Tellus (1987), *39B*, 140–154

Biospheric CO_2 emissions during the past 200 years reconstructed by deconvolution of ice core data

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(Manuscript received August 8; in final form August 21, 1986)

ABSTRACT

Measurements on air trapped in old polar ice have revealed that the pre-industrial atmosphere contained 280 ppm of CO_2 and that $\delta^{13}C$ of atmospheric CO_2 decreased by about 1.1‰ until 1980. These measurements show that considerable amounts of non-fossil CO_2 must have already been emitted into the atmosphere in the 19th century. Quantitative estimates of the emission rates were performed by deconvolving the CO_2 and $\delta^{13}C$ records, using models of the global carbon cycle (box-diffusion and outcrop-diffusion ocean, four-box biosphere). Depending on the structure of the ocean submodel, deconvolution of the CO_2 record yields a cumulative non-fossil production of about 90 to 150 Gt C until 1980, of which more than 50% were released prior to 1900. According to the model results, the net non-fossil production rate was roughly constant in the 19th and the first part of the 20th century. In the past 30 years, smaller values are obtained (0–0.9 Gt C yr^{-1}) which are at the lower limit or below current ecological estimates for deforestation and land use (1.6 ± 0.8 Gt C yr^{-1}). The difference might possibly be due to other sinks, e.g., stimulation of plant productivity by the enhanced CO_2 concentration. Calculated ^{13}C and ^{14}C time histories agree well with the observed changes. While the change of the atmospheric CO_2 concentration reflects more the cumulative carbon release, the isotope concentrations are more sensitive to short-term changes of the emission rate. The reason is that the oceanic uptake capacity is smaller for excess CO_2 by the buffer factor of ~ 10 than for an isotopic perturbation.

1. Introduction

For a long time, the pre-industrial atmospheric CO_2 concentration was not well-known and was the subject of many discussions. Through analyses of air trapped in old polar ice, it has become possible to reconstruct this concentration. Measurements carried out in Bern by means of 2 independent analytical methods, infrared laser absorption spectroscopy and gas chromatography, indicate that its pre-industrial (i.e., before about 1800) value must have been near 280 ppm. This is clearly lower than expected from carbon cycle model calculations that are based on the assumption that the atmospheric increase is due only to fossil CO_2 input; these calculations require a starting concentration of 294 to 298 ppm if the Mauna Loa CO_2 observations since 1958 (Keeling et al., 1976) are to be correctly simulated. The data obtained on an ice core from Siple Station, Antarctica (Neftel et al., 1985; Friedli et al., 1986), indicate a significant increase in the 19th century (Fig. 1), before fossil fuel consumption became a significant source. These results show that presumably large amounts of non-fossil CO_2 were released to the atmosphere in the past 200 years, probably because of deforestation and land use.

In order to get quantitative estimates of the magnitude of the non-fossil sources, we have calculated total CO_2 production rates (including fossil and net biospheric sources) for the measured atmospheric CO_2 concentration history. This can be done by solving the following equation, representing the atmospheric carbon balance, for the unknown total production rate $p_{tot}(t)$:

$$\frac{dN_a}{dt} = p_{tot}(t) - A_s F_{as}(t). \quad (1)$$

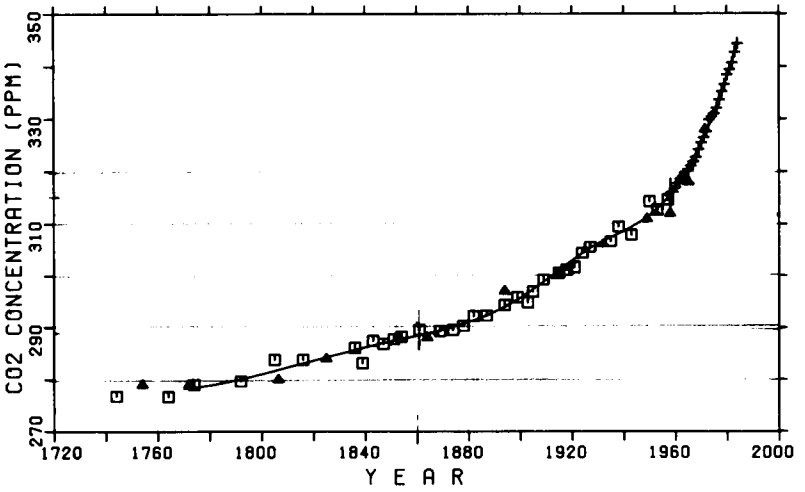

Fig. 1. Atmospheric CO_2 increase in the past 200 years as indicated by measurements on air trapped in old ice from Siple Station, Antarctica, measured by infra-red laser spectroscopy (full triangles; Neftel et al., 1985) and by gas chromatography (open squares; Friedli et al., 1986), and by the annual mean values from Mauna Loa Observatory (crosses; C. D. Keeling, personal communication). The full line is a spline fit through all data.

Here, N_a is the atmospheric CO_2 mass (proportional to concentration), A_s the surface area of the ocean and F_{as} the net CO_2 flux/m^2 from the atmosphere to the ocean; we assume that all excess CO_2 goes either into atmosphere, ocean or land biosphere. A possible additional CO_2 uptake by part of the biosphere is included in the net production term, $p_{tot}(t)$. Eq. (1) can re rewritten as

$$p_{tot}(t) = \frac{dN_a}{dt} + A_s F_{as}(t). \quad (2)$$

The flux to the ocean must be calculated by means of a suited carbon cycle model; in this study, we use the box-diffusion model (Oeschger et al., 1975) and its extension, the outcrop-diffusion model (Siegenthaler, 1983). The model determines F_{as} from the prescribed atmospheric and the calculated mixed-layer CO_2 concentrations. The net biospheric—or more precisely non-fossil—flux is calculated by subtracting from $p_{tot}(t)$ the relatively well known fossil CO_2 emission rate (Rotty and Marland, 1984).

In addition to the CO_2 concentration, the $\delta^{13}C$ value of CO_2 has also been measured on air trapped in the Siple ice core (Friedli et al., 1986). The atmospheric ^{14}C trend is known thanks to tree-ring measurements. This permits us to check whether the different records—concentration and isotopic composition—are consistent within the boundaries given by the carbon cycle models. Concentration, ^{13}C and ^{14}C histories contain different pieces of information. The flux of excess CO_2 into the ocean depends on chemical re-equilibration of seawater, which does not affect isotopic perturbations. The $^{14}C/C$ ratio in the atmosphere decreased until bomb tests produced large amounts of ^{14}C, because fossil carbon contains no ^{14}C. The $^{13}C/^{12}C$ ratio has responded to the input of fossil *and* of biospheric CO_2 that both have considerably lower $\delta^{13}C$ values ($\sim -25‰$) than atmospheric CO_2 ($\sim -7‰$). We will also discuss the sensitivity of the model results to uncertainties in the ice core data, to different model assumptions and to the (unlikely) possibility that the non-fossil CO_2 was not of biospheric, but rather of marine origin. The latter question can in principle be studied by means of a combined concentration—carbon-13 record, since biospheric carbon has low $\delta^{13}C$, while CO_2 evading from the ocean has a value near that of atmospheric carbon dioxide.

Similar deconvolution studies have been carried out based on tree-ring $\delta^{13}C$ data. I. G. Enting (private communication) has also deconvolved the ice core CO_2 data of Neftel et al. (1985) using a mathematical technique somewhat different from ours.

2. Input data and models

The concentration results from the Siple ice core plus the Mauna Loa record (C. D. Keeling, personal communication), smoothed by a spline fit (solid line in Fig. 1), are assumed to represent the global mean concentration history and used as input data to the model. This is possible because the Siple data overlap with those of Mauna Loa. For this study, we assume that the ice core data reflect the atmospheric increase in a representative way. Although the results will have to be confirmed by measurements on other ice cores and by other laboratories, the Siple record appears to be reliable; this is indicated by the excellent quality of the ice core (Stauffer and Schwander, 1984), by the agreement between the 2 analytical methods used, by good time resolution and the small scatter of the results and by the good agreement of the average pre-1800 concentration (278 $\pm$ 3 ppm) with the mean value from measurements on air trapped in South Pole ice samples, dating from ~800 to 1600 AD (283 $\pm$ 2 ppm) (Stauffer and Oeschger, 1985). The possible error of the absolute concentration values is estimated to 3 ppm, that of the mean gas age of the Siple samples to 10 years (B. Stauffer, personal communication).

Raynaud and Barnola (1985) have also reported ice core CO_2 results documenting the atmospheric increase. They obtained a lower pre-industrial value (260 to 270 ppm). The reason for the difference is not yet fully clear. Possibly, the extraction method of Barnola et al. may have led to low values (J. M. Barnola, personal communication). Pearman et al. (1986) also analysed an Antarctic ice core and found a mean value of 281 $\pm$ 7 ppm for the period 1600–1800, in good agreement with the results of the Bern laboratory.

The ice core data can be compared with direct measurements of the atmospheric CO_2 concentration made by a number of investigators towards the end of the 19th century. From an analysis of these data, Callendar (1958) proposed a value of 290 ppm for the turn of the century, while the high-quality data of a French group, Müntz and Aubin, indicate a probable mean value of 285–290 ppm around 1880 (Siegenthaler, 1984). These figures are in reasonable agreement with the Siple data (~291 ppm for 1880, 296 ppm for 1900).

The carbon cycle model used (Fig. 2) consists of 3 main reservoirs. The atmosphere is considered as well-mixed. The model ocean is divided into a surface mixed layer (75 m deep) and a diffusive deep sea (constant vertical eddy

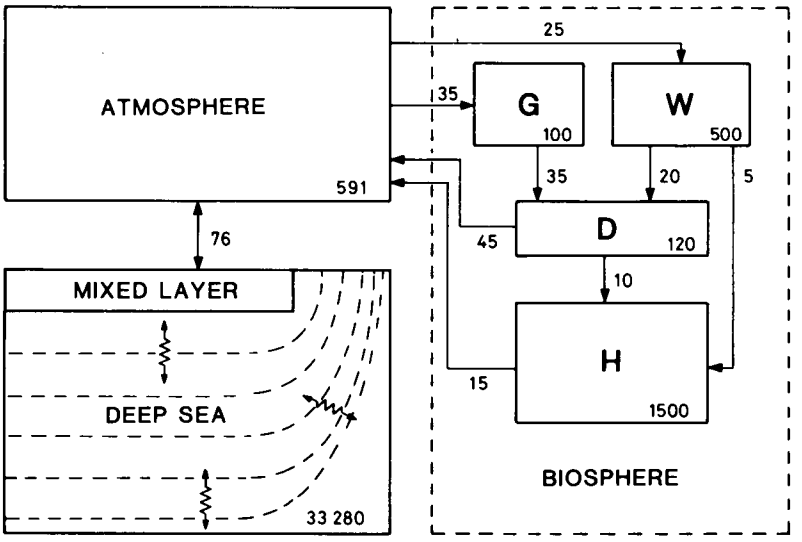

Fig. 2. Model of the global carbon cycle. Pre-industrial reservoir sizes and fluxes are given in Gt C and Gt C yr^{-1}. Meaning of symbols for biospheric carbon pools: G: ground vegetation plus nonwoody parts of trees; W: wood; D: detritus; H: soils.

diffusivity) without or with a high-latitude outcrop of deep water (box-diffusion (BD) or outcrop-diffusion (OD) model, respectively); see Oeschger et al. (1975) and Siegenthaler (1983) for a detailed discussion. The outcrop, permitting a direct ventilation of the deep sea in high latitudes, covers 10% of the whole ocean surface, and the gas exchange rate there is assumed to be higher by a factor 1.7 than for the rest of the ocean, as has been estimated by Siegenthaler (1986) from radon gas exchange data of Peng et al. (1979). The dynamic ocean model parameters—the gas exchange rate (or the corresponding atmosphere-ocean exchange coefficient, k_{as}) and the eddy diffusion coefficient K—can be determined from the distribution of radioisotopes. The best available analogue for the invasion of anthropogenic CO_2 into the ocean is the penetration of bomb-produced ^{14}C, since in temperate and low latitudes, both are governed by processes in the upper 1000 m. For longer time scales, exchange with the lower layers also becomes important, and a calibration based on the distribution of natural ^{14}C in the entire ocean would be more appropriate, involving smaller eddy diffusivities in our models (and therefore less oceanic uptake of excess CO_2). For the oceanic buffer factor ξ that summarizes the chemical re-equilibration of seawater with respect to CO_2 variations, 2 different values are used for warm and cold surface water, and they vary with CO_2 partial pressure, pCO_2, as given by Bacastow (1981). The concentration of dissolved inorganic carbon, $\sum CO_2$, is assumed constant in the whole ocean at the observed average surface water value, because the particle flux from the surface to depth, which is responsible for larger $\sum CO_2$ values at depth, is not included in our perturbation model. The justification is that the particles do not contribute to the sequestering of excess CO_2. For the numerical calculations, the deep sea is subdivided into layers 25 m apart down to 1000 m and ~550 m apart below 1000 m; the total ocean depth is 3729 m.

These models are obviously a very simple representation of the real ocean. In our opinion, the 2 model versions, BD and OD, probably provide lower and upper limits for the oceanic CO_2 uptake. Correspondingly, the true net non-fossil CO_2 flux (biospheric source minus any possible non-oceanic sinks) should be in the range given by the BD and OD results.

For the isotopic perturbations, size and structure of the land biosphere are important. A more realistic biosphere submodel has been used here than in earlier versions of these models. It consists of 4 well-mixed compartments: ground vegetation plus leaves (G), wood (W), detritus (D) and soils (H, for humus). This structure is adapted from the model of Emanuel et al. (1984). Fig. 2 shows the initial steady-state compartment sizes and fluxes. Any biospheric carbon release (or net growth) is distributed evenly through all 4 compartments; correspondingly, all compartment sizes and fluxes vary in the same proportion in response to a perturbation. This model is still rather coarse, but since in this context only the isotopic exchange fluxes with the atmosphere are of interest, further refinements in the biosphere modelling would probably not influence our results in a significant way.

The model is written in terms of perturbation equations, i.e., only deviations from an assumed initial steady state are considered. This is of advantage for the numerical precision of the results, and especially for isotopic perturbations (where ratios of the varying amounts of 2 isotopic species are of interest) it allows a more direct insight into the terms governing the considered changes than a formulation involving total amounts and fluxes. In contrast to earlier studies (Oeschger et al., 1975; Siegenthaler, 1983) where linear approximations were used, the exact isotopic equations have now been worked out, following the procedure of Heimann (1978). This explains the slightly different values for the parameters k_{as} and K (Table 1) compared to the paper by Siegenthaler (1983). (Another reason is that a somewhat unsatisfactory correction for the increase of total CO_2 with ocean depth in the calculation of the stationary oceanic ^{14}C profile, eqs. (17, 18) of Siegenthaler (1983), has now been dropped.)

For $\delta^{13}C$, isotopic fractionation at the interfaces air-sea and atmosphere-biosphere is taken into account, with kinetic fractionation factors α_{ij} accompanying the gross CO_2 fluxes F_{ij} from reservoir i to reservoir j (Table 1). The value $\alpha_{as} = 0.9980$ for the air-to-sea transfer is that calculated by Siegenthaler and Münnich (1981) and confirmed by direct experiments of

Table 1. *Main model parameters and pre-industrial values*

Symbol	Meaning	Value	
		BD	OD
N_a	Atmospheric CO_2 mass (278.3 ppm)	591 Gt C	
N_b	Biospheric carbon mass	2220 Gt C	
$\sum CO_2$	Oceanic total CO_2 concentration	2.05 mol m^{-3}	
a_c	Relative area of outcrop	0	0.1
k_{as}	Exchange coefficient atmosphere-ocean	1/7.80 yr	1/8.21 yr
F_{as}	CO_2 exchange flux atmosphere-ocean (for $N_a = 591$ Gt C)	17.4 mol m^{-2} yr^{-1}	16.5 mol m^{-2} yr^{-1}
K	Eddy diffusivity	4350 m^2 yr^{-1}	7100 m^2 yr^{-1}
ξ_m	Buffer factor for warm surface (mixed layer)	~9	~9
ξ_c	Buffer factor for cold surface (outcrop)	–	~14
R_a	^{14}C concentration in atmosphere	1	1
R_m	^{14}C concentration in mixed layer	0.953	0.961
R_{oc}	Average ^{14}C concentration in ocean	0.888	0.895
R_b	Average ^{14}C concentration in biosphere	0.990	
	$^{13}C/^{12}C$ fractionation factors:		
α_{as}	atmosphere → ocean	0.9980	
α_{sa}	ocean → atmosphere	0.9897	
α_{ab}	atmosphere → biosphere	0.9819	
α_{ba}	biosphere → atmosphere	1	

BD: box-diffusion model, no outcrop; OD: outcrop-diffusion model. F_{as} and oceanic ^{14}C concentrations are for a pre-industrial CO_2 level of 278.3 ppm.

Wanninkhof (1985). The value used for α_{sa} is taken from a review by Mook (1986). $\delta^{13}C$ of fossil fuel as a function of time is taken from Tans (1981).

3. Results for non-fossil CO_2 emissions

From the smoothed Siple-Mauna Loa concentration history, production rates were calculated by solving eq. (2) by means of the carbon cycle models. Fig. 3 shows the results for the total production rate $p_{tot}(t)$ (solid line), using the box-diffusion (Fig. 3b) and the outcrop diffusion (Fig. 3c) models. For the sake of comparison, model runs were also made in which the atmospheric CO_2 concentration was calculated for a fossil CO_2 input only (dashed line in Fig. 3a). In this case, the production rate was prescribed and the concentration was calculated, using eq. (1); the pre-industrial concentration value was adjusted such that the value observed at Mauna Loa in 1959, 315.6 ppm, is correctly simulated. The fossil CO_2 emission rate p_f (short-dashed line) is taken from Rotty and Marland (1984), and the biospheric CO_2 release (long-dashed) is $p_{bio} = p_{tot} - p_f$. p_f exhibits year-to-year fluctuations which are also reflected in the calculated values for p_{bio}, since p_{bio} represents the difference between a smooth (p_{tot}) and a fluctuating (p_f) curve. For this reason, the curves for p_f and p_{bio} in Figs. 3 and 4 were smoothed by applying a 7-year running mean.

According to these results, the biospheric production rate was roughly constant in the 19th century with average values of ~0.5–0.8 Gt C yr^{-1}, that is much larger than the fossil input in that period. Qualitatively, this has to be expected from the fact that the ice-core CO_2 concentrations exhibit a significant increase before 1900, which would not be expected if fossil fuels were the only CO_2 source (Fig. 3a). In the 20th century, the release from the biosphere no longer increases, but decreases to about zero in the period 1959–1983 (= period of Mauna Loa observations) according to the BD model, while it is about 1 Gt/yr in this period according to the OD model (Table 2a). The CO_2 uptake by the ocean calculated by the OD model is larger than that calculated by the BD model because of direct ventilation of the deep sea through the outcrop

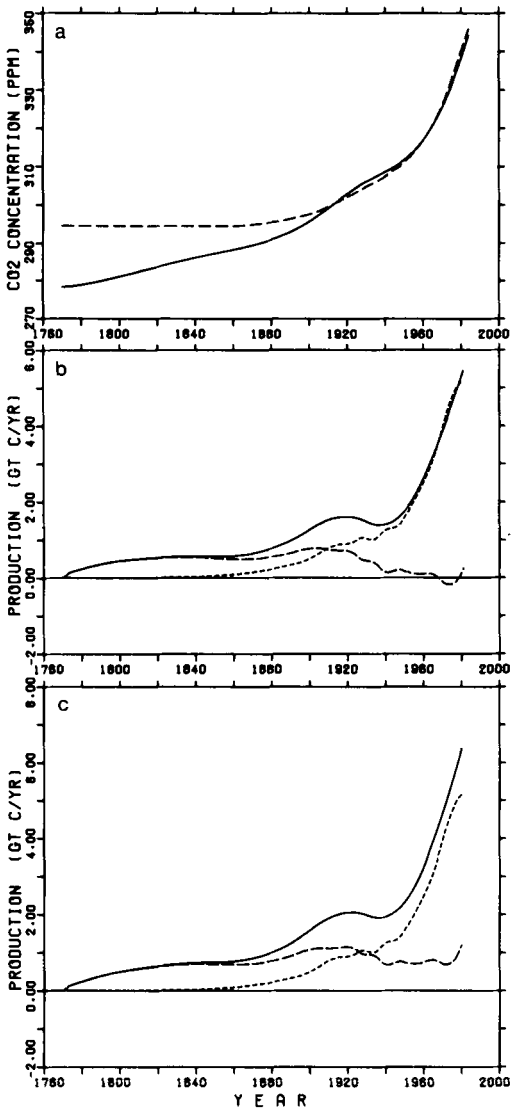

Fig. 3. (a) Observed atmospheric CO_2 concentration, *cf.* Fig. 1 (full line) and trend calculated by means of the box-diffusion model for fossil CO_2 input only (dashed line). (b) CO_2 production rates obtained by the deconvolution using the BD model. Solid line: total production; short-dashed: fossil; long dashed: biospheric production rate. (c) CO_2 production rates obtained using the OD model. Fossil and biospheric production rates shown in (b) and (c) represent 7-year running means.

area; this allows for a larger production rate than in the BD model, given the same atmospheric CO_2 history. According to the 2 models, the cumulative non-fossil production from 1770 (start of the calculations) to 1980 was 89 Gt C (BD) or 153 Gt C (OD), corresponding roughly to 50–100% of the cumulative fossil input (Table 2). Until 1900, the non-fossil input was 62 to 81 Gt C, compared to 12 Gt C of fossil carbon. Thus, more or at least as much biospheric CO_2 seems to have been released into the atmosphere in the 19th than so far in the 20th century.

The above results are affected by 3 kinds of possible errors. First, we assume that the pre-industrial atmospheric CO_2 concentration was constant and correspondingly that $p_{tot}(t)$ does not reflect any natural imbalance in the ocean-atmosphere exchange. The quoted CO_2 measurements on South Pole ice from the period 800 to 1600 AD (Stauffer and Oeschger, 1985) indicate that there were no major secular CO_2 fluctuations during that time, which supports this assumption; see also the discussion below in connection with the $\delta^{13}C$ changes. Second, the calculated net air-sea flux $F_{as}(t)$ in eq. (2) is subject to errors connected to uncertainties in the carbon cycle model. As mentioned above, we consider the model oceans with 10% outcrop area (OD) and without outcrop (BD) as limiting cases, and therefore the BD and OD model results for the biospheric production as lower and upper limits. Third, the input concentration data exhibit experimental errors. According to eq. (2), the calculated production rates depend on the time derivative of the atmospheric CO_2 concentration, which cannot be determined very precisely from the experimental data. Therefore, details of the structure of p_{tot} and p_{bio} in Fig. 3 are affected with uncertainty; they depend for instance on the choice of the method used for smoothing the original data, which is necessarily somewhat subjective.

The cumulative production is, from eq. (2):

$$P_{cum}(t) \equiv \int_{t_0}^{t} p_{tot}(t')\,dt' = N_a(t) - N_a(t_0) + A_s \int_{t_0}^{t} F_{as}(t')\,dt'. \quad (3)$$

P_{cum} depends on the absolute atmospheric concentration increase, which can be determined with better confidence from the ice core data than the time derivative. Thus, the cumulative input values are less dependent on errors of the input curve than the shape of the curves, $p_{tot}(t)$ and $p_{bio}(t)$ in Fig. 3.

Table 2. *Model results for CO_2*

(a) Production (in Gt C or Gt C yr^{-1}) obtained by deconvolution of CO_2 concentration history of Fig. 1 by means of box-diffusion (BD) and outcrop-diffusion (OD) model

	BD		OD	
	1900	1980	1900	1980
Cumulative production (Gt C):				
fossil (observed)	12	160	12	160
non-fossil	62	89	81	153
total	74	249	93	313
	BD		OD	
Average production rate, 1959–1983 (Gt C yr^{-1}):				
fossil (observed)	4.0		4.0	
non-fossil	0.0		0.9	

(b) Cumulative non-fossil production (in Gt C) obtained by deconvolution of shifted CO_2 concentration histories

	BD		OD	
	1900	1980	1900	1980
shifted by −6 ppm/−10 yr	77	121	100	195
shifted by +6 ppm/+10 yr	50	58	66	113

(c) Airborne fraction = ratio of atmospheric increase to total production in same period

	BD	OD
Deconvolution:		
1770–1980	0.510	0.405
1959–1983	0.581	0.479
Only fossil CO_2 input:		
1770–1980	0.612	0.519
1959–1983	0.625	0.533
Observed airborne fraction of *fossil* input:		
1959–1983	0.588	

In order to get a quantitative idea of the uncertainties, model runs were also carried out assuming lower and higher Siple CO_2 values. The input concentration histories were obtained by shifting the Siple data downwards or upwards by 6 ppm, and the gas ages back or forward by 10 years, respectively (in order to get a smooth transition to the unchanged Mauna Loa record) (Fig. 4a). The deconvolution results for these shifted records are shown in Fig. 4 which displays the biospheric release rate, $p_{bio}(t)$, for all model runs discussed. Fig. 4 thus gives the range of results that seem compatible with the Siple/Mauna Loa record and our carbon cycle model within the respective uncertainties. Inspection of Fig. 4 shows that a major difference between the results for p_{bio}, obtained from the unchanged and from the shifted ice core records, occurs in the period 1930–1970. The reason is that outside this period, the shape of the smoothed input concentration curves, and therefore dN_a/dt in eq. (2), are only slightly affected by the shift of the ice core data, while dN_a/dt is significantly affected by a shift between about 1930 and 1970, that is during the transition time between the Siple and the Mauna Loa records. The cumulative input values by 1980 obtained from the shifted records (Table 2b) are 30 to 40 Gt C higher or lower than for the original input.

We have identified the non-fossil production with the net biospheric CO_2 release, that is deforestation plus soil destruction minus regrowth minus CO_2 fertilization effect. According to the discussed model runs, average non-fossil

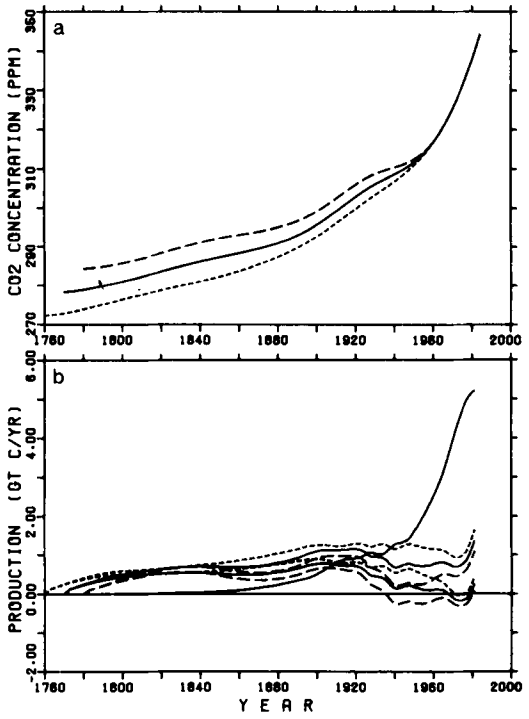

Fig. 4. (a) Smoothed CO_2 concentration histories obtained by shifting the Siple data by -6 ppm/-10 years (short-dashed line) and by $+6$ ppm/$+10$ years (long-dashed line); solid line: unshifted record of Fig. 1. (b) Smoothed biospheric CO_2 release rates calculated for different CO_2 concentration histories, i.e., for the record of Fig. 1 (solid lines), for the Siple data shifted by -6 ppm/-10 years (short-dashed) and for the Siple data shifted by $+6$ ppm/$+10$ years (long-dashed). The upper curve of each case was obtained with the OD model, the lower curve with the BD model. For comparison the fossil CO_2 release rate is also shown.

production rates in the past 20 years were in the approximate range 0 to 1 Gt C yr^{-1}. Current ecological estimates for the present biospheric release (without CO_2 fertilization) are 1.6 ± 0.8 Gt C yr^{-1}, and 150 ± 50 Gt C for the total release 1860–1984 (Bolin, 1986). Our deconvolution of the unshifted concentration curve yields for that time interval 51 (BD model) to 111 Gt C (OD model) and 90 to 159 Gt C for the whole period 1770–1984. The results from the model with outcrop are compatible with the direct estimates, while the BD results are somewhat lower, especially in the recent past. Our results indicate a decreasing trend or at most constancy in the 20th century. This is in contrast to ecological reconstructions (e.g. Houghton et al., 1985) that show a monotonous increase of the biospheric release rate since 1860 (although less steep than of the fossil CO_2). The question arises how this discrepancy can be explained. One possibility is that the assumptions underlying our results are not fully correct, i.e., that either the Siple ice core data deviate from the true atmospheric concentration history or that the carbon cycle models used do not yield the correct fluxes. If we dismiss these possibilities, then other carbon sinks than the ocean seem to exist.

One possible explanation for the difference in the recent past may be that stimulation of plant productivity due to elevated concentrations of CO_2, which is not included in the ecological estimate, has become effective with the high atmospheric CO_2 levels. There are many unknown questions regarding the importance of this effect. Kohlmaier et al. (1987) estimate by means of a biota model that CO_2 fertilization might presently account for 1.4 ± 0.7 Gt C yr^{-1}, while Bolin (1986) finds that such a sink at present probably does not exceed 0.5 Gt C yr^{-1}. In addition, other minor sinks may be active, like fertilization of marine or terrestrial biota by anthropogenic nutrient emissions, or charcoal formation during biomass burning.

It is interesting that the calculated biospheric production rates are already quite high around 1800. Data on deforestation and land use before 1860 are rather sparse, so that a comparison is difficult.

In Table 2c, calculated airborne fractions, defined as the ratio of cumulative total input to atmospheric CO_2 increase, are given. Interestingly, the airborne fraction of the total input until 1980, 0.51 for the BD model, is smaller than that calculated for fossil input only (0.61). This can be understood by considering the atmospheric CO_2 concentration response to a pulse input (Fig. 5): after a long time, a relatively large fraction of the CO_2 input has already been taken up by the ocean. Therefore, the airborne fraction of CO_2 produced before, e.g., 1900 is small in 1980. As emphasized earlier (Siegenthaler et al., 1978; Oeschger and Heimann, 1983), the atmospheric rate of increase depends not only on the current release rate, but also on the past input history. This is also reflected in the fact that the airborne

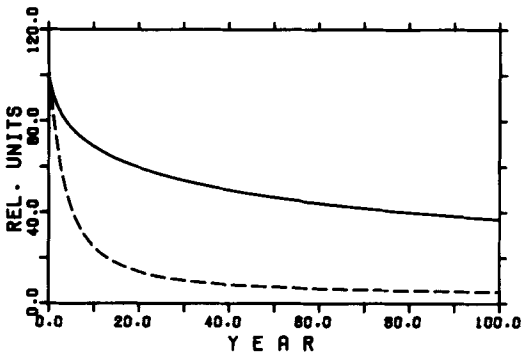

Fig. 5. Model response of atmospheric CO_2 (solid line) and $\delta^{13}C$ (dashed line) in response to a pulse input of isotopically spiked CO_2. Initial values are arbitrarily set at 100 units.

fraction for 1959–1983 is lower according to the deconvolution than according to the fossil-only input case (0.58 versus 0.62 for the BD model, see Table 2c): the large biospheric input in the 19th and early 20th centuries would, without fossil CO_2, yield a slightly decreasing CO_2 trend from 1959–1983, in consequence of the continuing oceanic uptake of that CO_2. Discussions of the global budget of anthropogenic carbon have often started from model simulations for a purely fossil input that typically yield airborne fractions of 0.60 ± 0.05, approximately corresponding to the observed airborne fraction of the fossil input alone during the Mauna Loa observation period. It has then been concluded that the geochemical models do not allow for an additional CO_2 input from deforestation; but this argumentation does not consider the fact that the airborne fraction is smaller for a total CO_2 production history with a smaller relative annual increase than for the rapidly growing fossil carbon release.

Our results allow for a biospheric input rate of 0–1 Gt C yr^{-1} in the past 20–30 years, which is in the lower range or somewhat below estimates for deforestation and land use. The reconstructed cumultative production is somewhat smaller, but not really incompatible with ecological estimates. Thus, the 2 methods of assessing biospheric fluxes seem to converge: there is no large discrepancy in the budget between anthropogenic carbon sources and sinks. It seems plausible that additional minor sinks exist, like CO_2 stimulation of plant productivity or enhanced biological productivity due to anthropogenic nutrient input (Bolin, 1986). If allowance is made for such sinks with a total size of 0.5–1 Gt C yr^{-1} during the past few decades, then the results of the 2 methods of reconstructing past biospheric releases agree within their limits of uncertainty.

4. Results for isotopic changes

On the same ice core from Siple Station on which the CO_2 data in Fig. 1 were obtained, Friedli et al. (1986) also measured $\delta^{13}C$ of the CO_2 in the trapped air. The results are shown in Fig. 6 (squares) together with direct atmospheric data (crosses) from California, 1956 (Keeling et

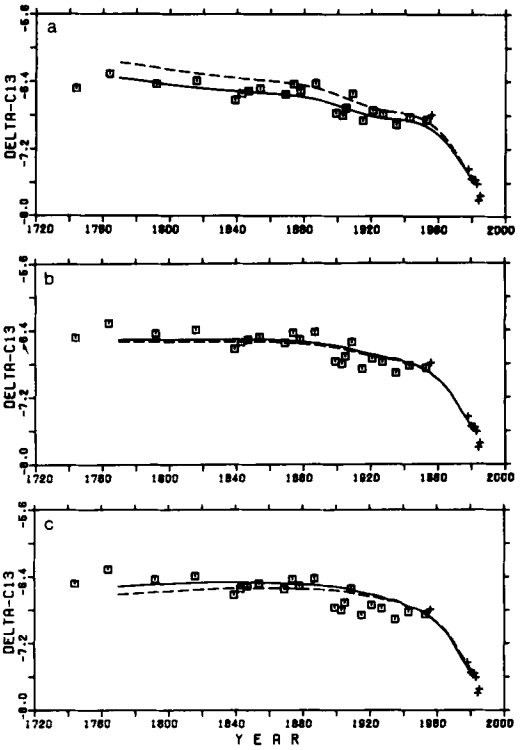

Fig. 6. Atmospheric $\delta^{13}C$ decrease of atmospheric CO_2 as indicated by measurements on air trapped in ice from Siple Station, Antarctica (squares) and by direct measurements on atmospheric CO_2 (crosses). Continuous lines are trends calculated by means of the BD model (solid line) and the OD model (dashed line): (a) from the deconvolution, (b) for purely fossil CO_2 input, (c) for the assumption that the calculated non-fossil CO_2 input is of oceanic origin.

al., 1979; N_2O-corrected according to Mook and van der Hoek, 1983) and Mauna Loa, 1978 to 1985 (Mook et al., 1983; M. Heimann, C. D. Keeling and W. G. Mook, personal communication). The data indicate a decrease from the 18th century to 1980 of 1.14 ± 0.15‰. This can be compared with tree-ring $\delta^{13}C$ records. Different individual tree-ring records show rather different changes, because the biological $^{13}C/^{12}C$ fractionation depends on variable plant physiological and environmental factors. Stuiver et al. (1984) have tried to reduce the influence of these factors by normalizing on tree-ring area and obtained a decrease of about 0.9‰ from about 1800 until 1975, which is compatible with the results from ice core plus atmospheric measurements. Freyer (1986) constructed a mean trend from all published northern hemisphere tree-ring data with a total change of 1.6‰ until 1980, larger than indicated by the ice core data. Freyer (personal communication) has suggested that the northern hemisphere trees might record a larger shift than the global mean atmosphere, because the main fossil sources are located there. However, according to observational data and 2- and 3-dimensional model calculations (M. Heimann, C. D. Keeling and W. G. Mook, personal communication; Pearman and Hyson, 1986), $\delta^{13}C$ at Mauna Loa approximately corresponds to the global mean value, and the free-air value in the northern hemisphere is no more than 0.1‰ lower. On the other hand, the agreement is not so bad when keeping in mind that the looked-for change of about 1‰ is small compared to the natural fractionation of ~18‰ between plants and atmospheric CO_2.

By means of the carbon cycle models, we have calculated isotopic changes simultaneously with the production rates, by assigning the appropriate isotope concentrations ($\delta^{13}C \approx -25$‰ and $\Delta^{14}C \approx 0$‰ before 1954) to the biospheric CO_2 input. The 4 biospheric pools were assumed to contribute to the CO_2 release in proportion to their sizes. For all model runs, $\delta^{13}C$ for the atmosphere in 1980 was adjusted to the value of −7.55‰ measured for Mauna Loa by Mook et al. (1983). Fig. 6 shows the model results, and overall changes until 1980 are given in Table 3.

For comparison, isotopic changes were also calculated using a biospheric submodel consisting of only one (instead of four) well-mixed compartment, with a mean residence time of 14 years and containing 700 Gt C, about as much as the four-box biosphere without soils. These model runs yield slightly (by 0.1‰) larger changes from 1770 to 1980 than those with the four-box submodel,

Table 3. *Isotopic changes for different model runs*

	BD model	OD model
Shift of atmospheric $\delta^{13}C$ until 1980 (‰)		
deconvolution	−1.19	−1.38
deconvolution, one-box biosphere	−1.30	−1.50
deconvolution, non-fossil CO_2 = oceanic	−1.03	−0.89
fossil-only input	−1.05	−1.02
observed	−1.14	
Shift of atmospheric $\Delta^{14}C$ (Suess effect), 1860–1950 (‰)		
deconvolution	−17.8	−17.3
fossil-only input	−17.6	−17.1
observed	−17	
Isotopic shift in the mixed layer (deconvolution) (‰)		
$\delta^{13}C$, 1770–1970:		
deconvolution	−0.46	−0.54
observed	−0.4 to −0.5	
$\Delta^{14}C$, 1860–1950:		
deconvolution	−4.7	−4.9
observed	−6 to −12	

The biosphere is represented by a four-box model, except where indicated otherwise. References for the observed values are given in the text.

because the larger four-box biosphere provides a stronger dilution of the perturbation. The shape of the computed $\delta^{13}C$ curves is similar for the one-box as for the four-box biosphere runs given in Fig. 6. Since the one-box submodel is not a very realistic representation of the biosphere, we will not discuss these results in more detail.

For a case where only CO_2 input due to fossil fuel combustion is considered, the BD model predicts a larger CO_2 increase than the OD model, but the $\delta^{13}C$ changes until 1980 calculated by the 2 models are only 0.03‰ different (Table 3). This can be understood such that the oceanic uptake of isotopic perturbation, in contrast to CO_2, via the deep-sea outcrop is not very different from that via the mixed layer, as a consequence of the fact that the buffer factor ξ affects only CO_2, but not the isotopic perturbations. For the deconvolution of the Siple-Mauna Loa record, however, the difference BD − OD is significant, about 0.2‰. The reason is that the OD model allows for a considerably larger release of biospheric CO_2 (with low $\delta^{13}C$) into the atmosphere than the BD model, so that the intput of isotopic perturbation is larger. The $\delta^{13}C$ change until 1980 obtained from the BD model (−1.19‰) agrees well with the observed change of -1.14 ± 0.15‰, while the OD result of −1.38‰ slightly exceeds the indicated error range. Keeling et al. (1980) determined, from measurements on atmospheric CO_2, a $\delta^{13}C$ decrease of 0.65 ± 0.13‰ in the period 1956–1978. From the deconvolution, we expect for this interval a change of 0.52‰ or 0.57‰ according to the BD and the OD models, respectively, which is within the error limits of the observations.

The shape of the calculated $\delta^{13}C$ trend (Fig. 6a) agrees well with the observed data. There is a marked shift in the data just before 1900 and subsequently a pleateau until about 1950, which is also simulated by the model. The plateau around 1920–1940 in the model curves has its origin in a similar but less well pronounced feature in the CO_2 record at the same time (Fig. 1). The step-like change in the ice core $\delta^{13}C$ data is striking, and the question arises if it indeed reflects the atmospheric trend or perhaps is an artefact. But if for instance the experimental age scale were wrong, such that in reality all gas samples attributed to the period 1900–1950 would have about the same age, then also the CO_2 concentrations would have to be constant in this interval, which is not the case. It is interesting to note that many tree-ring records also exhibit constant or even increasing $\delta^{13}C$ between 1920 and 1950 (Tans and Mook, 1980; Freyer, 1986). The isotopic data therefore corroborate the existence of a maximum in the biospheric carbon release rate around 1900 or slightly later.

The observation that the $\delta^{13}C$ curve exhibits more structure than the CO_2 curve can be understood by comparing the model responses of the CO_2 concentration and of $\delta^{13}C$ to a pulse input (Fig. 5). The isotopic perturbaton vanishes faster than the CO_2 excess, because the isotopic signal is diluted by the whole carbon amount in the equilibrated oceanic reservoir. In contrast, the oceanic uptake capacity for CO_2 is reduced, compared to that for the isotopic perturbation, by the buffer factor of about 10. Therefore, a fluctuation in the input rate is less strongly attenuated in the atmospheric $\delta^{13}C$ trend than in the CO_2 concentration trend.

The $\delta^{13}C$ change calculated for purely fossil input is not much smaller than that obtained from the deconvolution of the Siple-Mauna Loa record (Table 3); the computed shift until 1980 would be compatible with the observed change. The reason for this is explained by the above discussion. However, the fossil-only simulation does not reproduce the marked shift around 1900 and the plateau thereafter.

The calculations that led to the ^{13}C results of Fig. 6a are based on the assumption that the non-fossil CO_2 input is of biospheric origin. While this certainly is the most likely assumption, one may ask the question of whether an input of CO_2 from the ocean, due to some natural imbalance in the ocean-atmosphere CO_2 exchange, can be distinguished by means of $\delta^{13}C$ from a biospheric CO_2 input. The pre-industrial atmospheric $\delta^{13}C$ value was determined by an isotopic equilibrium with dissolved inorganic carbon in the ocean surface water, and CO_2 released by the ocean into the atmosphere therefore has a $\delta^{13}C$ value very near that of atmospheric CO_2. Therefore, such an oceanic CO_2 input would affect the atmospheric $^{13}C/^{12}C$ ratio only very little, in contrast to CO_2 from biomass destruction. Fig. 6c shows the model results for the assumption that the whole non-fossil input, as calculated in the

deconvolution (eq. (2)), came from the the oceanic mixed layer. As expected, the results are similar to those for the fossil-only input. Again, there is a discrepancy with the ice core data between the late 19th century and 1950. The decrease from 1770 to 1980, as obtained from the BD model, is compatible with the observed overall change, while the OD model result (0.89‰) is smaller than that for the fossil input and is outside the error range of the experimental data (Table 3). The answer to the above question is that the model results for the 2 assumptions are indeed different, but not as much as might be expected at first.

The decrease of the atmospheric $^{14}C/C$ ratio before 1950 (Suess effect) was caused only by the input of fossil carbon, the rate of which is well known, in contrast to the biospheric flux. Furthermore, the ^{14}C decrease is well-documented by tree-ring measurements from different authors, while the Siple data represent the only ice core $\delta^{13}C$ obtained so far. Therefore, the Suess effect provides a good test for validation of carbon cycle models. As seen from Table 3, the BD and OD model results are nearly identical, and the deconvolution results are also virtually indistinguishable from results for fossil-only input. The predicted change, -17 to -18‰, agrees perfectly with the data of Stuiver and Quay (1981) who observed by means of tree-ring ^{14}C measurements a decrease of 20‰ from 1860 to 1950, of which they attributed 3‰ to changing ^{14}C production connected with variations of the solar magnetic field. Deconvolution runs with the one-box biosphere mentioned above give larger ^{14}C changes than obtained with the four-box biosphere; the difference from the values of Table 3 is 2‰.

Nozaki et al. (1978) and Druffel and Benavides (1986) reported results of ^{13}C analyses of a coral and of a sclerosponge that indicate a $\delta^{13}C$ decrease in ocean surface water from 1800 to 1970 of 0.4–0.5‰. This fits well the model results of -0.46‰ to -0.54‰ (Table 3). The predicted $\Delta^{14}C$ shift in the mixed layer until 1950 is 5‰ (Table 3). Druffel and Suess (1983) measured ^{14}C decreases between 6 and 12‰ in corals from Galapagos, Florida and Belize, somewhat larger than expected. This is possibly due to the fact that the surface ocean, in contrast to the atmosphere, cannot be considered as horizontally well-mixed within a few years. In the ocean regions, where these corals grew, the exchange between surface and deeper waters may be slower than elsewhere. It is somewhat surprising that observations and model agree for ^{13}C but not for ^{14}C; this can, however, not be discussed here any further.

5. Comparison with $\delta^{13}C$ deconvolution studies

A number of authors have attempted to estimate past biospheric CO_2 inputs and pre-industrial CO_2 levels by deconvolving tree-ring $\delta^{13}C$ data. Siegenthaler et al. (1978) found that for a linear decrease of about 1.1‰ from 1860 to 1974, about 157 Gt C would have to be released by forest burning. Peng (1985) obtained an input of $\sim$144 Gt C from the biosphere until 1980 by deconvolving the average trend of Freyer (1986), with a maximum production at the beginning of the 20th century and a decrease afterwards. This maximum corresponds to the mentioned slowing down of the $\delta^{13}C$ decrease seen in the tree-ring record between 1910 and 1940; qualitatively it agrees with our results. Stuiver et al. (1984) deconvolved an unsmoothed average record from 6 trees. Not surprisingly, in this way, they obtained strong fluctuations in the biospheric carbon flux and in the atmospheric CO_2 concentration during pre-industrial time, which can hardly be considered as realistic, but rather reflects the natural variability of $\delta^{13}C$ in plants. They estimate a cumulative bio-flux of carbon from 1600 to 1975 of 150 ± 100 Gt C and a pre-industrial CO_2 concentration of about 270 ppm; Peng (1985) reconstructed a pre-industrial CO_2 level of about 266 ppm. Thus, the deconvolutions of tree-ring data tend to yield somewhat higher cumulative inputs than our deconvolution of the Siple-Mauna Loa record and lower pre-industrial CO_2 concentration than recorded in the ice from Siple Station and from the South Pole. Besides the deviations of the tree-ring record from the ice core $\delta^{13}C$ data, the results are also affected by the fact that the authors of the mentioned studies used somewhat different models.

For comparison, we have also performed a deconvolution of the smoothed Siple-Mauna Loa $\delta^{13}C$ record. As can be expected, the resulting

biospheric carbon release curve exhibits a maximum around 1900, required to produce the observed strong $\delta^{13}C$ shift. As pointed out above, rapid production rate changes are better recorded in $\delta^{13}C$ than in the CO_2 concentration, so that the isotope data support the result that there was indeed an input peak early in this century. The cumulative biospheric CO_2 production obtained from the $\delta^{13}C$ deconvolution (38 Gt C until 1900, 47 Gt C until 1980 using the BD model) is smaller than that calculated from the CO_2 concentration deconvolution. However, the latter result seems more reliable, since, as discussed above, $\delta^{13}C$ has not as good a memory for past carbon inputs as the CO_2 concentration.

6. Conclusions

Deconvolution of the combined CO_2 concentration records from the Siple Station ice core and from Mauna Loa Observatory yields a net cumulative biospheric carbon release until 1980 of ~90 to 150 Gt C, and an annual input in the period 1959–1983 of 0–0.9 Gt C yr^{-1}. Direct estimates considering rates of deforestation and land use for the recent past are somewhat higher, 1.6 ± 0.8 Gt C yr^{-1} according to Bolin (1986), but they do not include a possible additional carbon storage in parts of the terrestrial biosphere due to stimulation of plant productivity by the enhanced CO_2 concentration. The existence of such a sink might partly explain the difference; in addition, other minor sinks may have been active, like fertilization of marine and terrestrial biota by anthropogenic nutrient release or elementary carbon formation during biomass burning.

Our deconvolution indicates that biospheric CO_2 release rates were already high in the 19th century and decreased or were at most constant in the course of the 20th century. Thus, the ocean has had time to take up a considerable fraction of the early biospheric input. When this is taken into account, there is no contradiction between an airborne fraction of >0.5 calculated for purely fossil CO_2 production and the existence of a major emission of carbon from the biosphere in the past.

The model-calculated $\delta^{13}C$ trend, based on the CO_2 concentration record, agrees well with the observed $\delta^{13}C$ values of CO_2 trapped in ice core air bubbles. This consistency between concentration data, isotopic results and model is very encouraging and strengthens the confidence in the experimental techniques and in our understanding of the global carbon cycle. Concentration and isotopic data complement each other: the atmospheric CO_2 concentration history reflects more the integrated CO_2 input and acts as a low-pass filter, while the $\delta^{13}C$ record behaves like a high-pass filter and reacts more strongly to short-term changes of the production rate. In this way, the 2 kinds of information complement each other.

7. Acknowledgements

We acknowledge the contributions of M. Heimann who was involved in the modelling in an early stage of this study. We wish to express our thanks to B. Stauffer, H. Friedli and H. Lötscher for discussions on experimental aspects of the Siple data, to T. Wenk for discussions of modelling problems, and to B. Bolin and I. Levin for valuable suggestions for improvements of the manuscript. This work was supported by the Swiss National Science Foundation.

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