Global Carbon Monoxide Fluxes: Inappropriate Measurement Procedures

Bartholomew and Alexander have calculated (1) that the global CO uptake by soil is 4.1 × 10^14 g/year. Although we should be satisfied to see Seiler’s earlier estimates (2) confirmed, we are deeply concerned about the experimental procedure used by Bartholomew and Alexander (1) and what we feel are misquotations from Seiler’s earlier paper (2). Their calculation is based on laboratory experiments that represent disturbed conditions, whereas our experiments are based on measurements made in the field under natural conditions. We are also concerned about the application of an unrealistically high CO mixing ratio of 3 parts per million by volume (ppmv) and the use of the radiotrace technique with ^14CO as the tracer.

The CO uptake depends on concentration and, observed ambient CO mixing ratios in the lower troposphere are of the order of 0.05 to 0.30 part per million (ppm); thus reported uptake rates based on mixing ratios of 3 ppm must be overestimated by approximately one order of magnitude. Furthermore, the report by Bartholomew and Alexander totally neglects the fact that CO is not only destroyed but also produced in soil. In summer at high soil surface temperatures and ambient CO mixing ratios (< 0.30 ppmv), the production sometimes exceeds the destruction. Under these conditions the soil acts as a source of atmospheric CO. Extrapolation of results obtained at 3 ppm to low ambient mixing ratios, however, indicates that the soil is always a net sink, an incorrect generalization.

The existence of simultaneous production and destruction of CO by different processes in the soil clearly demonstrates the inapplicability of a radiotracer technique that measures only the oxidation of ^14CO to ^12CO and not the production of CO by soil. The use of ^14CO is therefore inappropriate for the determination of the CO net flux between the soil and atmosphere. Thus we feel that agreement between Seiler’s earlier data and those obtained by Bartholomew and Alexander (1) is fortuitous.

The global CO uptake rate of 5 × 10^14 g/year (2) is based on in situ measurements carried out under ambient natural conditions, different types of soil, and different seasons and weather conditions, covering soil temperatures of 3° to 50°C. This is well documented in (2); we therefore do not understand the statement of Bartholomew and Alexander that Seiler’s estimate is based on “measurements of a few European soils in the laboratory.”

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References
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We are surprised that Seiler and Conrad missed the crucial difference between their studies and ours. Atmospheric scientists accept the fact that the properties and behavior of CO, SO_2, and N_2O are different, and they would not assume that the average values of some properties of five gases could be used to predict the properties of all gases. If it is inappropriate to conclude that, “once you have seen one atmospheric component, you have seen them all,” it would also seem reasonable to suggest that soils differ markedly, and that averaging numbers for five soils, all from one geographical area, does not provide a meaningful mean value for all soils. Soil taxonomists have labored long and hard to develop a meaningful and useful scheme for the categorization of soils, and it is incumbent upon atmospheric scientists, microbiologists, and others to base their extractions on, or at least link them to, the classification systems such as...
oped. We are critical of our own study (1) because of the few samples representing the soil orders and the limited geographic scope of our sampling, but surely the extent of our sampling is broader than that of studies published earlier.

We agree that field measurements are, in theory, better than laboratory studies, but there is enormous variability between estimates of microbial processes occurring at immediately adjacent sites in the field. Until appropriate analyses are made of the variation in activity at sites representing what soil scientists, oceanographers, or limnologists deem to be a single type of soil or water, caution must be used in extrapolations made from single samples taken in the field. The issue is now new: the greater relevance but lower reproducibility of field samples versus the lower relevancy but higher reproducibility of laboratory tests. Clearly, more work is needed to establish the causes and extent of variation in field tests and to validate laboratory assays as approximations of field values.

We do not dispute that soils both produce and destroy CO and that \( ^{14}\text{CO} \) should not be used to assess net flux between the soil and the atmosphere. However, we assume that a reader of a report entitled "Soil as a sink for atmospheric carbon monoxide" (1), in which the authors propose a soil uptake rate, would not conclude that the investigators are evaluating net fluxes. To obtain meaningful estimates of global fluxes, data should be obtained with appropriate methodologies and with truly representative samples of the environments in which the pollutant is being generated. Seiler (2) does not list soil as a major global source of CO, and hence use of the highly sensitive radiotracer technique seems to be eminently suitable for studies of CO transformations mediated by soils and their microbial inhabitants.

The utility of the procedure for environmental studies can be illustrated by another example. Despite the dependence of the CO oxidation rate on CO concentration (1), a relationship between the rate of microbial processes and substrate concentration that is well known, microbiologists who are inclined to draw ecological conclusions solely from studies of species tested in pure culture investigate isolates that are obtained at CO concentrations three or more orders of magnitude greater than those prevailing in nature. Because of the means of isolating these microorganisms, the isolates so obtained use CO as a carbon source as classical heterotrophs or as an energy source as autotrophs. In contrast, data obtained by exposing soils to \( ^{14}\text{CO} \) at concentrations similar to those in the atmosphere show that (i) essentially none of the \( ^{14}\text{C} \) appears in the soil organic fraction containing microbial cells, (ii) \( \text{CO}_2 \) fixation in soil is not enhanced in the presence of \( \text{CO} \), and (iii) populations growing by using \( \text{CO} \) as either a carbon or an energy source do not appear to grow when soils are exposed to such CO concentrations (3). Such data, which suggest that the species destroying \( \text{CO} \) in soil act by cometabolizing the pollutant rather than by growing at its expense, could not be obtained, or at least not readily, by methods not involving radiotracer methodology.

Our use of 3 parts per million by volume (ppmv) was deliberate, even though our data (1) indicate that the rate of oxidation at this concentration is higher than would be expected if the CO concentration over the soil was equivalent to that found in nature. As we mentioned in (1), no mixing of the headspace occurred during incubation of the samples. Heichel (4) 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 overlaying air. In addition, the method we used did not permit acidification of the soil prior to the trapping of \( ^{14}\text{CO}_2 \) formed from the added \( ^{14}\text{CO} \). Thus, a portion of the \( ^{14}\text{CO}_2 \) formed remained in the soil solution and was not detected; this resulted in an underestimated rate of CO oxidation. We therefore feel that the use of 3 ppmv of CO in our experiments did not result in appreciable errors in estimates of the in situ rate of oxidation of ambient concentrations of CO.

We did err in stating that Seiler's (2) estimate was made from a few European soils in the laboratory tested at a single temperature. Field determinations were in fact made with variable temperature but only for five soils, and all these soils were from the vicinity of Mainz. The validity of using Mainz soils classified as an eolian sand, a clay, a brown soil, a loess loam, and a chernosol—a categorization unacceptable to any modern soil scientist—to represent the universe of soils is left to the reader to decide.

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References
3. G. W. Bartholomew and M. Alexander, unpublished data.
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