matters arising

The interpretation of tree-ring $\delta^{13}C$ records

RECENTLY Farmer[1] reported on the decline of $\delta^{13}C$ in the tree rings of the American elm from 1883 to 1933 and generally supports the net biospheric CO_2 release theory due to the so-called pioneer agricultural expansion of the late nineteenth century. Other data from various parts of the Northern Hemisphere show a similar decline in the $^{13}C/^{12}C$ ratio in tree rings[2-5]. However, the tree-ring records produced after 1930 are less uniform in trend, with the American elm indicating a dramatic increase in $\delta^{13}C$ from 1930 to 1970. Several explanations of this increasing trend have been put forward, including a cessation of the net biospheric CO_2 flux; but as Farmer notes, more complicated interactions may be at work. I wish to point out that these investigations have ignored the shift in the fossil fuel consumption pattern of coal, petroleum and natural gas during the period 1850–1970 which may have a significant effect on atmospheric $\delta^{13}C$.

From data presented by Stuiver[4] and Wedepohl and Althaus[6], I have taken $\delta^{13}C$ fossil fuel values of −24.5‰ (coal), −28.5‰ (oil) and −41.5‰ (gas) and multiplied the appropriate $^{13}C/^{12}C$ ratios by the per cent production estimates provided by Rotty[7] for 1950–74 and Dorf[8] for pre-1950 data. The result of this calculation, an estimate for the $\delta^{13}C$ of fossil fuel produced CO_2 as a time function which appears in Fig. 1, is to modify the equation for computing the change in atmospheric $\delta^{13}C$ caused by fossil fuel CO_2 used by Stuiver[4] and Farmer[1] from

$$\Delta(\delta^{13}C) = 0.18S \qquad (1)$$

to

$$\Delta(\delta^{13}C) = (\gamma/100)S \qquad (2)$$

where γ takes the values of Fig. 1 less 7 (the per mil atmospheric $\delta^{13}C$) and S is the per cent ^{14}C change.

Equation (1) is a good approximation for the $\delta^{13}C$ change before 1930; however, by 1970, when the fossil fuel $\delta^{13}C$ declines to −29 per mil, a 22% error is incurred by not using equation (2). Note that this error amplifies the unexplained upward trend of the tree-ring data after correction for the fossil fuel CO_2 atmospheric input. Although the $\delta^{13}C$ upward trend (Fig. 1*c* of ref. 1) may be correlated with a local[1], and perhaps global[9], temperature decrease during the post-1930 period, this effect may also be interactive. The biospheric CO_2 input of 120 BMT (10^9 metric tonnes = 1 BMT) computed by Stuiver[4] and Wilson[5], if sufficiently concentrated around the year 1900, could cause a temperature effect of the magnitude and timing noted in the global records for the Northern Hemisphere[9].

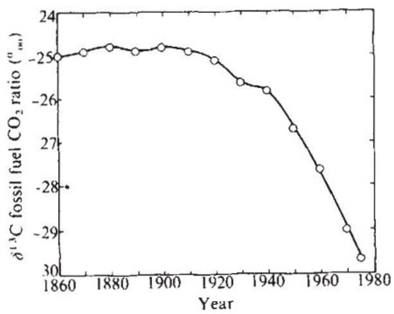

Fig. 1 Estimate of ^{13}C content of combusted fossil fuels with respect to their historical use pattern. The change in relative deficiency beginning in the early part of this century and continuing to the present indicates the shift from coal to petroleum and later to natural gas. This curve resolves part of the deficiency in ^{13}C in tree-ring data due to fossil fuel combustion.

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FARMER REPLIES—The insertion of a varying $\delta^{13}C$ of fossil fuel CO_2 (Fig. 1) in equation (2), as proposed by Mulholland, would alter the estimated decline in atmospheric $\delta^{13}C$ due to fossil fuel CO_2 input (Fig. 1*b* of ref. 1) by 0.01‰ from 0.28‰ to 0.29‰ by 1940, 0.03‰ from 0.35‰ to 0.38‰ by 1950 and 0.07‰ from 0.47‰ to 0.54‰ by 1960. These alterations are insignificant in the context of correcting the observed tree-ring $\delta^{13}C$ variations for the effects of fossil fuel CO_2 input on atmospheric $\delta^{13}C$ (Fig. 1*a*, *c* of ref. 1) and suggest that the use of 18 for γ is a good approximation to at least 1950.

Although the alteration would be more marked by 1970, amounting to a change of 0.16‰ from 0.70‰ to 0.86‰, the net result of all such alterations, as Mulholland observes, would in any case be the enhancement of the upward trend since 1933 of the fossil-fuel CO_2 corrected $\delta^{13}C$ curve for the American elm (Fig. 1*c* of ref. 1). Thus the apparent 'fossil-fuel CO_2 corrected' $\delta^{13}C$–atmospheric temperature correlation for the elm post-1933 remains. The need for investigation of tree-ring $^{13}C/^{12}C$ ratios before the onset of major anthropogenic activity, to aid resolution of perturbatory parameters since 1850, is re-emphasised.

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Oxidation–reduction potentials of haem proteins

STELLWAGEN[1] has compared oxidation–reduction potentials of seven haem proteins with respect to parameters of haem accessibility and polarity of the haem crevice calculated on the basis of known three-dimensional structures.

One point, however, has been overlooked. Kassner[2] presented a model not for estimation of whole E'_0, but only for an increment of E'_0 (assigned as $\Delta E'_0$) which must be added to the E'_0 value of the cytochrome *c* model system to obtain values which correspond better to the experimental ones. Kassner's equation for $\Delta E'_0$ expresses the fact that greater thickness and apolarity of the haem apolar environment leads to higher values of the increment $\Delta E'_0$.

The values of $\Delta E'_0$ should then be added to E'_0 for haem protein models. For the

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