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Net terrestrial carbon exchange from mass balance calculations: an uncertainty estimate

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ABSTRACT

One classical method of determining the net exchange of carbon between the atmosphere and the terrestrial biosphere is to perform a mass balance on atmospheric CO_2 through time. In this calculation, the residual flux needed to balance the carbon budget when fossil fuel emissions, ocean uptake, and the documented increase of atmospheric CO_2 concentrations are taken into account, is interpreted as being net terrestrial carbon exchange. In this study, the uncertainties in such a calculation are investigated and related to the magnitude of the "missing carbon sink" as a function of time. The uncertainty in the CO_2 growth rate is found to be of the order of ± 1 GtC/yr (~ 0.5 ppmv/yr) prior to the start of direct atmospheric measurements in 1959. The difficulties in assigning a precise uncertainty estimate for the CO_2 growth rate from the ice core record are illustrated. It is then shown that the missing sink is significantly different from zero from the 1950s to the present day, even when all the uncertainties are taken into consideration. Finally, it is pointed out that the uncertainties in the cumulative carbon budget imbalance may be larger than previously thought. This has implications for model studies where conclusions are based on the ability to tune a given model to reproduce the cumulative missing sink curve.

1. Introduction

Estimates of CO_2 emissions from fossil fuel combustion and land use modifications are not consistent with the measured accumulation of CO_2 in the atmosphere and the modelled net uptake of CO_2 in the world's oceans (Watson et al., 1990; Schimel et al., 1995). This apparent imbalance in the global carbon budget has come to be known as the problem of the "missing sink". Apart from highlighting our incomplete knowledge of the carbon cycle, the mismatch between sources and sinks of atmospheric CO_2 is of practical significance since future CO_2 projections are sensitive to the nature of the carbon budget imbalance (Wigley, 1994; Craig and Holmén, 1995). Establishing the link between CO_2 emissions and atmospheric CO_2 concentrations is therefore a crucial part of climate change research.

Of the major net fluxes in the global carbon budget, the flux between the atmosphere and the terrestrial biosphere is the most uncertain (Schimel et al., 1995). One classical indirect method of estimating the biospheric contribution is by performing a mass balance on atmospheric CO_2 through time and solving for the net biosphere-atmosphere flux by difference (Siegenthaler and Oeschger, 1987). The mass balance equation for atmospheric CO_2 can be written

$$dM/dt = F - O + X, \quad (1)$$

where dM/dt is the rate of increase of the mass of CO_2 in the atmosphere; F is the fossil fuel emission rate; O is the rate of net CO_2 uptake by the oceans; and X is the residual flux that is usually interpreted as the net CO_2 exchange between the atmosphere

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and the terrestrial biosphere. X can be further divided into a flux from land use modifications and a flux from other processes that may be of importance such as CO_2 fertilisation, nitrogen deposition, mid-/high latitude forest regrowth, and climate variability (Schimel et al., 1995). All carbon fluxes are given in units of GtC/yr.

Although many mass balance calculations have been performed (Siegenthaler and Oeschger, 1987; Keeling et al., 1989; Wigley, 1991; Siegenthaler and Joos, 1992; Sarmiento et al., 1992; Wigley, 1993; Schimel et al., 1995), there has been limited discussion of the uncertainties inherent in such a calculation. While there is little doubt that carrying out the mass balance is a worthwhile exercise to check the consistency of independent estimates of net terrestrial fluxes with the rest of the global carbon budget as we know it, it is nevertheless warranted to examine the uncertainty in the residual flux so obtained. To what extent have we pinned down the net terrestrial CO_2 flux by using this method?

The uncertainty in X in eq. (1) is a function of the uncertainties in the other terms. Fossil fuel emissions since 1950 are known to within 10% (Marland and Rotty, 1984), while data before that time may be in error by up to 20% (Keeling, 1973). Average annual fossil fuel emissions for 1980–89 are estimated to be 5.5 ± 0.5 GtC/yr (Schimel et al., 1995). Ocean CO_2 uptake for 1980–89 is constrained by tracer measurements to be 2.0 ± 0.8 GtC/yr (Siegenthaler and Sarmiento, 1993; Schimel et al., 1995). dM/dt can be estimated from direct CO_2 concentration measurements since the late 1950s and ice core data prior to that time. The direct measurements of atmospheric CO_2 provide the best known term in the global carbon budget. 3.2 ± 0.2 GtC/yr accumulated in the atmosphere as CO_2 on average from 1980–89 (Schimel et al., 1995). The rate of accumulation of CO_2 in the atmosphere estimated from ice core data is more uncertain, however.

The quoted analytical uncertainty in measuring CO_2 concentrations from most ice cores is ± 3 ppmv (Friedli et al., 1986; Anklin et al., 1995). Etheridge et al. (1996) give an analytical uncertainty of ± 1.2 ppmv (one standard deviation) for their high resolution data from Law Dome in Antarctica. Additional uncertainties associated with in situ production of CO_2 in the ice through acid-base reactions are most certainly small for the Antarctic ice cores that document the rise of CO_2 concentrations over the past few centuries (Delmas, 1993). Estimating dM/dt and its uncertainty from the ice core data is complicated by two factors. The first is that the data are unevenly spread out in time. The second is that there is an uncertainty in the dating of each concentration measurement that is slightly less than the finite close-off time for the bubbles in the core (Enting, 1985). This uncertainty (2 standard deviations) is estimated to be ± 10–11 years for the Siple Station core (Schwander and Stauffer, 1984; Neftel et al., 1985) and ± 4 years for the Law Dome cores (Etheridge et al., 1996). These features are illustrated using the Siple Station data in Fig. 1.

To our knowledge, the first mass balance calculation using ice core data to estimate dM/dt over time was performed by Siegenthaler and Oeschger (1987). They acknowledged the difficulty in estimating the uncertainty in dM/dt but claimed that there is much less uncertainty in the integral of eq. (1) over time. They carried out a sort of sensitivity test by shifting the ice core data up and down by 6 ppmv but obtained little difference in X since dM/dt isn't affected by this process. The other mass balance studies listed above did not address the uncertainty in dM/dt and its effect on the residual flux, X.

In this study, we provide a range of estimates for the uncertainty in dM/dt and combine it with the quoted uncertainties in the other terms of the mass balance equation to obtain a complete uncertainty estimate for the net terrestrial carbon exchange. This net carbon exchange is then compared to independent estimates of emissions from land use change to allow the evolution of the missing sink and its uncertainty to be analysed. Finally, the uncertainty in the integral of eq. (1) and thus the cumulative missing sink is discussed and related to the amount of information that can be obtained by tuning models to fit this curve. We find that the missing sink is significantly different from zero from the 1950s to the present day in all the tests we perform. Furthermore, we find that uncertainties in the cumulative missing sink are likely to be large. Inferences about the nature of the carbon budget imbalance made by tuning models to fit the cumulative missing sink curve must therefore be made with caution.

The layout of the paper is as follows. The data and model used in the study are outlined in Section 2. Section 3 contains a description of the methodology employed, after which the results are

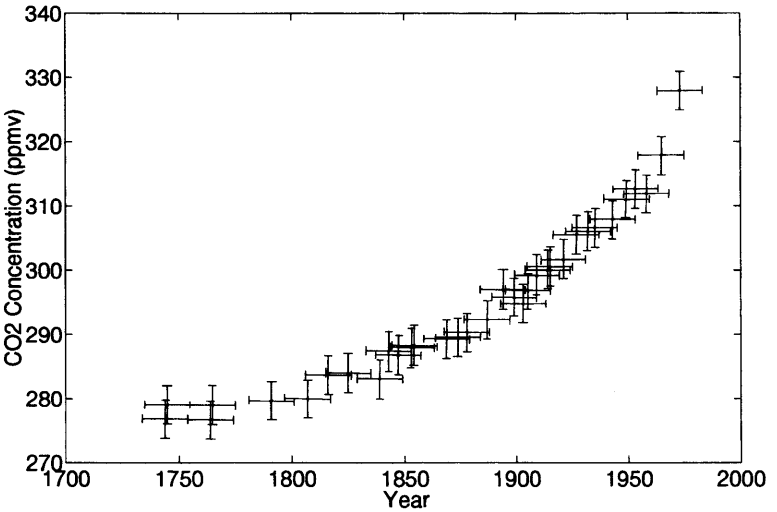

Fig. 1. CO_2 concentrations from the Siple Station ice core (Neftel et al., 1994). The error bars indicate a ± 10 year dating uncertainty and a ± 3 ppmv concentration uncertainty (Neftel et al., 1985; Friedli et al., 1986).

presented and discussed in Section 4. In Section 5 we draw some conclusions.

2. Data

To perform the mass balance calculation, CO_2 concentration data and fossil fuel emission data are required along with an ocean carbon cycle model to calculate the ocean CO_2 uptake. We use fossil fuel emissions from Keeling (1991) and Marland and Boden (1991) with the exception of data for 1985 to 1990 that are from G. Marland as reported by Enting et al. (1994). The fossil fuel emissions data set is linearly extrapolated back to zero emissions in 1844 as in Enting et al. (1994). The modern CO_2 concentration record comes from direct atmospheric measurements at Mauna Loa since 1959 as compiled by Keeling and Whorf (1991). Prior to that time, CO_2 concentrations from ice cores in Antarctica are used. We perform experiments with data from both the Siple Station ice core (Neftel et al., 1994) and the DE08 and DE08–2 cores from Law Dome (Etheridge et al., 1996). Independent estimates of CO_2 emissions from land use change that we compare with our derived terrestrial carbon exchange are from R. A. Houghton as listed by Enting et al. (1994). These land use change emissions are linearly extrapolated back to zero in 1693.

Ocean uptake is calculated using the box-diffusion model of Oeschger et al. (1975). In this model the atmosphere-ocean system is divided into 3 main reservoirs: the atmosphere, the oceanic mixed layer, and the deep sea. The atmosphere and the mixed layer are assumed to be well-mixed with respect to carbon. The deep sea is divided into layers between which carbon exchange is governed by eddy diffusivity. The eddy diffusivity coefficient is assumed to be constant with depth and is determined during model calibration. The option of including a "deep-sea outcrop" in polar regions as introduced by Siegenthaler (1983) is omitted in this study since its inclusion leads to unrealistically high total CO_2 uptake (Siegenthaler and Joos, 1992). The model is run using parameters from the calibration with a globally averaged, steady state (preindustrial) ^{14}C depth profile. This gives an average CO_2 uptake during the 1980s of 1.9 GtC/yr, close to the middle of the IPCC range of 2.0 ± 0.8 GtC/yr for the same period. Full details of the box-diffusion model and its calibration can be found in Oeschger et al. (1975) and Siegenthaler (1983).

3. Methodology

3.1. *Uncertainty in CO_2 growth rate*

Estimating the uncertainty in the growth rate of CO_2 concentration from the ice core data is

not straightforward. The data are unevenly spaced in time and there are uncertainties in both the x (time) and y (concentration) coordinates. Moreover, it is not clear to what extent the CO_2 concentration in air bubbles in Antarctic ice is representative of the atmosphere as a whole. We ignore this uncertainty here and assume that the CO_2 content of the air bubbles is indicative of the global average CO_2 concentration.

A simplification can be made by noting that the dating uncertainty is highly correlated between ice core data points. This is due to the fact that the main source of uncertainty is in the determination of the age difference between the air in the bubbles and the ice surrounding the bubbles (Neftel et al., 1985; Friedli et al., 1986). The age of the ice can be determined relatively accurately by counting seasonal variations in electrical conductivity. The uncertainty in the age of the ice is therefore only ± 2 years (Neftel et al., 1985; Friedli et al., 1986; Etheridge et al., 1996). The uncertainty in the age of the air in the bubbles is due to the finite time that it takes for a bubble to become closed-off from contact with the atmosphere as the firn in which it resides is slowly compressed to ice. We take the Siple Station core as an example although similar arguments apply for the Law Dome cores. At Siple Station, the age difference between the air in the bubbles and the surrounding ice is 83 years with a close-off time of 20–22 years (Schwander and Stauffer, 1984; Neftel et al., 1985; Barnola et al., 1995). This close-off time leads to the quoted uncertainty of ± 10–11 years although this is likely to be an overestimate since diffusion of air in the firn is not considered (Barnola et al., 1995; Schwander et al., 1993). A high correlation of errors in dating between data points is likely since the difference between air bubble age and ice age is to a first approximation constant throughout the core. There will be some variations in the age difference due to precipitation and temperature variations at the site of the core, but the effects should be small compared to the quoted ± 10–11 year error range (Etheridge et al., 1996). Support for this assertion comes from the data set itself where the mean spacing of the data points is considerably less than the ± 10–11 year uncertainty. Since the ordering of the points is determined by the stratigraphy of the core, the dating uncertainty cannot be uncorrelated from point to point because it would violate this ordering. For these reasons, we assume that the ± 10–11 year uncertainty shifts the whole data set forward or backward in time but leaves the internal spacing unchanged. Since the rate of growth of CO_2 concentration is not affected by shifting the whole curve back and forth, we can make the simplification that the dating uncertainty does not contribute to the uncertainty in the growth rate, dM/dt. When we augment the ice core data with the Mauna Loa record, dM/dt will be affected at the join if the ice core record is shifted while the Mauna Loa data are fixed, but we ignore this effect here.

The precision of the gas-chromatographic measurement of CO_2 concentrations in the Siple Station ice core is given as ± 3 ppmv (Friedli et al., 1986; Barnola et al., 1995). We assume that the errors in concentration are uncorrelated from point to point, but it is not clear what statistical level the ± 3 ppmv refers to. We test 2 assumptions both of which assume a normal distribution of measurements about the stated concentration. In the first case we assume that 99% (2.6 SD) of the measurements are within ± 3 ppmv of the mean. This corresponds to an SD (σ) of 1.165 ppmv. In the second case we assume that 90% (1.6 SD) of the measurements are within ± 3 ppmv of the mean which corresponds to a σ of 1.824 ppmv. Any systematic error in CO_2 concentrations due to gravitational fractionation (Craig et al., 1988) will not affect dM/dt and it is ignored here. For the Law Dome cores, the precision is ± 1.2 ppmv (1σ) (Etheridge et al., 1996).

The next step in the calculation is to calculate dM/dt and its uncertainty through time. In the absence of a simple analytical function that can describe the CO_2 record we fitted cubic splines to the data set. We used NAG routines E02BEF and E02BBF (NAG, 1991) to compute the spline fit. The trade-off between closeness of fit and smoothness of fit is controlled by a parameter, S, that we vary from 5 to 500 to obtain a family of curves that follow the oscillations in the CO_2 record to varying degrees. Specifically, the sum of the squares of the discontinuities in the third order derivatives at the interior knots is minimised subject to the constraint that the sum of the squares of the weighted residuals cannot exceed S. A very large value of S gives a weighted least-squares cubic polynomial that underfits the data. A value of $S=0$ returns an interpolating spline,

thereby overfitting the data. Small values of S lead to large oscillations early in the CO_2 record where the average spacing of the data is large. We added two CO_2 concentrations to the data sets in the years 1650 and 1700 to help stabilise the early record. A further concentration was added to the Law Dome data in 1750 since the first data point in this data set is not until 1832. The concentration in these years was set to the best guess preindustrial value of 278 ppmv (Enting et al., 1994), although we acknowledge that the concept of a single preindustrial CO_2 concentration is not strictly correct (Etheridge et al., 1996). The spline fitting routine does not allow multiple concentrations in a given year so the Law Dome concentrations in 1905, 1924 and 1953 were averaged to give one point for each of these years. Similarly, the Siple Station concentrations in 1744 and 1745, and 1764 and 1765 were averaged to give one concentration in 1744 and one in 1764 in order to additionally stabilise the early record. Spline fits to the CO_2 record with S values of 5, 10 and 20 are shown in Fig. 2 for the Siple Station and Law Dome ice cores respectively. All three S values give curves that follow the data well. Note the beginnings of an ocsillation in the early Law Dome record with $S=5$. Large values of S give curves that do not capture the shorter timescale variations in the data (e.g., 1935–45 in the Law Dome record) that are thought to be real (Etheridge et al., 1996), and for this reason we do not consider them further here. The CO_2 growth rate, dM/dt, is shown in Fig. 3 for the spline fits of Fig. 2. Notice how the small differences in the curves of Fig. 2 give relatively large differences in the CO_2 growth rate in Fig. 3. This sensitivity indicates that it is not possible to unambiguously determine the CO_2 growth rate as a function of time from ice core data since a curve fitting routine will always be necessary and the degree of smoothing involved will always be arbitrary, at least to some extent.

To obtain an uncertainty estimate for dM/dt as a function of time in the Siple Station data, we created 500 perturbed ice core data sets assuming a σ of 1.165 ppmv, and then another 500 assuming a σ of 1.824 ppmv. 500 random numbers were generated at each point in the record assuming a normal distribution centred on the stated concentration with either the 1.165 ppmv or the 1.824 ppmv standard deviation. Each perturbed ice core data set was then joined to the Mauna Loa record and the spline fits recalculated. dM/dt was then calculated for each of these spline fits. The process was repeated for the Law Dome data with $\sigma=1.2$ ppmv. The uncertainty estimate for dM/dt is taken as ± 2 SD of dM/dt for the 500 curves that pass through each year from 1650 to 1990. It is discussed in Subsection 4.1.

3.2. *Mass balance calculation and the missing sink*

We solved eq. (1) for the residual, X, from 1650 to 1990. Fossil fuel emissions, F, are from Keeling (1991) and Marland and Boden (1991). Ocean uptake, O, is calculated using the box-diffusion model (Oeschger et al., 1975). The CO_2 growth rate, dM/dt, comes from the spline fits to the unperturbed CO_2 record.

The exact meaning of "uncertainty" as used in the literature is often obscure. In this study we assume that "uncertainty" refers to ± 2 SD unless stated otherwise. Our conclusions are not sensitive to this assumption.

The uncertainty in X is a function of the uncertainties in the other terms. Since to a very good approximation, errors in the other terms are independent of each other, the uncertainty in X will be the square root of the sum of the squares of the uncertainties in these other terms. The uncertainty in the fossil fuel emissions figures since 1950 is stated as 6–10% (Marland and Rotty, 1984). If uncertainties in the emissions from the different fuel types (gases, liquids, solids, and flared gas) are mutually independent, the uncertainty is 6%; if they are not independent, the uncertainty is 10%. Prior to 1950, the data are uncertain to $\pm 20\%$ (Keeling, 1973). As a first approximation, we employ a constant uncertainty of 10% for the entire fossil fuel emissions data set. Ocean uptake for the 1980s is given as 2.0 ± 0.8 GtC/yr (Schimel et al., 1995). The relative error will not have been less in earlier years and we adopt a constant relative error of $\pm 40\%$ for ocean CO_2 uptake. The uncertainty estimate for dM/dt comes from the perturbed CO_2 records discussed above.

X is usually interpreted as being net terrestrial carbon exchange. A number of processes contribute to this term. Firstly, there is the net flux to the atmosphere from deforestation and land use changes calculated by Houghton and coworkers (see Houghton et al. (1983) for an explanation of the methods used). Other processes include CO_2

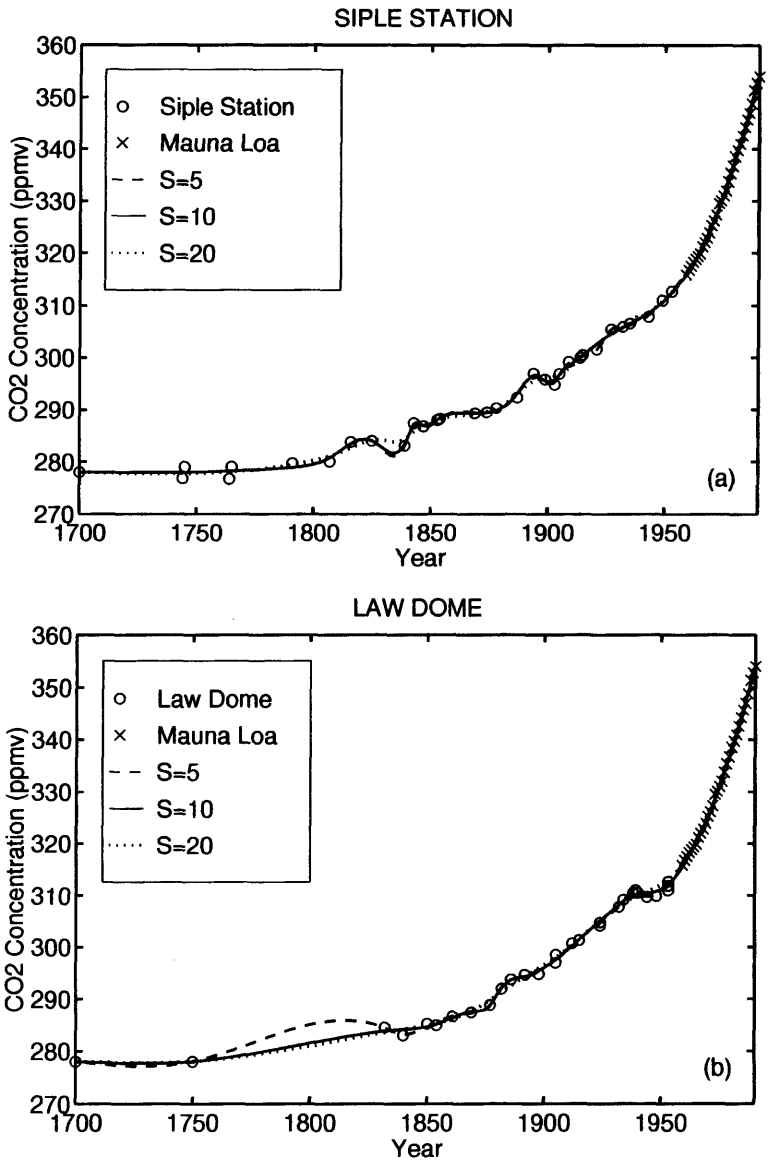

Fig. 2. Cubic spline fits to the CO_2 concentration record (circles) from: (a) the Siple Station ice core (Neftel et al., 1994); and (b) the DE08 and DE08–2 ice cores from Law Dome (Etheridge et al., 1996), both joined to the Mauna Loa direct measurements (crosses) (Keeling and Whorf, 1991). Spline fits for $S=5$ (dashed line), $S=10$ (unbroken line), and $S=20$ (dotted line) are shown (see text for details).

fertilisation, nitrogen fertilisation, mid-/high latitude forest regrowth, and climatic effects (Schimel et al., 1995). These other processes have proven to be far more difficult to quantify and only recently have tentative estimates begun to emerge (Schimel et al., 1995). For this reason, the difference between Houghton's land use change emissions and X has traditionally been termed the missing CO_2 sink with the other processes being likely explanations.

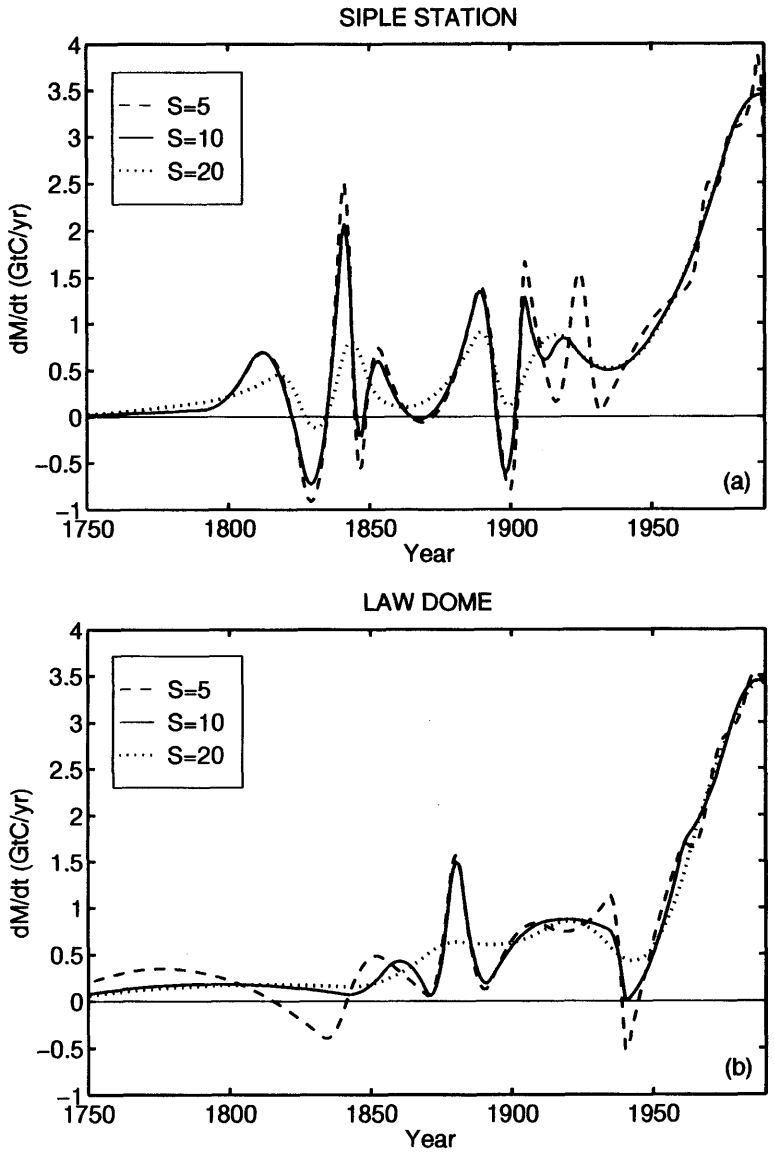

Fig. 3. The growth rate of the mass of CO_2 in the atmosphere, dM/dt, obtained from the cubic spline fits in Fig. 2.

Although the magnitude of the missing sink itself does not tell us a great deal about the mechanisms involved, its evolution since preindustrial times might. In particular, it is pertinent to ask when the missing sink became significantly different from zero taking into account all the uncertainties. We have investigated this question using our uncertainty estimate for X and the quoted uncertainty in the land use change flux. Schimel et al. (1995) give the land use change flux as 1.6 ± 1.0 GtC/yr for the 1980s. As is the case for ocean uptake, the relative uncertainty can hardly be less further back in time, so we use a relative uncertainty of $\pm 60\%$ for the entire land use change emissions data set. The results of this analysis are discussed in Subsection 4.2.

One caveat in such a calculation is that it assumes the carbon cycle to be in steady state in preindustrial times which is unlikely to be true (Enting, 1992; Etheridge et al., 1996). The DSS ice core at Law Dome clearly shows depressed CO_2 concentrations during the Little Ice Age, for example (Etheridge et al., 1996). This means that the early rise in CO_2 concentrations may partly reflect the natural recovery of the carbon cycle from the Little Ice Age rather than anthropogenic emissions. For this reason, derived fluxes prior to 1850 should be interpreted with caution. We calculate cumulative emissions from 1850 as discussed below.

3.3. *Cumulative missing sink*

Siegenthaler and Oeschger (1987) claim that the integral of eq. (1) has fewer uncertainties than eq. (1) itself since the CO_2 concentration is better known than its growth rate. We examine the extent to which this is the case and what significance it might have.

If the uncertainty in the cumulative net terrestrial carbon exchange (integral of X) and the cumulative missing sink is to be small, then errors in ocean uptake, land use change emissions, and fossil fuel emissions must be largely uncorrelated from year to year so that they cancel to a significant extent when integrated over time. It is not obvious that this will be the case. The largest uncertainties in the derivation of the fossil fuel (Marland and Rotty, 1984) and land use change (Houghton et al., 1983) emissions data sets come from uncertainties in the data that individual countries report concerning fuel production and clearing of land respectively. We suspect that the errors from this source are more likely to be systematic rather than random from year to year, in which case they will accumulate rather than cancel. Further, the large uncertainty range in the estimate for ocean uptake arises mainly from differences in ocean carbon cycle models (Schimel et al., 1995). These errors are most certainly systematic through time since a given model will not give an uptake estimate higher than the mean one year and then lower the following year. Hence, even in this case, the errors will accumulate through time.

In the final part of the study, we calculate the cumulative missing sink and its uncertainty since 1850 assuming that the uncertainties in fossil fuel emissions, ocean uptake, and land use change emissions are systematic from year to year. The uncertainty in these terms is then the relative uncertainty for a given year times the cumulative total. We assume that the uncertainty in the integral of dM/dt in a given year is equal to the uncertainty in CO_2 mass obtained from the spline fits to the 500 perturbed data sets. This is strictly true only if the CO_2 concentration in 1850 is exactly known but the error is insignificant. The results and their implications are given in Subsection 4.3.

4. Results

4.1. *Uncertainty in CO_2 growth rate*

dM/dt and its uncertainty are shown as a function of time in Fig. 4 where the Siple Station data with $\sigma = 1.165$ ppmv are used. Note how a lower value of S leads to a larger uncertainty since the cubic spline follows all the oscillations in each of the perturbed data sets. A cubic spline with a larger value of S is unable to do this and the estimated uncertainty is consequently less. The spurious oscillations in the early record with low values of S are clearly visible. dM/dt and its uncertainty as a function of time are also shown in Fig. 5, but here $S = 10$ in all three figures. Fig. 5a is the Siple Station data with $\sigma = 1.165$ ppmv; Fig. 5b is the Siple Station data with $\sigma =$ 1.824 ppmv; and Fig. 5c is the Law Dome data. The larger standard deviation in Fig. 5b leads to a larger uncertainty than in (5a) as is to be expected. The similar standard deviations in Figs. 5a, c give similar uncertainty estimates although the shapes of the curves vary. Note that the uncertainty is not constant in time.

The sensitivity of the uncertainty in dM/dt to the value of S and to the standard deviation of the Siple Station data makes its unambiguous quantification impossible. For the most recent data from Law Dome, however, the uncertainty is approximately ± 1 GtC/yr (~ 0.5 ppmv/yr) for most of the ice core record using S values of 5–20. Average values of dM/dt during the 1980s range from 3.3 to 3.4 GtC/yr with uncertainties of 0.1–0.3 GtC/yr using the different values of S and σ. This compares well with the IPCC figure of 3.2 ± 0.2 GtC/yr (Schimel et al., 1995).

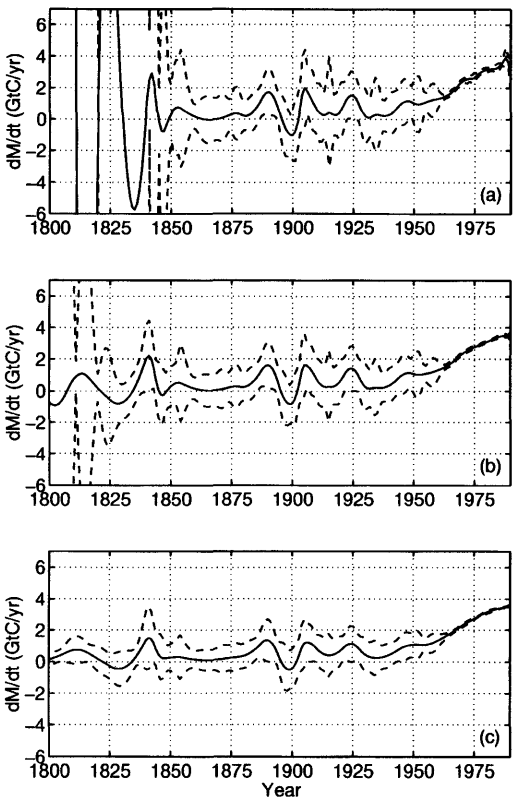

Fig. 4. The CO_2 growth rate, dM/dt, (unbroken lines) and its uncertainty ($\pm 2\sigma$, dashed lines) as a function of time for the Siple Station record with: (a) $S=5$; (b) $S=10$; and (c) $S=20$. The curves assume that 99% of the samples lie within the quoted ± 3 ppmv uncertainty (Friedli et al., 1986). This corresponds to a standard deviation (σ) of 1.165 ppmv assuming that the data are normally distributed about the mean.

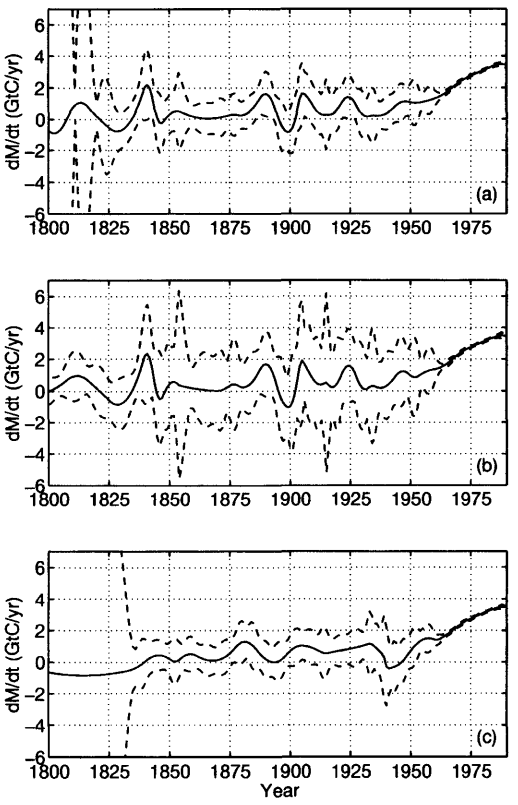

Fig. 5. The CO_2 growth rate, dM/dt, (unbroken lines) and its uncertainty ($\pm 2\sigma$, dashed lines) as a function of time for $S=10$ and: (a) the Siple Station data assuming $\sigma=1.165$ ppmv; (b) the Siple Station data assuming $\sigma=1.824$ ppmv; and (c) the data from Law Dome ($\sigma=1.2$ ppmv).

4.2. *Mass balance calculation and the missing sink*

The residual flux, X, from eq. (1) and its uncertainty are shown in Figs. 6a–c. The curves for $S=10$ are given along with the land use emission data of R. A. Houghton (Enting et al., 1994). After some oscillations in the early Siple Station record (Figs. 6a, b), the residual flux declines steadily from roughly 0.5 GtC/yr in 1920 to sub-zero values after 1950. The residual is almost constant at about 0.5 GtC/yr in the early 1900s in the Law Dome data, but in the 1930s it plummets below zero and stays there for most of the ensuing period. We see that the terrestrial biosphere was a source of carbon prior to 1950, according to the Siple Station data, and 1940, according to the Law Dome data, after which it was mainly a sink. When the uncertainties are taken into account, however, we cannot say that X was significantly different from zero using either data set.

The land use change emissions data are similar to X until the early 1900s with emissions around 0.5 GtC/yr. After that time, X declines while land use change emissions slowly increase. Their error ranges overlap, however, and the difference may not be significant. After 1960, X is negative while land use emissions increase to larger positive values and the discrepancy is significant, even when all the uncertainties are included.

The traditional way of expressing this discrepancy is to calculate the difference between the two

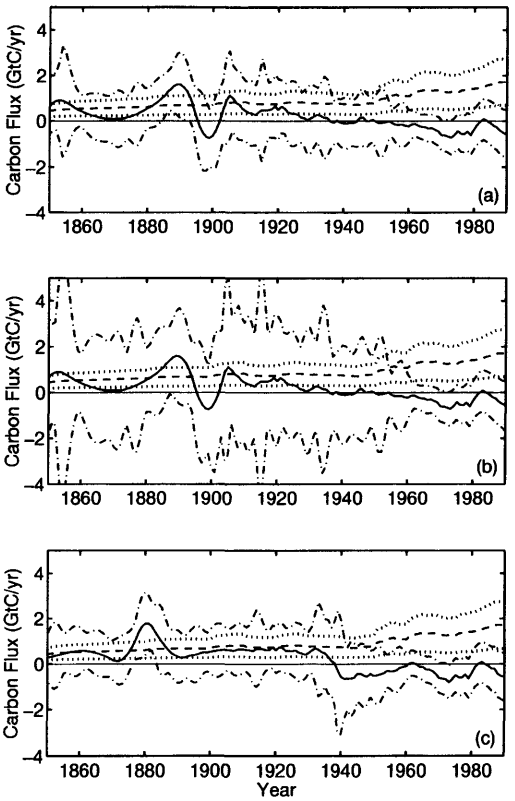

Fig. 6. The residual flux, X, from the mass balance calculation (unbroken lines) along with its uncertainty ($\pm 2\sigma$, dash-dotted lines) as a function of time. The results are for the curves shown in Fig. 5. Also shown are R. A. Houghton's land use emission data (dashed lines) as listed by Enting et al. (1994) with a relative uncertainty of $\pm 60\%$ (dotted lines).

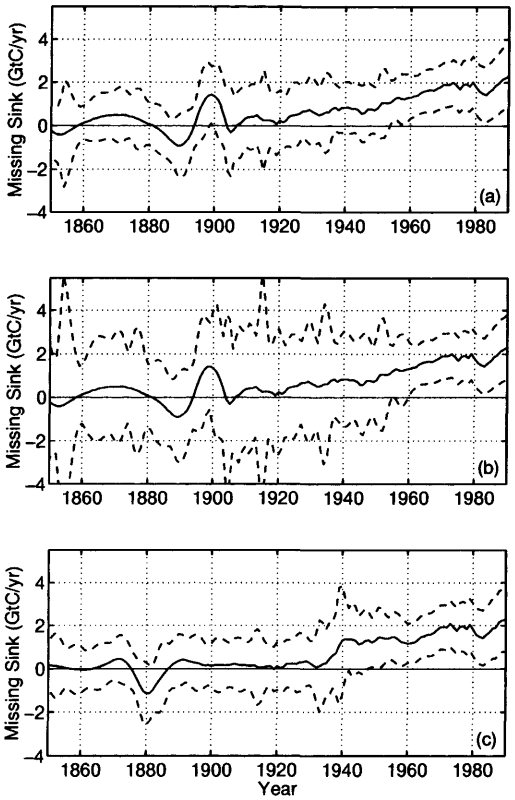

Fig. 7. The "missing sink" (unbroken lines), defined as the land use emission data minus the residual fluxes from Fig. 6, as a function of time along with its uncertainty ($\pm 2\sigma$, dashed lines).

fluxes and call it the missing sink. We do this and plot the results in Fig. 7. From these figures we can conclude that the missing sink is not significantly different from zero until the 1950s, but since that time it most certainly is. Other sink processes in the terrestrial biosphere must be active and their strength must have increased substantially since the early 1900s. Unless the uncertainties in the data have been grossly underestimated or major perturbations in ocean uptake not taken into account by the models have occurred, there is no other conclusion that can be drawn.

We note finally that our estimate of the average magnitude of the carbon budget imbalance and its uncertainty during the 1980s (1.8 ± 1.3 GtC/yr) is close to the IPCC estimate (1.9 ± 1.4 GtC/yr) if the same method of calculation is used.

4.3. *Cumulative missing sink*

The cumulative missing sink since 1850 and its uncertainty calculated with $S = 10$ and the Law Dome data are shown in Fig. 8. The Siple Station data and other values of S and σ give similar results since the errors in CO_2 concentration are uncorrelated from year to year which makes their contribution to the cumulative uncertainty small. We see that if the errors in fossil fuel emissions, land use change emissions, and ocean uptake are largely systematic as might well be the case, then the uncertainty in the cumulative missing sink is large. In fact the cumulative sink doesn't become

significantly different from zero until the late 1980s.

It is tempting to try to gain information about the nature of the carbon budget imbalance by tuning models to fit the missing sink or cumulative missing sink curves. Indeed some information should be able to be gleaned from their shape at least. However, if the uncertainties are in fact as large as shown in Fig. 8, then caution is required. For example, Friedlingstein et al. (1995) estimated the contribution of CO_2 fertilisation to the carbon budget imbalance by tuning their model to the cumulative missing sink curve. They postulated that the CO_2 fertilisation effect is the sole mechanism responsible for the missing sink from 1850 up to some year, *Tcalib*. Hence, they forced the integrated amount of carbon assimilated through CO_2 fertilisation in their model to be equal to the cumulative missing sink in the year *Tcalib*. The cumulative CO_2 fertilisation sinks for *Tcalib*= 1920, *Tcalib*=1950, and *Tcalib*=1990 are also shown in Fig. 8. The uncertainties in the cumulative missing sink dwarf the differences between model runs with different *Tcalib* values upon which Friedlingstein et al. (1995) based their results, hence the need for caution. Note that in Fig. 8 the cumulative fertilisation sink curves don't pass through our cumulative missing sink curve exactly in the year *Tcalib* since the ocean model we use to derive the cumulative missing sink is not the same as the one used by Friedlingstein et al. (1995) and we show results with the Law Dome ice core data.

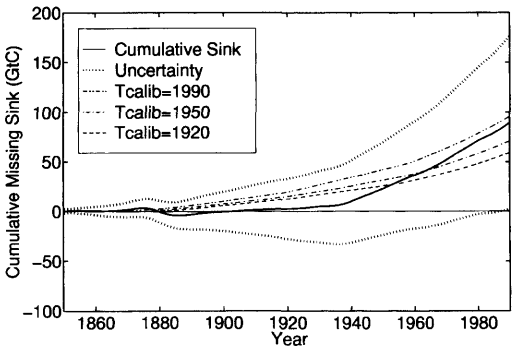

Fig. 8. The cumulative "missing sink" (unbroken line) and its uncertainty ($\pm 2\sigma$, dotted lines) since 1850 for the Law Dome ice core data and $S=10$. Also plotted are results from Friedlingstein et al. (1995): The cumulative CO_2 fertilisation sink is shown as a function of time for *Tcalib*=1920 (dashed line), *Tcalib*=1950 (dash-dotted line), and *Tcalib*=1990 (dash-double dotted line) (see text for details).

5. Conclusions

The uncertainty in the growth rate of CO_2 concentration in the atmosphere derived from ice cores is sensitive to the way these data are smoothed. For this reason it is difficult to quantify exactly but an estimate of ± 1 GtC/yr (~ 0.5 ppmv/yr) seems appropriate for most of the CO_2 record from the DE08 and DE08–2 cores at Law Dome, Antarctica (Etheridge et al., 1996).

A robust result from our study is that the carbon budget imbalance is significantly different from zero since the 1950s, even when all the uncertainties are taken into consideration. This means that other terrestrial sink processes must be active and that they must have increased substantially in strength since the early 1900s. The likely candidates are CO_2 fertilisation, nitrogen deposition, mid-/high latitude forest regrowth, and climatic effects as listed by the IPCC (Schimel et al., 1995). Improved quantification of these processes is imperative. The mass balance calculation will maintain its place as a valuable check on the estimates of various fluxes in the global carbon cycle. Its precision would be bettered significantly if the uncertainties in ocean uptake and land use change emissions could be reduced. All of the above would substantially improve our ability to make accurate projections of CO_2 concentrations using a given future emissions scenario. This is a crucial part of predicting future climate change.

Finally, while tuning models to match the missing sink may give some useful information, the uncertainties are as yet large and the results of such calculations must be interpreted with caution. Flux estimates from mechanistic models calibrated independently of other fluxes in the carbon budget are likely to provide the most reliable results.

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