

# Emission of Carbon Monoxide by Vegetation and Soils

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## A literature review and recommendations for STOCHEM

### 1. Introduction

Carbon monoxide (CO) is one of the most important reactive trace gases in the troposphere. Using a global burden of 370 Tg (Warneck, 1999) and a global source of 2780 Tg y<sup>-1</sup> (see section 2), the residence time for CO in the troposphere is about 50 days. It does not absorb enough infrared radiation to be classified as a greenhouse gas, but may affect concentrations of other greenhouse gases such as methane via its effect on levels of the hydroxyl radical (OH), because reaction with CO is the major sink for the hydroxyl radical. It is estimated that emitting 100 Tg of CO (1 Tg = 10<sup>12</sup> g) has the same overall radiative forcing perturbation as emitting 5 Tg of methane (Wild and Prather, 2000). The perturbation to the methane levels lasts 12 years, and ozone levels would also increase (IPCC, 2001). Over half of the current CO emissions originate from anthropogenic activities, and the northern hemispheric burden is roughly twice that of the southern hemisphere. Despite many evaluations of the global carbon monoxide budget, its global burden is less certain than those of methane and nitrous oxide (IPCC, 2001).

### 2. Sources of Carbon Monoxide

Carbon monoxide has both anthropogenic and natural sources, and the sum of these emissions is estimated as 2780 Tg y<sup>-1</sup> (IPCC, 2001). Anthropogenic sources, principally the burning of fossil fuels and biomass, amount to about 1350 Tg y<sup>-1</sup> (IPCC, 2001). CO is generally emitted directly by these processes, although the total figure includes production from the oxidation of hydrocarbons. In contrast, the natural sources of CO are more indirect, as most of the CO attributed to natural sources comes from hydrocarbon oxidation. The principal sources include the oxidation of methane emitted from wetlands and ruminants, and the oxidation of higher hydrocarbons such as isoprene (C<sub>5</sub>H<sub>8</sub>) and terpenes which are emitted by vegetation. However, CO is emitted directly from the oceans, vegetation and soils. Natural CO sources are thought to contribute about 800 Tg y<sup>-1</sup> (IPCC, 2001) to the total CO source. In this report, the literature describing the direct emission of CO by vegetation and soils will be reviewed, and recommendations of the magnitudes of these sources for use in STOCHEM will be given.

#### 2.1 Direct Emission of Carbon Monoxide by Vegetation

The direct emission of CO by living green plants when exposed to sunlight was first reported by Wilks (1959). Since then, there have been several laboratory studies on the photo-production of CO (Seiler and Conrad, 1987, and references therein; Warneck, 1999, and references therein; Tarr et al., 1995). The emission of CO from living plants increases linearly with solar actinic irradiance (Fischer and Lüttge, 1978), even up to 800 W m<sup>-2</sup>, where net photosynthesis is inhibited (Warneck, 1999). The source of the CO is probably direct photooxidation of the plant material followed by transport to the stomata, as opposed to photolysis of a gas-phase compound, although the exact mechanism is not known (Tarr et al., 1995). The CO fluxes from laboratory studies on irradiated plant leaves are summarised in Table 1. Despite the different species studied,

the fluxes are of the same magnitude. Tarr et al. (1995) reported a mean emission of  $2.3 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  for an irradiance of  $650 \text{ W m}^{-2}$ . Assuming the flux is linearly proportional to the irradiance, it was reduced to an irradiance of  $50 \text{ W m}^{-2}$  for comparison with the other data.

Table 1. Laboratory measurements of the photoproduction of CO by plants.

| Reference                 | CO flux / $10^9$ molecules $\text{cm}^{-2} \text{s}^{-1}$ |
|---------------------------|---|
| Fischer and Lüttge (1978) | 2.6   |
| Seiler et al. (1978)      | 6.45  |
| Bauer et al. (1979)       | 94.6 <sup>a</sup>   |
| Tarr et al. (1995)        | 1.8   |

<sup>a</sup>Production at noon; irradiance not given.

Using the flux of CO from plant leaves measured by Seiler et al. (1978), Seiler and Conrad (1987) and Warneck (1999) both estimated the global emission flux to be  $75 \pm 25 \text{ Tg y}^{-1}$ , although no details on the method used to calculate this value are given by either authors. Bauer et al. (1979; cited by Logan et al., 1981) used estimates of leaf surface areas and light intensities to calculate a similar global emission flux of  $70 \text{ Tg y}^{-1}$ .

Tarr et al. (1995) found that dead and decaying plant matter also emitted carbon monoxide when exposed to sunlight, at significantly greater rates than living tissue. Combining their experimental results with estimates of sunlight intensity, length of day and dry season, leaf area index and areas covered by vegetation, they estimated that dead plant material in savannah regions could emit between 30 and 60  $\text{Tg CO y}^{-1}$ . More recent data on this phenomenon have been reported by Schade et al. (1999) from both laboratory and field measurements. These authors discovered a thermal source of CO from litter on the soil surface in addition to the photochemical source. In agreement with the findings of Tarr et al. (1995), Schade et al. (1999) found that UV radiation (330 - 400 nm) was the most effective in producing CO. Using data from the field measurements of Schade et al. (1999) and estimates of areas of various ecosystems, Schade and Crutzen (1999) estimated that  $60 \pm 30 \text{ Tg CO y}^{-1}$  are emitted globally from the photochemical degradation of decaying plant material. An additional flux of  $40 \text{ Tg y}^{-1}$  was calculated for thermal emissions from the litter on the surface of the soil, although Schade and Crutzen (1999) state that this value has an error of a factor of 2. Overall, Schade and Crutzen (1999) estimate the total source of CO from dead and decaying plant material to be 60 - 90  $\text{Tg y}^{-1}$ .

Other estimates of the global source of CO from vegetation have been made more indirectly. Logan et al. (1981) used a global model to estimate the magnitude of the various CO sources. They calculated a direct vegetative source of  $130 \text{ Tg y}^{-1}$ , with the possible range being 50 - 200  $\text{Tg y}^{-1}$ . Crutzen (1983; cited by Seiler and Conrad, 1987) calculated a range of 20 - 200  $\text{Tg y}^{-1}$  from a modelling study. Lelieveld and van Dorland (1995) used measurements of CO concentrations and a model describing losses by reaction with the hydroxyl radical, advection and dry deposition to calculate the CO emissions required to balance the losses. From this study, they calculated a source of 100  $\text{Tg y}^{-1}$  from vegetation. The estimates of direct global emissions of CO from plants reported in the literature are summarised in Table 2.

Table 2. Estimates of global photoproduction fluxes of CO by vegetation.

| Reference                                | Magnitude / Tg y <sup>-1</sup> |
|--|--------------------------------|
| IPCC (2001)                              | 150                            |
| Lelieveld and Dentener (2000)            | 115 <sup>a</sup>               |
| Marufu et al. (2000)                     | 74.6 <sup>a</sup>              |
| Schade and Crutzen (1999)                | ~ 100 <sup>b</sup>             |
| Seiler and Conrad (1987); Warneck (1999) | 75 ± 25 <sup>c</sup>           |
| Lelieveld and van Dorland (1995)         | 100                            |
| Müller (1992)                            | 165 <sup>d</sup>               |
| Hough (1991)                             | 75 <sup>c</sup>                |
| Khalil and Rasmussen (1990)              | 100                            |
| Crutzen (1983)                           | 20 - 200                       |
| Logan et al. (1981)                      | 130 (50 - 200)                 |
| Bauer et al. (1979)                      | 70 <sup>c</sup>                |

<sup>a</sup>Vegetation and Soils

<sup>b</sup>Flux from dead and decaying vegetation only

<sup>c</sup>From live vegetation only.

<sup>d</sup>Sum of animal, microbial and foliage emissions.

## 2.2 Emission of Carbon Monoxide by Soils

In this section, the direct production of carbon monoxide by soils is discussed. This source is distinct from the thermal production in leaf litter described in the previous section. In a study of natural emissions of trace gases from North America, Guenther et al. (2000) concluded that any CO produced in the soil would be oxidised by other organisms and so no net emission would occur. In the GIM/IGAC intercomparison of modelled tropospheric CO distributions (Kanakidou et al. (1999) and references therein), none of the three-dimensional models used included emission of CO from soils. In a study of land-use changes, King (2000) found that land used for crop production had a reduced soil organic content and an increased consumption of CO compared to undisturbed land (e.g. pine forest). Hence, no emission of CO from arable land is expected.

Tropical savannah soils appear to be net emitters of carbon monoxide. Sanhueza et al. (1994) performed a study of CO emissions in the savannah regions of Venezuela. They found that these soils were net CO emitters during the day, and sinks at night. Ploughed soils were net sinks, as the daytime emission was greatly reduced compared to the unperturbed areas. An earlier study by Scharffe et al. (1990) in the Guyana Shield of Venezuela found that the savannah soils were net CO emitters, whereas a nearby deciduous forest was a sink. Conrad and Seiler (1985) studied CO production in soils in the Transvaal region (again savannah) of South Africa, and found that the soil was a net source of CO when the soil temperature exceeded 30 - 40 °C, but was a net sink for atmospheric CO at other times. The CO emissions were strongly dependent on the organic content of the soil, and the soil temperature.

Wetlands have also been reported to be sources of carbon monoxide. Moxley and Smith (1998) found that peatlands in Scotland emitted CO during the wetter months of the

year. Using their data and the global area of bogs estimated by Matthews and Fung (1987),  $2.9 \times 10^{12} \text{ m}^2$ , they estimated a global CO emission of just  $0.2 \text{ Tg y}^{-1}$ . Funk et al. (1994) studied the influence of the height of the water table on emissions of trace gases from Alaskan wetland cores in a laboratory, and found that the cores were net CO emitters providing the water table was maintained at a high level. Using their observed emission rates ( $1 - 2 \text{ mg CO m}^{-2} \text{ d}^{-1}$ ), a given growing season of 130 days, and the same area of wetlands used by Moxley and Smith (1998), a global CO emission of  $0.38 - 0.76 \text{ Tg y}^{-1}$  may be estimated. Although these estimates are highly uncertain, they indicate that emission of CO by wetland soils is very small.

The emission of carbon monoxide from rice paddies has been measured by Conrad et al. (1988). Using observed ratios of emitted CO and CH<sub>4</sub>, and estimates of methane emissions by rice paddies, these authors calculated an upper limit for the CO emission of  $0.24 \text{ Tg y}^{-1}$ . This flux is very small, and, like natural wetlands, indicates that CO emissions from rice paddies are unimportant.

Zepp et al. (1997) found that burned forest sites in Canada were emitters of CO, whereas the unburned sites were sinks. Using their measured emission fluxes and areas of burned forest areas for the 1990s, Zepp et al. (1997) estimated a source of  $0.65 \text{ Tg y}^{-1}$ , but a sink of  $3.9 \text{ Tg y}^{-1}$  for the unburned forests. Hence the forests remain a sink for CO, but some localised changes from sink to source after burning are possible.

Conrad and Seiler (1985) estimated that the global CO flux from soils lies between  $2.9$  and  $32.1 \text{ Tg y}^{-1}$ . However, the global soil sink for CO is considerably larger, and they concluded that soils should be a net sink for CO. Seiler and Conrad (1987) reviewed the available data and concluded that dry soils in tropical regions would be sources of CO, but humid tropical regions and temperate zones would be sinks. Using the global soil CO source of Conrad and Seiler (1985), they estimated that  $10 \pm 9 \text{ Tg y}^{-1}$  were produced in hot dry tropical regions. More recently, Potter et al. (1996) used a gridded dataset of soil carbon contents, and an assumed CO production rate to estimate a global source of just  $10 \text{ Tg y}^{-1}$  from soils.

### 3. Recommendations for STOCHEM

The production of carbon monoxide from plants and soils only makes a small contribution to the global CO budget. Using the highest estimates of thermal and photoproduction of CO from plants ( $60$  and  $190 \text{ Tg CO y}^{-1}$  respectively), an upper limit of about  $250 \text{ Tg CO y}^{-1}$  may be placed on this source. This value is about 9 % of the overall global CO source. However, the majority of the photoproduction is expected to occur in tropical regions, where sunlight intensities are high, plants are abundant, and the growing seasons are long. Seiler and Conrad (1987) calculated that, of their global estimate of  $75 \pm 25 \text{ Tg y}^{-1}$  CO from living plants, 80 % of this flux ( $60 \pm 20 \text{ Tg y}^{-1}$ ) was emitted in tropical regions. Although a lack of measurements makes this value uncertain, the photoproduction of CO by plants in tropical areas is not negligible, and needs to be included in chemistry models.

The data of Tarr et al. (1995) and Schade et al. (1999) indicate that production of CO (both photolytically and thermally) from dead and decaying plant material is also important. Using the photoproduction flux of CO from living plants of  $75 \text{ Tg y}^{-1}$  (Seiler

and Conrad, 1987) and a flux from dead plant material of  $60 \text{ Tg y}^{-1}$  (Schade and Crutzen, 1999), a total source of about  $130 \text{ Tg y}^{-1}$  from standing plant material seems reasonable. Adding a small additional thermal source of CO from plant litter on the soil surface, a total global source of  $150 - 170 \text{ Tg CO y}^{-1}$  may be estimated. These findings support the value of  $150 \text{ Tg y}^{-1}$  listed by the IPCC (2001), and it is recommended that this value is used in the STOCHEM model.

There have only been a small number of studies on the emission of carbon monoxide by soils. These studies indicate that some tropical soils (savannah) and wetlands (both natural and rice paddies) are sources of CO for at least part of the year. However, such emissions are very small compared to the global CO source of  $2780 \text{ Tg y}^{-1}$  (IPCC, 2001). From the data presented in section 2.2, the global emission of CO from soils appears to be of the order of  $20 \text{ Tg y}^{-1}$ , and distributed over a large surface area. Estimates of the soil sink of CO are also uncertain ( $240 - 650 \text{ Tg y}^{-1}$ ; IPCC, 2001), but are considerably larger than the soil sources. Given the scarcity of measurements of carbon monoxide emission by soils, the small global source, and the fact that the soil sink is much larger, it is recommended that a parameterisation of soil emissions of CO should not be added to the STOCHEM model.

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