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Processes controlling the ^{14}C content of soil carbon dioxide: Model development

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Carbon-14 dates from soil carbonates have been considered unreliable estimates of the age of pedogenesis because of unknown initial $^{14}C/^{12}C$ ratios in the carbonate and the possibility of subsequent contamination with environmental ^{14}C. Comparison of carbonate ^{14}C ages with ^{14}C ages of coexisting organic matter suggests that radiocarbon dates calculated from pedogenic carbonate in arid areas were ~500–7000 radiocarbon years too old. On the other hand, radiocarbon dates of pedogenic carbonate from the sub-humid part of southeastern Australia were much younger than either the known age of deposition in which the carbonate was segregated, or the likely age of pedogenesis. These discrepancies have been attributed to an initial low ^{14}C content of soil carbonate due to the "limestone dilution" effect and/or secondary contamination by environmental ^{14}C. The "limestone dilution" effect states that soil carbonate derives half of its C from "dead" calcium carbonate and another half from atmospheric CO_2, suggesting that radiocarbon age of such carbonate would be about one half-life of ^{14}C (~5570 yr) older than the true age. However, studies on soil CO_2 and $\delta^{13}C$ of soil CO_2 and pedogenic carbonates indicate that the CO_2 and its isotopic species in a soil system are in isotopic equilibrium. This implies that the ^{14}C content of pedogenic carbonate should be determined by ^{14}C content of soil CO_2 and inherited "dead carbon" should not affect the age of soil pedogenic carbonate.

We present here a diffusion-reaction model that analyzes the $^{14}CO_2$ distribution in soils. Carbon dioxide is produced in soils by biological processes and is transported to the atmosphere by diffusion. The diffusion mechanism applies to its isotopic species $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ as well. Different isotopic species of CO_2 react and diffuse independently of each other according their own concentration gradient and their own sources and sinks. Since the concentration of $^{14}CO_2$ in a soil profile is controlled by the production and decay of $^{14}CO_2$, and by diffusion through the soil to the atmosphere, the concentration of $^{14}CO_2$ can be described by a diffusion-reaction equation:

$$\frac{\partial C_s^{14}}{\partial t} = D_s^{14}\frac{\partial^2 C_s^{14}}{\partial z^2} + \Phi_s^{14} - \lambda C_s^{14} \qquad (1)$$

where C_s^{14} represents the $^{14}CO_2$ concentration in the soil air (mol cm^{-3}); D_s^{14} is the diffusion coefficient of $^{14}CO_2$ in the soil (cm^2 s^{-1}); Φ_s^{14} is the production of $^{14}CO_2$ in the soil (mol cm^{-3} s^{-1}); and λ the decay constant of ^{14}C ($3.84 \cdot 10^{-12}$ s^{-1}). To model $^{14}CO_2$, information is needed regarding the production of $^{14}CO_2$ (Φ_s^{14}) in a soil. With the simplified assumption that soil CO_2 is primarily produced (a) by root respiration with practically no dif-

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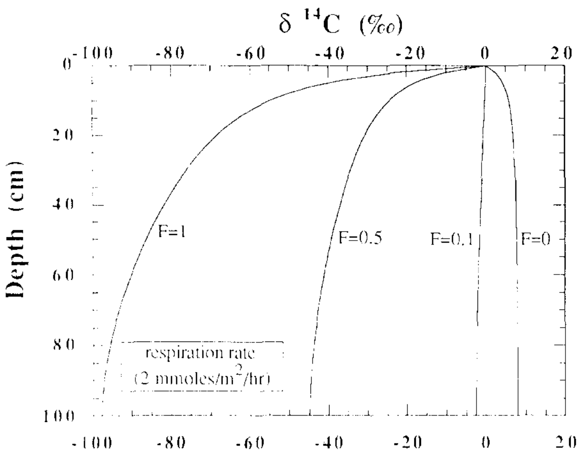

Fig. 1. $\delta^{14}C$ value of soil CO_2 vs. depth for a model soil. *F* is relative contribution of CO_2 from organic matter decomposition. It shows that the $\delta^{14}C$ values of soil CO_2 vary with depth from the (pre-atomic bomb) atmospheric value at the soil–atmosphere interface to more negative or more positive values at depth depending on the value of *F*.

ference in ^{14}C from atmospheric CO_2, and (b) by decomposition of soil organic matter with the same ^{14}C content as decomposing organic matter, $^{14}CO_2$ ($\delta^{14}C$) profiles in soils can be calculated for various conditions. Fig. 1 shows how the $\delta^{14}C$ value of soil CO_2 varies with depth in a model soil where the $^{14}CO_2$ concentration is diffusion controlled. The parameters for the model soil are listed in Table 1.

Our model shows that the ^{14}C content of soil CO_2 is not the same as that of atmospheric CO_2 and varies with depth depending on various factors. The most important factors affecting the ^{14}C content of soil CO_2 include the ^{14}C content of soil organic matter, the relative contribution of root respired CO_2 to total CO_2 production, soil respiration rate, atmospheric CO_2 concentration and $^{14}CO_2$ content, soil properties, temperature, etc. Our model suggests that soil CO_2 could be enriched in ^{14}C relative to atmospheric CO_2 when soil CO_2 is derived from root respiration and/or decomposition of short-lived organic matter which has the same ^{14}C content as atmospheric CO_2. On the other hand, soil CO_2 could be depleted in ^{14}C relative to atmospheric CO_2 if decomposition of older organic matter contributes to the soil CO_2 production. Therefore, the ^{14}C dates of soil carbonate could be younger or older than the true ages of pedogenesis. However with appropriate evaluation of different factors affecting $^{14}CO_2$ distribution in soils, the ^{14}C content of soil carbonate could lead to reliable dates of pedogenesis.

TABLE 1

Parameters for the model soil described in the text

$\delta^{14}C_{o.m.}$	−10	−50	−100	−150	−200	−225	−250	−275	−300	−325
Depth (cm)	10	40	60	80	100	120	140	160	180	200

$\delta^{14}C_{o.m.}$ = 1.1176 − 1.7317*depth; temperature = 15°C; pressure = 1 atm; respired CO_2: $\delta^{13}C$ = −26‰; atmospheric CO_2: 300 ppm, $\delta^{13}C$ = −6‰; porosity = 0.5; tortuosity factor = 0.61.