less than the amount of CO produced by fossil fuel combustion (6.4×10^{14} g/year) and is equal to the estimate of the amount of CO produced by CH_4 oxidation (4.0×10^{14} g/year) (*1*). Our estimate of the amount of CO removed by soil represents 33 and 8 to 20 percent of the total global sink for CO in the budget proposed by Seiler (*1*) and Zimmerman *et al.* (*4*), respectively.

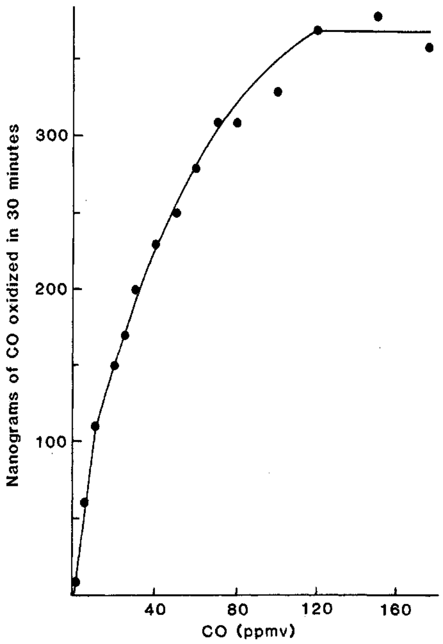

Fig. 1. Effect of CO concentration on the rate of its oxidation to CO_2 in soil.

Gene W. Bartholomew*
Martin Alexander

Laboratory of Soil Microbiology,
Department of Agronomy,
Cornell University,
Ithaca, New York 14853

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* Present address: Department of Environmental Science and Engineering, University of North Carolina, Chapel Hill 27514

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