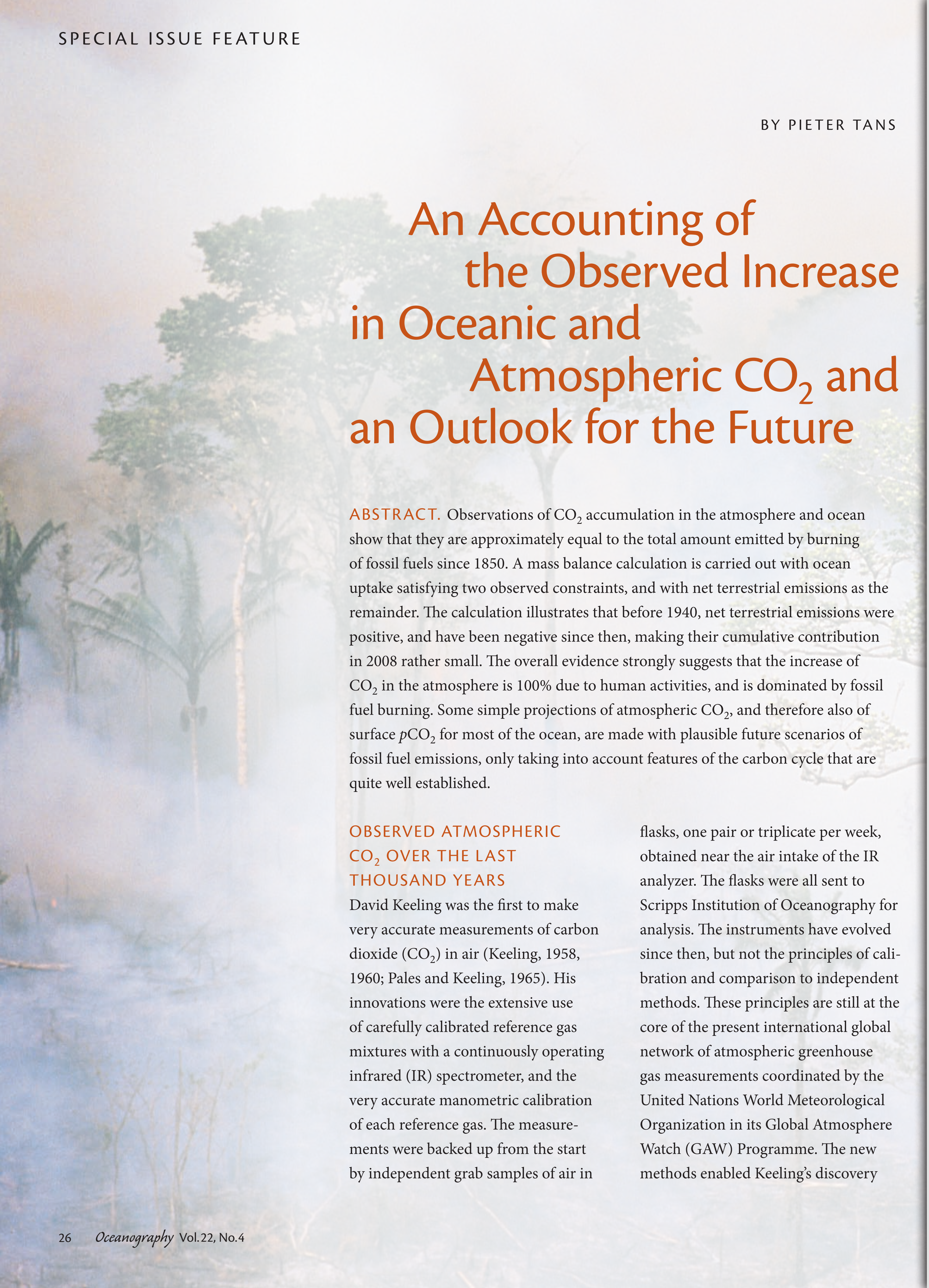
SPECIAL ISSUE FEATURE



BY PIETER TANS

An Accounting of the Observed Increase in Oceanic and Atmospheric CO_2 and an Outlook for the Future

ABSTRACT. Observations of CO_2 accumulation in the atmosphere and ocean show that they are approximately equal to the total amount emitted by burning of fossil fuels since 1850. A mass balance calculation is carried out with ocean uptake satisfying two observed constraints, and with net terrestrial emissions as the remainder. The calculation illustrates that before 1940, net terrestrial emissions were positive, and have been negative since then, making their cumulative contribution in 2008 rather small. The overall evidence strongly suggests that the increase of CO_2 in the atmosphere is 100% due to human activities, and is dominated by fossil fuel burning. Some simple projections of atmospheric CO_2, and therefore also of surface pCO_2 for most of the ocean, are made with plausible future scenarios of fossil fuel emissions, only taking into account features of the carbon cycle that are quite well established.

OBSERVED ATMOSPHERIC CO_2 OVER THE LAST THOUSAND YEARS

David Keeling was the first to make very accurate measurements of carbon dioxide (CO_2) in air (Keeling, 1958, 1960; Pales and Keeling, 1965). His innovations were the extensive use of carefully calibrated reference gas mixtures with a continuously operating infrared (IR) spectrometer, and the very accurate manometric calibration of each reference gas. The measurements were backed up from the start by independent grab samples of air in flasks, one pair or triplicate per week, obtained near the air intake of the IR analyzer. The flasks were all sent to Scripps Institution of Oceanography for analysis. The instruments have evolved since then, but not the principles of calibration and comparison to independent methods. These principles are still at the core of the present international global network of atmospheric greenhouse gas measurements coordinated by the United Nations World Meteorological Organization in its Global Atmosphere Watch (GAW) Programme. The new methods enabled Keeling's discovery of the increase of CO_2 every year, the seasonal cycle, the spatial gradient from the Northern Hemisphere to the Southern Hemisphere, and the concept of "background" air with a CO_2 concentration that is representative of very large areas. One important consequence is that we are very certain of the global increase of CO_2 measured directly and accurately in the atmosphere from 1957 to today.

Accurate measurements of CO_2 in air bubbles trapped in ice cores and, subsequently, in air in firn (compressed snow before it turns into ice), are essential to our knowledge of past atmospheric CO_2. The most highly time-resolved records are from Law Dome near the coast of Antarctica (Etheridge et al., 1996; MacFarling Muere et al., 2006). The combined records (Figure 1) show how dramatically different CO_2 has behaved since about 1850. In fact, before the nineteenth century, CO_2 fluctuated between 170 and 300 ppm for at least the last 2.1 million years (e.g., Lüthi et al., 2008; Hönisch et al., 2009). During the last 1000 years, CO_2 varied between ~ 276 and 284 ppm, the range of pre-industrial CO_2 against which the current rise is best compared. The variations are correlated with climate. The 1550 to 1800 low-CO_2 period coincides with the Little Ice Age known from European paintings and other records. When estimating how much atmospheric CO_2 has increased since pre-industrial times, the uncertainty lies in where we started from, not in how much there is today. At the beginning of 2009, the increase stood at 385–280 (±4) ppm = 105 ± 4 ppm, which corresponds to 223 ± 8 GtC in the entire atmosphere (1 GtC equals one billion metric tons of carbon, or 3.67 billion metric tons of CO_2).

WHERE DID THE CO_2 INCREASE COME FROM?

We know that humankind has been consuming the fossil fuels coal, oil, and natural gas at steadily increasing rates since the nineteenth century. The cumulative amount of CO_2 produced between 1850 and early 2009 is approximately 345 GtC (± 5–10%), of which 7 GtC is from cement production, based on estimates by the Carbon Dioxide Information Analysis Center (CDIAC; Marland and Rotty, 1984; Andres et al., 1999), using energy statistics compiled by the UN Statistical Office. The CDIAC estimates are updated annually at http://cdiac.esd.ornl.gov/ and now run through 2006. We extrapolated CO_2 data for 2007–2008 using energy statistics from British Petroleum (BP, 2009).

Because CO_2 is fairly soluble, a considerable portion of the emissions from fossil fuels must have moved from the atmosphere into the ocean. The cumulative increase in the ocean over the industrial period was measured during the 1990s by the World Ocean Circulation Experiment/Joint Global Ocean Flux Study (WOCE/JGOFS) international series of scientific cruises. Gruber et al. (1996) developed a method to distinguish the amount of dissolved CO_2 due to biological processes internal to the ocean from the slow increase caused by CO_2 invading from the atmosphere. When applied to the WOCE/JGOFS data, the total ocean increase in CO_2 from the atmosphere, integrated over time and normalized to the year 1994, was 118 ± 19 GtC (Sabine et al., 2004). A second, and independent, observational constraint on the current rate of ocean uptake of CO_2 is provided by the measured trend of the ratio of oxygen to nitrogen in the atmosphere, which works as follows. Oxygen is

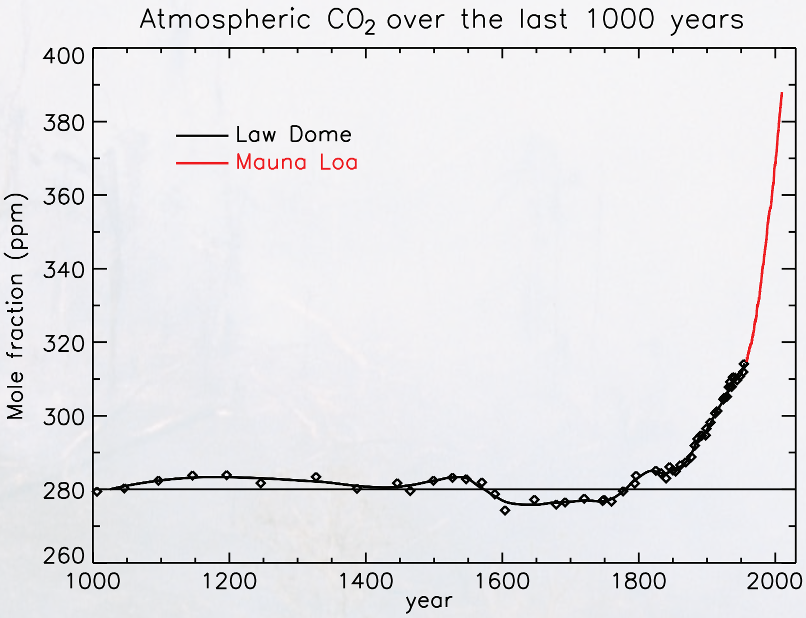


Figure 1. Recent atmospheric CO_2 history. The Law Dome (black) curve has been smoothed to the data (diamond symbols), and matches up well with the Mauna Loa Observatory (red) record. The seasonal cycle has been removed from the latter.

removed from the atmosphere when the reduced carbon in fuels is oxidized to CO_2. Subsequently, if plants absorb the added CO_2 through photosynthesis, oxygen is returned to the atmosphere. But, if the added CO_2 dissolves in water, the O_2 is not returned to the atmosphere. Using this method, Manning and Keeling (2006) determined that the average rate of ocean net uptake of CO_2 during 1993–2002 was 2.2 ± 0.6 GtC yr^{-1}.

Because we would like to make prognoses of future CO_2, it is important to know how the ocean uptake developed over time, and what role land use has played, especially through the destruction of forests to clear land for agriculture. The past can be reconstructed if we employ an ocean carbon cycle model, which can be stand-alone or embedded in an ocean circulation model. One such model is the Hamburg Ocean Carbon Cycle model (HAMOCC3; Maier-Reimer, 1996). It is used here because Martin Heimann (Max-Planck-Institute for Biogeochemistry, *pers. comm.*, 2009) made available a pulse response function (PRF). The PRF describes the decay of an instantaneous addition of CO_2 to the atmosphere as the ocean gradually takes up most of the added CO_2. The PRF calculated with the full ocean model is then approximated by a sum of exponentials (Table 1), which allows for numerically efficient calculations of the fate of any CO_2 emissions history, as in Equation 1, with $C_{atm}(t)$ as the amount remaining in the atmosphere, t as the present time, t' as the past time, $t' < t$, $E(t')$ as total emissions at time t', and the sum of exponentials in square brackets as the atmospheric PRF to one unit of emissions:

$$C_{atm}(t) = \int_{-\infty}^{t} dt' E(t') \left[x_0 + \sum_{i=1}^{n} x_i e^{a_i (t'-t)} \right]. \quad (1)$$

We have $x_0 + x_1 + \cdots + x_n = 1$. x_0 represents the “permanently” airborne fraction of emissions, and a_i are rate constants. For example, $a_i = 0.05\ yr^{-1}$ corresponds to a time constant for uptake of 20 years. The reconstruction of past emissions proceeds as follows. At each one-month time step, the net total emissions are equal to the change of $C_{atm}(t)$ plus the amount taken up by the ocean:

$$C_{oce}(t) = \int_{-\infty}^{t} dt' E(t') \left[1 - x_0 - \sum_{i=1}^{n} x_i e^{a_i (t'-t)} \right], \quad (2)$$

where the total emissions, from terrestrial biomass and natural changes through land use, and from fossil fuel combustion combined, can be made consistent with the atmospheric increase and uptake by the ocean. The net terrestrial emissions are then estimated separately by subtracting the fairly well-known fossil fuel component as estimated by CDIAC from the total emissions. For estimating the industrial atmospheric CO_2 anomaly, a pre-industrial CO_2 level of 280 ppm is assumed to be in long-term equilibrium with the ocean, and the calculation starts in the year 1090. Figure 2 shows the results, in which fossil fuel emissions plus net terrestrial emissions are equal to atmospheric plus oceanic increases. Note that in 1850, the ocean cumulative uptake starts out negative. During the Little Ice Age, mass balance required net terrestrial uptake that was partially compensated by slowly responding cumulative carbon losses from the ocean. At its peak around 1760, the estimated cumulative terrestrial emissions were –33 GtC, and cumulative ocean uptake peaked slightly later at –22 GtC. In 1850, the ocean was still at –10 GtC, whereas the atmosphere and terrestrial biosphere recovered more quickly. The HAMOCC3 ocean model does not fit the observed cumulative ocean uptake in 1994. Three other published PRFs (Sarmiento and Orr, 1992) also do not provide a good fit.

To overcome the lack of fit to the

Table 1. Pulse response functions

HAMOCC3		Empirical	
time constant years ($1/a_i$)	coeff. x_i	time constant years ($1/a_i$)	coeff. x_i
∞	0.1551	∞	0.17
461.1	0.0342	300	0.18
187.3	0.3705	60	0.40
62.16	0.1449	10	0.25
23.13	0.1028		
7.29	0.1198		
1.78	0.0727		

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observations, we construct what can be called an empirical PRF as a sum of exponentials, subject to the constraints that it is consistent with both the integrated ocean uptake in 1994 (Sabine et al., 2004) and with the rate of uptake during 1993–2002, centered on late 1997 (Manning and Keeling, 2006). There is a further constraint for the rate of uptake, based on an ocean inverse model using interior ocean distributions of carbon, of 2.2 ± 0.3 GtC yr^{-1} during the nominal period 1995–2000 (Gruber et al., 2009), fully consistent with the Manning and Keeling (2006) estimate. Also, as before, the coefficients x_i have to sum to 1. A first guess can be obtained by fitting an exponential to the fossil fuel emissions since 1945, when they were already dominating the terrestrial contribution. Eighty-five percent of all fossil emissions until 2009 have taken place since then, 75% since 1962, and 50% since 1982. The emissions are thus described as

$$E_{fos}(t') = E_{fos}(t)e^{b(t'-t)} \quad t' < t, t = 2009, \tag{3}$$

in which b is the average annual rate of increase of 2.9% per year (doubling time ~ 24 years). The use of an exponential approximation of the fossil fuel emissions history enables the two constraints to be written as linear algebraic equations,

$$\begin{aligned} ABF_{ins} &= 1 - \sum_{i=0}^{n} x_i\left(\frac{a_i}{a_i + b}\right) \\ ABF_{cumul} &= \sum_{i=0}^{n} x_i\left(\frac{b}{a_i + b}\right), \end{aligned} \tag{4}$$

and solved by standard methods, together with the constraint on the sum of x_i, to obtain a first-guess solution for the coefficients x_i after the time constants $1/a_i$ have been chosen. Note that the time constant a_0, corresponding to the "permanently" airborne term x_0, equals zero. ABF_{ins} is the observed "instantaneous" airborne fraction of emissions in 1997, and ABF_{cumul} is the "cumulative" airborne fraction in 1994. The first Equation 4 expression is obtained by differentiating Equation 1 with respect to time t,

$$\frac{dC_{atm}(t)}{dt} = E(t)\sum_{i=0}^{n} x_i - \int_{-\infty}^{t} dt' E(t') \sum_{i=0}^{n} x_i a_i e^{a_i(t'-t)},$$

then substituting Equation 3 for fossil fuel combustion, integrating over t', and dividing by current emissions $E_{fos}(t)$. The second expression is obtained by substituting Equation 3 into Equation 1, integrating over time t', and dividing by the integrated fossil emissions until time t.

Note that both *ABF*s are calculated as (1–ocean uptake)/(fossil fuel emissions). We choose not to use *ABF*s relative to the sum of fossil fuel emissions and land use, as is often done, for two reasons. First, with our definition, clean constraints on the problem are obtained from ocean observations. Second, *ABF*s as used here are very well-defined quantities based directly on observations, whereas when land use emissions are included in the definition, the uncertainty becomes much larger, and trends may appear that could be artifacts caused by our poor quantitative understanding of land use emissions. We prefer to derive net terrestrial emissions as a residual from better-determined terms in the budget.

Total emissions were not exponential, with an early peak of net terrestrial emissions. Also, fossil fuel emissions rose

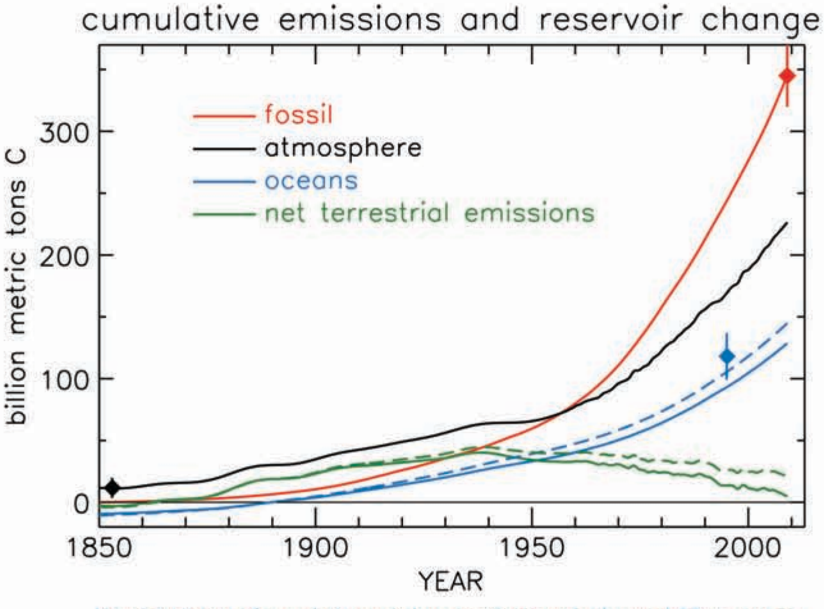

Figure 2. History of cumulative emissions consistent with observed CO_2 increases in the atmosphere and ocean. Uncertainties in the fossil fuel emissions and the accumulations in the atmosphere and ocean are plotted for the year in which they apply. The Hamburg Ocean Carbon Cycle (HAMOCC3) model does not fit the observed cumulative ocean uptake. Therefore, there are two versions of cumulative ocean uptake and net terrestrial emissions: solid lines indicate HAMOCC3 and dashed lines indicate empirical pulse response function.

faster during the period 1945–1973 than during 1974–2000. Thus, the first guess PRF is entered into the full atmospheric history, and coefficients are adjusted to approximately fit both constraints. Table 1 gives the derived empirical response function. It turns out that, with a permanent airborne fraction term and three exponentials, the two constraints of Equation 4 cannot be simultaneously satisfied exactly. When the predicted cumulative ocean uptake is 118 GtC in 1994, the rate of increase in 1997 is too high, and when the rate of ocean uptake at the end of 1997 is 2.2 GtC yr^{-1}, the integral increase in 1994 is too low. The empirical fit is a compromise, giving an integral uptake in 1994 of 105 GtC, and a rate of increase in 1997 of 2.5 GtC yr^{-1} (dashed lines in Figure 2). The empirical PRF predicts that at the end of 2008, cumulative ocean uptake has increased to 145 GtC, and the rate of uptake to 3.2 GtC yr^{-1}.

The most striking feature of Figure 2 is that, within their respective uncertainties, the measured increases in the atmosphere and the ocean add up to the total amount emitted by burning fossil fuels. The atmospheric increase was primarily caused by land use until the early part of the twentieth century, but the net cumulative emissions from the terrestrial biosphere peaked in the late 1930s at ~ 45 GtC, dwindling to ~ 20 GtC in the first decade of the twenty-first century.

Figure 3 is a plot of the calculated rates of uptake. The upper panel shows the rate of total (fossil plus net terrestrial) emissions necessary to satisfy the observed atmospheric history, both in the case of HAMOCC3 and the empirical ocean uptake function. After subtraction of the fossil fuel component, the net terrestrial rate of emissions is plotted in the lower panel. The required mass balance manifests itself again. When ocean uptake is larger, the required total emissions to the atmosphere need to increase (upper panel), which decreases the net terrestrial sink (lower panel) since the mid-twentieth century. Remember that "net terrestrial" includes emissions from deforestation. If global deforestation causes emissions of 1.5 GtC yr^{-1}, our mass balance implies that there has to be terrestrial uptake between 1.5 and 3 GtC yr^{-1} in the second half of the twentieth century, more than compensating for the deforestation.

Suggestions that the carbon cycle is becoming less effective in removing CO$_2$ from the atmosphere (e.g., LeQuéré et al., 2007; Canadell et al., 2007) can perhaps be true locally, but they do not apply globally, not over the 50-year atmospheric record, and not in recent years. To the contrary, despite global fossil fuel emissions increasing from 6.57 GtC in 1999 to 8.23 in 2006, the five-year smoothed global atmospheric growth rate has not increased during that time, which requires more effective uptake either by the ocean or by the terrestrial biosphere, or both, to satisfy atmospheric observations. When calculating ABF_{ins} for the entire Mauna Loa record and fitting a linear slope, it is weakly negative, decreasing from 0.61 in 1958 to 0.53 in 2009. In this approach to the carbon budget, the required enhanced uptake does not depend on models, only on the observed atmospheric increase and estimates of fossil

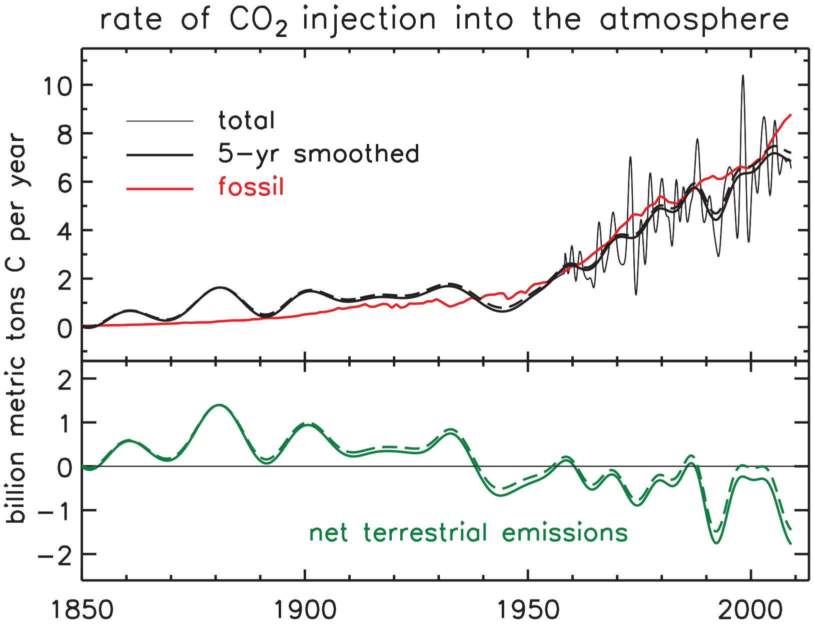

Figure 3. Rates of emissions and uptake. Total emissions (fossil fuel plus net terrestrial) required to reproduce the observed atmospheric growth rate. The thinner black solid line is the result using HAMOCC3 ocean uptake; the thicker black solid line is five-year smoothed of same; the black dashed line is five-year smoothed of same, with empirical ocean uptake; and the difference between required net total emissions and fossil fuel emissions is indicated by the green solid and dashed lines, for HAMOCC3 and empirical ocean uptake, respectively.

fuel emissions. There are two ways to avoid the conclusion that overall sinks have strengthened in *proportion* to emissions (or slightly faster). The first is to include land use in the denominator of *ABF*, written here as ABF_{F+L}, requiring that actual values be assigned to land use emissions as a function of time. The choice of assigned values gives some control on the value of ABF_{F+L} and on its trend. With the continuing growth of fossil fuel emissions, the relative contribution of land use emissions has diminished over time, which in itself can cause a trend of ABF_{F+L}. However, as already argued, this approach distances ABF_{F+L} from direct observations by injecting models into the denominator. The second is to hypothesize that the recent increases in global fossil emissions have been dramatically overstated. It is more likely that we are currently in a period of anomalously large terrestrial uptake similar to the early 1990s.

The mass balance outlined above leaves no serious doubt that our own activities, in particular the burning of fossil fuels, have caused the increase in CO_2. There is additional supporting evidence from atmospheric observations of isotopic ratios of CO_2. The $^{13}C/^{12}C$ ratio has declined in such a way that the source of CO_2 must be of organic origin. The time history of the $^{14}C/^{12}C$ ratio shows, despite the large injection of $^{14}CO_2$ due to nuclear weapons testing, that the source of CO_2 must be at least ~ 20,000 years old. Furthermore, the spatial gradient of CO_2 between Mauna Loa, Hawaii, and the South Pole has steadily increased from 1957 to the present, which is consistent with a growing source that primarily resides in the Northern Hemisphere.

A FUTURE SCENARIO FOR ATMOSPHERIC CO_2

We have a problem when trying to predict atmospheric CO_2 for the rest of this century and beyond. To name a few issues, it is likely that ocean circulation will be affected by climate change. We don't even know to what extent today's ocean circulation is in steady state. A lack of steady state would invalidate, for example, the representation by a constant sum of exponentials as used above. The rate of exchange between surface and deeper waters could change, as could the long-term partitioning of CO_2 between the atmosphere and the ocean. The latter is affected strongly by biological processes in surface waters and by the residence time of water masses in the surface mixed layer. In the analysis above we have seen that the overall role of terrestrial emissions has been quite small in the last five decades. Total terrestrial biomass appears to have been somewhat buffered against human intervention and modest climate anomalies, but will that remain so? A serious candidate for large sustained emissions of both CO_2 and CH_4 is degradation of organic matter in permafrost soils as a result of Arctic warming (Schuur, 2008). The total amount is estimated to be ~ 1400 GtC, or ~ 1700 GtC when northern peat lands are included. That amount is almost five times the cumulative fossil fuel emissions through 2008. Permafrost disintegration is being observed (Walter et al., 2006), but is currently not pervasive enough to be measurable as enhanced CH_4 mole fractions in air in the larger Arctic basin (Dlugokencky et al., 2009). The situation is aptly described as a Sword of Damocles. There is a geologic event, the Paleocene-Eocene Thermal Maximum (PETM) 55 million years ago, for which there is strong evidence of a geologically sudden release of massive amounts of carbon coinciding with abrupt warming (Zachos et al., 2008). Feedbacks between the carbon cycle and climate are likely to have played a prominent role in the PETM event.

Arctic permafrost degradation is a good example of the severe difficulty of climate prediction in general. It is a likely and potentially large positive feedback expected to play out over many decades, while the rate and the specific mechanisms have not been quantified or identified. There are rapid climate feedbacks, such as water vapor, as well as very slow ones, and thus the overall "effective" feedback factor amplifying the effect of greenhouse gases is time dependent. It might reasonably be expected that we will only be able to unravel the slow feedback effects while they are actually happening, so that our hypotheses can be informed by observations. Then, it is also too late, however. We do know that there are plausible feedbacks that could lead to catastrophic climate change, large enough to threaten the stability of our civilization. The probability is not vanishingly small. We understand the fundamental character of feedback and its uncertainty. It explains the long tail of climate predictions, especially the non-negligible chance of catastrophic climate change (Roe and Baker, 2007), which appears to be of the order of one in five, depending on a subjective assessment of what might constitute "catastrophic."

Despite the difficulty of long-term CO_2 projections, some things are clear: fossil fuel burning has driven the CO_2 increases thus far, the ocean will eventually take up the largest portion of the emissions, and the enhancement of CO_2 in the atmosphere and ocean will last for a very long time (Zachos et al., 2008; Archer et al., 2009). The second point is incorporated into the pulse response function. As time progresses, the ocean's share of the emitted CO_2 increases. It is also visible in the *ABF*s defined above. The observed rate of ocean uptake as a fraction of fossil fuel emissions (ABF_{ins}) centered on 1997 is 2.2/6.56 = 34%, whereas the total cumulative ocean uptake divided by cumulative fossil fuel emissions (ABF_{cumul}) in 1994 equals 118/243 = 49%. The third point implies that the effect of CO_2 on climate forcing is cumulative; it depends primarily on the total amount emitted, not on the rate of emissions. Unfortunately, the IPCC reports have not helped public understanding of this fact by choosing, somewhat arbitrarily, a rather short time horizon (100 years is most commonly used) for climate forcing by CO_2. It is useful to convey all three points in any projection.

To construct the CO_2 scenarios shown in Figure 4, we first need to make a projection for fossil fuel consumption. Instead of adopting the common economic point of view, which, through its emphasis on perpetual growth, implicitly assumes infinite Earth resources, or at least infinite substitutability of resources, let us start with an estimate of global fossil fuel reserves. Table 2 presents both conventional and unconventional fossil fuels, as compiled by the World Energy Council (WEC, 2007), after applying carbon fractions to each category. Cumulative extraction of fossil fuels now stands at ~ 345 GtC, and there still appear to be another ~ 640 GtC of proved reserves, making the total original conventional reserves ~ 1000 GtC. The resource and reserve estimates are uncertain, partially for political reasons. For example, OPEC export quotas depend on it, as do stock valuations of energy companies. It is known that the easiest deposits are typically exploited first, and when their extraction peaks, deposits that are more expensive and energy intensive to extract are opened up. The up-front energy investments (and water pollution) necessary to bring oil from the Canadian tar sands (bitumen) to market are an order of magnitude larger than for Saudi fields. Therefore, a logistic model is more appropriate than an exponential model, and it can be expected to play an important role in a future world where we have to take guidance from economic theories predicated on sustainability instead of on growth.

Initially, when the resource still appears vast, there is exponential growth, but the logistic model takes into account that it becomes gradually harder to extract more. The model is defined by Equation 5

$$E = dQ/dt = kQ(1 - Q/N), \qquad (5)$$

in which N is the total resource, Q is cumulative extraction, k is the initial exponential rate of growth, and E is the rate of extraction. The factor $(1 - Q/N)$ expresses the increasing difficulty of extraction, which results in slowing of growth. The peak rate of extraction occurs when Q equals half of the total resource.

There are many examples of historical extraction following a logistic function. To name a few, Pennsylvania anthracite extraction peaked in ~ 1920 and is now exhausted (Höök and Aleklett, 2009), crude oil extraction in the United States has been firmly on the declining side for decades, and oil and gas from the North Sea are now also declining. It can

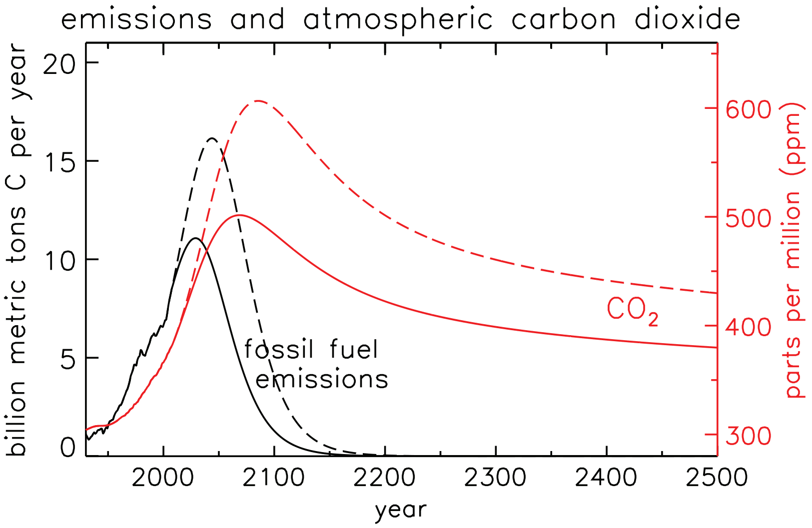

Figure 4. Two potential atmospheric CO_2 futures using a logistics function for the emissions of fossil fuels. Potential emissions (using left axis) for Scenario A (black solid line) total 1000 GtC, and for Scenario B (black dashed line) 1500 GtC. Using the right axis, resulting atmospheric CO_2 for Scenario A is shown by the solid red line for the 1000 GtC case, and the dashed red line shows Scenario B for the 1500 GtC case. The right-hand axis starts at the pre-industrial level of 280 ppm.

be debated to what extent technological innovation can add to the extractable resource base, but history seems to show that as costs (labor, energy, regulation) increase, extraction slows because alternatives become competitive. In the case of energy, unconventional resources can be considered to have their own logistics function, starting out at a substantially higher cost level than conventional reserves. In essence, the picture being painted by a logistics curve is that the energy, financial, environmental, and also geopolitical costs of fossil fuel extraction will tend to increase even without climate considerations, and that technical innovation can bring costs down, but not enough to overturn the overall picture. The world's attempt to slow down climate change can be expected to add significant environmental costs to fossil fuel extraction and processing. Rapid invention, technical development, and scaling up of alternatives, including efficiency and conservation, is crucial. Without them, the increasing demand for better living standards for more people will almost certainly force us into the large-scale exploitation of unconventional fossil fuel resources with little regard for the consequences of climate change, accompanied by accelerating environmental destruction, acidification of ocean waters, resource wars, and other negative impacts.

Table 2. Fossil fuel resources

CONVENTIONAL	Proved Reserves[1] (GtC)	Consumption 2005 (GtC yr^{-1})
Bituminous coal (+anthracite)	258	2.66
Sub-bituminous	107	0.23
Lignite	45	0.26
Oil	136	3.20
Natural gas	93	1.47
Total	639	7.82

UNCONVENTIONAL	Resources[2]
Shale oil	347
Bitumen	343
Heavy oil	277
Total	967

[1] Proved reserves are defined as the amount that can be recovered with existing available technology under present and expected local economic conditions.

[2] Resources constitute a wider category. The deposits are less well characterized and include potential reserves when extraction technology improves.

Thus, long-term sustainable economics and action to avoid the worst of climate change are part of the same package. In Figure 4, we present two illustrative scenarios. In Scenario A, we took actual emissions through 2008, $N = 1000$ GtC, and after 2008 grafted a logistics curve for the remainder of the reserves onto the actual emissions by adjusting k and the timing of peak extraction. The adjustments allowed for a smooth transition of actual emissions to post-2008 projected emissions, and allowed for the average rate of growth of extraction during 2009–2013 to be set at 2.0% per year. In Scenario B, it is assumed that a significant amount of unconventional resources is extracted in addition to conventional reserves, for a cumulative total of 1500 GtC, with actual emissions through 2008, and average growth rate of extraction during 2009–2013 set at 3.0% per year.

In Figure 4, the peak rate of emissions in Scenario A occurs in 2029 at 11.1 GtC yr^{-1}. Atmospheric CO_2 peaks 40 years later in 2069 at ~ 500 ppm when the rate of emissions drops below the rate of global sinks from the atmosphere, and does not return to below 400 ppm for two centuries. This CO_2 prognosis corresponds with the three known features already mentioned—the dominating role of fossil fuel burning, the ocean absorbs most of the added CO_2, and the long time scale. Scenario B emissions peak in 2044 at 16.1 GtC yr^{-1}. Although 250 GtC have been added before half of the total resource is consumed, it only takes an additional 15 years before the emissions peak is reached. As with pure exponential growth, resources that may look very large are invariably consumed surprisingly fast. That it is the cumulative emissions that matter is illustrated by the CO_2 enhancement over pre-industrial being about 50% larger in Scenario B than in Scenario A.

Figure 5 shows the consequences for climate forcing by CO_2 and for surface ocean pH for the two emissions scenarios. Future climate forcing (F) due to CO_2 alone is estimated (IPCC, 2001, p. 358) as

$$F\ (\text{Watt m}^{-2}\text{, globally averaged}) = 5.35 \cdot \ln(X/280), \tag{6}$$

in which ln is the natural (base e) logarithm, and X is the mole fraction of CO_2 in ppm. The pH change is estimated in a simple way as follows. From the first

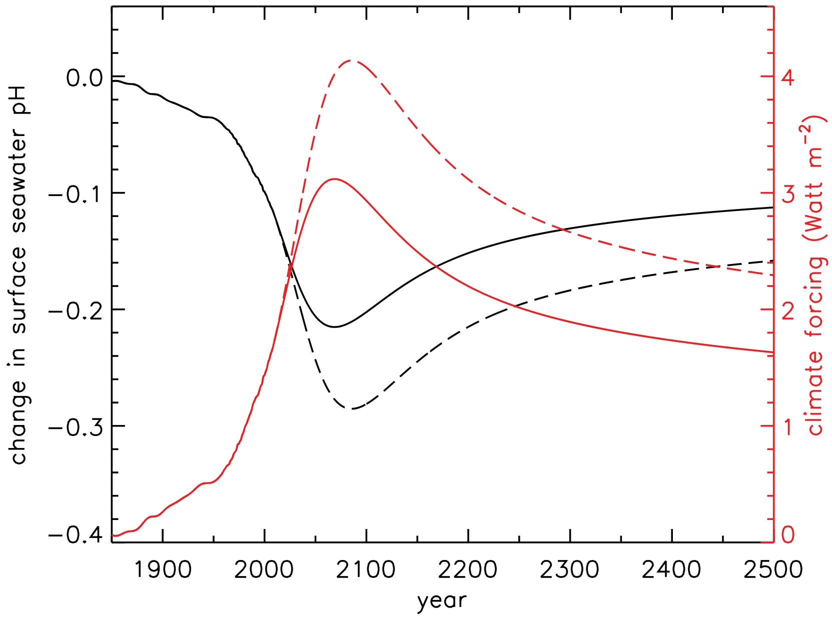

Figure 5. Changes in pH for global average surface ocean water (black lines, left axis) and climate forcing (red lines, right axis) since pre-industrial times by added CO_2, for emissions scenarios A (solid lines) and B (dashed lines).

carbonate dissociation equilibrium, $CO_2(aq) + H_2O \rightleftarrows H^+ + HCO_3^-$, we have $[H^+] = K_1 \cdot [CO_2(aq)] / [HCO_3^-]$, with K_1 the first dissociation constant of carbonic acid, and square brackets denoting the concentration. Thus, the pH is given by

$$\begin{aligned} pH &= -\log[H^+] = -\log(K_1) \\ &- \log[CO_2(aq)] + \log[HCO_3^-], \end{aligned} \tag{7}$$

and the difference from pre-industrial times by

$$\begin{aligned} pH - pH_0 &= \\ -\log([CO_2(aq)] / [CO_2(aq)]_0) & \\ + \log([HCO_3^-] / [HCO_3^-]_0), & \end{aligned} \tag{8}$$

in which the subscript "0" denotes pre-industrial values. For most of the ocean surface, dissolved $CO_2(aq)$ is very nearly in equilibrium with the overlying atmosphere, and thus Equation 8 can be written as

$$\begin{aligned} pH - pH_0 = -\log(X/280) + \\ \log([HCO_3^-] / [HCO_3^-]_0). \end{aligned} \tag{9}$$

X is again the mole fraction of CO_2 in the atmosphere (ppm), and log is the logarithm base 10. The dominant term in Equation 9 is $\log(X/280)$ because the relative changes in atmospheric CO_2 (and thus $CO_2(aq)$) are much larger than the relative changes in bicarbonate concentration. The changes in bicarbonate are, of course, related to the changes in $CO_2(aq)$. A more complete treatment of ocean chemistry, including the reaction of CO_2 with borate ions (Tans, 1998) shows that Equation 8 is closely approximated by

$$pH - pH_0 \sim -0.85 \cdot \log(X/280). \tag{10}$$

In the above estimate, we used the following values for average pre-industrial surface waters (Takahashi et al., 1981): temperature 16°C, salinity 34.78 g kg^{-1}, $[CO_2(aq)] = 10.0$ µmol kg^{-1}, $[HCO_3^-] = 1769$ µmol kg^{-1}, $[CO_3^{2-}] = 223$ µmol kg^{-1}, and titration alkalinity 2311 µ-equiv. kg^{-1}.

The empirical response function (Table 1) was used in Figure 4, but the results are not strongly dependent on the choice of a particular ocean model. The use of a response function implies that we have neglected the fact that, as the ocean surface acidifies, the proportion of emissions taken up by the ocean diminishes (not a large effect in these scenarios). The reason for a decreasing ocean uptake fraction is that the majority of the CO_2 added to the ocean reacts with carbonate ions in the equilibrium $CO_2(aq) + CO_3^{2-} \rightleftarrows 2HCO_3^-$, forming bicarbonate ions. This equilibrium is pushed to the right with added $CO_2(aq)$, obeying the equilibrium condition $[HCO_3^-]^2 / [CO_2(aq)][CO_3^{2-}] = K_1/K_2$ (K_2 is the second dissociation constant of carbonic acid, $HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$). Very approximately, assuming $[HCO_3^-]$ does not change because its concentration is so much larger than the other components, a 20% relative increase in $CO_2(aq)$, and thus of the atmospheric CO_2 mole fraction, goes together with a 20% relative decrease in carbonate ions. As the concentration of the latter becomes smaller, the same relative increase in $CO_2(aq)$ goes together with a progressively smaller absolute decrease in total carbonate ions, which equals most (neglecting borate) of the absolute amount taken up by the ocean. The expected progressive decrease in carbonate ions associated with increasing CO_2 is precisely what is threatening the health of coral reefs and other calcium carbonate forming organisms. Other uncertainties mentioned above, such as changes in ocean circulation and ocean biology, have also been ignored because they cannot be credibly predicted at this time. In addition, the dissolution of

$CaCO_3$ in the ocean that will eventually neutralize the added acid has also been ignored because the expected time scale is 3,000–7,000 years (Archer et al., 2009), which is too slow to have much of an effect in the next few hundred years.

Finally, we assumed that net terrestrial emissions were zero from 2009 onward because of our finding that the cumulative net terrestrial contributions have been minor thus far. If there should be significant net emissions, out of our control, from permafrost carbon or other sources, CO_2 will become much higher than in our scenarios. Because those emissions are not point sources, it may be imperative for society to have developed by that time techniques for extracting CO_2 from free air (e.g., Keith, 2009).

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