Atmospheric lifetime of fossil-fuel carbon dioxide

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Abstract

CO_2 released from combustion of fossil fuels equilibrates between the various carbon reservoirs of the atmosphere, the ocean, and the terrestrial biosphere on time scales of a few centuries. However, a sizeable fraction of the CO_2 remains in the atmosphere, awaiting a return to the solid earth by much slower weathering processes and deposition of $CaCO_3$. Common measures of atmospheric CO_2 lifetime, including the e-folding time scale, disregard the long tail. Its neglect in the calculation of global warming potentials leads many to underestimate the longevity of anthropogenic global warming. Here we review the past literature on the atmospheric lifetime of fossil fuel CO_2 and its impact on climate, and we present initial results from a model intercomparison project on this topic. The models agree that 20-35% of the CO_2 remains in the atmosphere after equilibration with the ocean (2-20 centuries). Neutralization by $CaCO_3$ draws the airborne fraction down further on time scales of 3-7 kyr.

Introduction

The fate and lifetime of fossil fuel CO_2 released to the atmosphere is not inherently scientifically controversial, but the packaging of this information for public consumption is strewn with such confusion that Pieter Tans proposed in print that the entire concept should be “banished“(Tans et al 1990). How long is global warming from CO_2 going to last, policymakers and the public would like to know. If there is a trade-off possible between emissions of CO_2 versus emissions of other greenhouse gases, how shall they be

compared? The lifetimes of greenhouse gases are incorporated into the construction of global warming potentials, the time-integrated climate impact of each gas relative to CO_2.

The question of the atmospheric CO_2 lifetime is also important for predicting the impact of human activity on slowly-responding aspects of the climate system such as the major ice sheets (Archer & Brovkin in press), permafrost (Gavrilov et al 2003, Lawrence & Slater 2005), and geochemical impacts of changing the temperature of the deep sea (Archer et al 2004). Many of the most profound changes in the Earth's surface, such as sea level, take place on time scales of thousands of years and longer.

There is a strong consensus across models of global carbon cycling, as exemplified by the ones presented here, that the climate perturbations from fossil fuel CO_2 release extend hundreds of thousands of years into the future. This is consistent with sedimentary records from the deep past, in particular a climate event known as the Paleocene Eocene thermal maximum, which consisted of a relatively sharp increase in atmospheric CO_2 and ocean temperature, followed by a recovery, which took perhaps 150,000 years (Kennett & Stott 1991, Pagani et al 2006) .

The gulf between the widespread preconception of a relatively short (hundred-year) lifetime of CO_2 on the one hand, and the evidence of an much longer climate impact of CO_2 on the other, arguably has its origins in semantics. There are rival definitions of a lifetime for anthropogenic CO_2. One is the amount of time it takes until a substantial portion, say 50% or perhaps 1-1/e which is about 63%, of the excess CO_2 goes away. Another is the average lifetime, or transit time, of the individual carbon atoms before they leave the atmosphere. The misinterpretation which has plagued the question of the

atmospheric lifetime of CO_2 seems to arise from confusion of these two very different definitions.

In the simplest of worlds, the decay of a perturbation might follow first-order linear kinetics. Radioactive decay is an example of this. The resulting concentration trajectory through time will follow an exponential decay function. In this case the mean lifetime of the carbon atoms in the atmosphere is closely approximated by the "most of it goes away" criterion; the mean lifetime is in fact equal to the e-folding time scale, the time at which only 1/e, about 37%, of the original pulse remains. If fossil fuel CO_2 in the atmosphere was expected to diminish according to linear kinetics, then it would be possible to calculate the lifetime simply using the present-day excess CO_2 concentration in the atmosphere (about 100 ppm or 200 Pg C) and the natural uptake rate, currently about 2 Pg C / yr each into the oceans and into the land biosphere. Dividing the inventory by the flux yields an apparent lifetime of 50-100 years, depending on whether you count the terrestrial uptake in addition to the oceanic. This calculation has been most recently re-done by Jacobson (2005), who determined an "atmospheric lifetime" of 30-95 years. For the nonlinear CO_2 uptake kinetics as predicted by carbon cycle models, however, this apparent lifetime would increase with time after the CO_2 is released. Some CO_2 from the release would remain in the atmosphere thousands of years into the future, and the atmospheric lifetime calculated at that time would be thousands of years.

The most fundamental problem with the linear-kinetics formulation is that even the simplest atmosphere / ocean carbon cycle models decay to a different atmospheric CO_2 level, higher than the concentration before the spike was released. If the ocean and atmosphere were held in a non-reactive container, that excess CO_2 would remain in the

atmosphere forever, an eternal airborne fraction of the CO_2 slug of 15-40% (Archer 2005). If the ocean were infinitely large or caustic (high-pH), the airborne fraction might approach zero, but given the size and chemistry of the ocean, an airborne fraction of tens of percent can be calculated from simple thermodynamics, as if the ocean were a bucket of homogeneous seawater in equilibrium with about two buckets-full of a gas phase.

In the real world, the leftover CO_2 in the atmosphere after ocean invasion interacts with the land biosphere, and is taken up by pH-neutralization reactions with calcium carbonate ($CaCO_3$) and the CaO component of igneous rocks. The time scales for these processes range from thousands to hundreds of thousands of years. Keeling and Bacastow (1961) predicted that it would take at least 10,000 years for atmospheric CO_2 to return to preindustrial levels. Walker and Kasting (1992) reached a similar conclusion but extended the duration of the long tail to hundreds of thousands of years. Broecker and Takahashi (1978) described the neutralization reaction with $CaCO_3$. Many other carbon cycle models of a variety of configurations and resolutions (Archer 2005, Caldeira & Kasting 1993, Lenton & Britton 2006, Montenegro et al 2007, Ridgwell & Hargreaves 2007, Sundquist 1990, Tyrrell et al 2007), and essentially all of them have found the same result. The mean lifetime (or transit time out of the atmosphere) of fossil fuel CO_2 molecules has been calculated to be tens of thousands of years (Archer et al 1997), not at all similar to the 50-100 year lifetime calculated using the linear approximation based on fluxes immediately following a release of CO_2 to the atmosphere. Clearly the linear approximation, using a single characteristic time scale for the removal of CO_2 from the atmosphere, is a poor representation of the way we think the carbon cycle works. An analogy can be drawn with radioactive waste, for which the decay of its radioactivity as a

whole will not conform to any single measure, since it is composed of a variety of different radionuclides with a wide range of half-lives.

As the ocean is acidified, its ability to hold more CO_2 decreases, so that the airborne fraction of a kilogram of CO_2 is higher if lots of CO_2 has been released previously. The change in buffering provided by seawater can be readily calculated and is encapsulated in the 'Revelle Factor' (Zeebe & Wolf-Gladrow 2001). For a system in which CO_2 re-partitions only between ocean and atmosphere, an analytical expression can be derived for the CO_2 concentration in the air as a function of time (Goodwin et al 2007). To include ocean-sediment interactions, Khesghi and Archer (2004) developed an analytical Greens-function type approximation to the results of an ocean and sediment carbon cycle model. These formulations had an explicit accounting of the change in carbon buffer chemistry with ocean acidification. The buffering capacity and pH of the ocean are ultimately restored by dissolution of $CaCO_3$ (Broecker & Takahashi 1978, Ridgwell & Zeebe 2005). Even for linear uptake kinetics, the decay time scale from an impulse CO_2 release is different from the decay time scale after ongoing emissions are stopped (Caldeira & Kasting 1993, Gaffin et al 1995a), or in other words, the decay time for an additional kilogram of CO_2 depends on the state of the system into which that CO_2 is released.

As more and more CO_2 is emitted, the airborne fraction increases because of the depleted carbon buffer chemistry of the ocean, while the radiative impact of a further kilogram added to the air decreases, because of the absorption band saturation effect. Caldeira and Kasting (1992) find that these two effects largely counteract each other, so that the radiative impact of a kilogram of CO_2 is nearly independent of whether that

kilogram is released early or late in the fossil fuel era. Montenegro et al (2007) find that the logarithmic dependence of radiative forcing on CO_2 concentration acts to extend the long tail of the radiative forcing from the CO_2 to a longer time scale than they calculate from the CO_2 concentration itself.

The extent and longevity of the climate impact from CO_2 release will also depend on transient uptake by the terrestrial biosphere, taking up 2 Pg C / year today and shortening the apparent lifetime of CO_2, but which could become saturated in the coming decades, leaving pCO_2 to follow the slower uptake kinetics of the ocean (Moore & Braswell 1994). If the terrestrial biosphere including soil carbon turned into a new source of CO_2 to the atmosphere at some point in the future (Friedlingstein et al 2006), then it would act to prolong the apparent lifetime of CO_2. In addition, high plant primary productivity in a high CO_2 world may also act to enhance the rate of weathering of soil minerals and bedrock, leading to an acceleration of the longest term, silicate weathering process (Lenton & Britton 2006).

An appropriate appreciation of the lifetime(s) of CO_2 is important because the benefits of mitigating different types of greenhouse gases are compared using global warming potentials ("GWP"), which are time integrals of the radiative impacts of the different gases. The long tail of the CO_2 lifetime is a problem for calculating the global warming potentials of all gases, since CO_2 is taken to be the reference case against which other gases are compared. Most of the linear-kinetics studies (Caldeira & Kasting 1993, Gaffin et al 1995a, Moore & Braswell 1994) explicitly acknowledge that they are not considering the long lifetime of the CO_2 that remains in the atmosphere after initial equilibration with the ocean. This initial decay time scale is a useful and helpful quantity

to measure, but it is not by itself appropriate for calculating the global warming potential, because it doesn't represent the entire climate impact. In practice, the tail is generally thrown out of GWP calculations by truncating the integral at 100 years, a time scale that arises from our own lifetimes, we would argue, rather than anything intrinsic about the carbon cycle.

The 1990 IPCC report included in its Summary for Policymakers a table showing the properties of various greenhouse gases, including an atmospheric lifetime of CO_2 listed as 50-200 years, with a footnote caveat that "the way in which CO_2 is absorbed in the ocean and biosphere is not simple and a single value cannot be given….". It was carefully explained in technical Chapter 1, Greenhouse Gases and Aerosols, that on human time scales CO_2 really has no sinks, it just equilibrates between the atmosphere, ocean, and biosphere, with some residual remaining in the atmosphere after the equilibration is done. The time scale of 50-200 years was based on a pair of ocean carbon cycle model responses to a pulse CO_2 input (Maier-Reimer & Hasselmann 1987, Siegenthaler & Oeschger 1987). This 50 to 200 years represents a time scale for equilibration with the ocean, a process which leaves a significant fraction of CO_2 in the atmosphere. This time scale is not equivalent to the mean transit time of the CO_2 molecules before they are removed from the system, nor is it a statement about how long the climate impacts of CO_2 release will last. But this distinction was confused in the Summary for Policymakers where the time scale is referred to as an atmospheric lifetime, which is incorrect, and it is used to calculate global warming potentials, which is inappropriate. The footnote quoted above explains why a range of lifetimes is given, rather than a single value as for methane and other gases, but gives no indication of the new equilibrium or the long tail.

On this question, Gaffin (1995b) wrote that "the door to misunderstanding had been left open. Others have and continue to walk through it."

Subsequent IPCC reports in 1995 and 2001 compounded the mistake, revising the lower limit of the lifetime estimate down to only 5 years. Presumably the lower end of the range was a reflection of CO_2 exchange with the atmosphere or the terrestrial biosphere, although short-term uptake and release, or exchange of one carbon for another, have no impact on the altered climate. Finally the 2007 IPCC report removed the table from the summary, and wrote a bullet point that "Carbon dioxide cycles between the atmosphere, oceans and land biosphere. Its removal from the atmosphere involves a range of processes with different time scales. … The remaining 20% may stay in the atmosphere for many thousands of years." This change encountered significant resistance in internal IPCC deliberations.

To summarize, with few exceptions (Jacobson 2005) there has been no disagreement within the carbon cycle scientific community about the long tail to the fossil fuel CO_2 lifetime. But there has been considerable divergence on the way in which the behavior of that carbon pulse should be expressed and evaluated. The result has been an erroneous conclusion throughout much of the popular treatment of the issue of climate change that global warming will be a century-time scale phenomenon. Simple thermodynamics of CO_2 dissolved in seawater, plus paleo-evidence from 55 million years ago (the PETM) tell us otherwise.

A Model Intercomparison Experiment

We have assessed the range of possibilities for the long-term fate of fossil fuel CO_2 in the atmosphere, ocean, and terrestrial biosphere by means of a model intercomparison

experiment that we call LTMIP (for Long Tail Model Intercomparison Project). Model intercomparisons have proven extremely useful in climate dynamics (such as the AR4 climate forecast simulations) and paleoclimate modeling (PMIP (Weber et al 2007)), and this project takes as its template the intercomparison ocean carbon and nutrient cycling models called OCMIP (Orr 1999). In the intercomparison results we present here, we limit the time scale of our model simulations to 10,000 years, which is arguably not as long as we would like, but is still too long for primitive-equation atmosphere circulation codes. Hence most of the models in our group are streamlined in some computational way.

Models

CLIMBER-2 consists of a fully climate-responsive two-dimensional atmosphere coupled to a two-dimensional 3-basin dynamic ocean, a terrestrial biosphere model (VECODE), an oceanic biogeochemistry model, and a phosphate-limited model for marine biota (Brovkin et al 2002, Brovkin et al 2007, Ganopolski et al 1998). The sediment model resolves the diffusive pore-water dynamics, assuming oxic-only respiration and 4.5-order $CaCO_3$ dissolution kinetics (Archer 1996, Brovkin et al 2007). Weathering rates scale to runoff on the land surface grid cells, with separate carbonate and silicate lithological classes.

CC_SED was described by (Archer 2005), and uses the HAMOCC2 stationary annual mean flow field code to advect geochemical tracers. The sediment model is the same as in CLIMBER (Archer 1996). The temperature of the ocean is offset uniformly with a 1000-year response time, relaxing to a target temperature determined by a deep-ocean climate sensitivity of 3°C. A weathering feedback has been added to the

code since its description (Archer 2005), scaled to CO_2 according to Berner and Kothavala (2001), with some of the parameters as described by Berner (2004).

GENIE (Ridgwell & Hargreaves 2007) consists of a 3-D non-eddy resolving frictional geostrophic ocean circulation model, and 2-D sea-ice and energy moisture balance atmospheric models (Edwards & Marsh 2005). GENIE incorporates a representation of the marine geochemical cycling of carbon and other biologically mediated tracers and a representation of sedimentary stratigraphy and preservation of carbonates in deep-sea sediments (Ridgwell et al 2007). The sediment diagenesis zone at each ocean grid point is treated as a single (1cm) box and is coupled to an accumulating column below. $CaCO_3$ dissolution in the diagenesis zone is calculated based on the model of (Archer 1996) modified as described in (Ridgwell 2007). Carbonate and silicate weathering rates are parameterized as a function of mean global surface air temperature over land, following (Berner & Kothavala 2001) and (Lenton & Britton 2006) and are initially equal in magnitude. A fixed CO_2 out-gassing rate balances the baseline silicate weathering rate.

GENIE16 is similar to GENIE8, except it has 16 (rather than 8 depth levels in the ocean) and is seasonally insolation forced. The climate model component is described in (Singaraye et al in press).

GEOCYC is an on-line zero-dimensional descendent of the Berner and Kothavala (2001) GEOCARB III model, with the addition of time-dependent equilibration of the atmosphere and a homogeneous ocean using a time constant of 1 Pg C yr^{-1} per 300 ppm difference in surface ocean pCO_2, and with time-resolved $CaCO_3$ neutralization where the burial rate of $CaCO_3$ is a linear function of ocean $CO_3^{=}$ concentration using

a dependence of 3 E-3 Pg C yr^{-1} for every micromolar change in ocean $CO_3^{=}$ concentration, from the model results of Archer et al (1997). This model was designed for educational purposes, and can be run interactively on the web at http://understandingtheforecast.org/Projects/geocarb.html.

LTCM is a derivative of the HILDA (Shaffer & Sarmiento 1995) box advection / diffusion model with the inclusion of an OCMIP-type geochemical component. The sediment model is similar in formulation but of different origin to that used in HAMOCC and CLMBER. Weathering rates interact with climate following Berner and Kothavala (2001).

MESMO (Matsumoto et al 2008) is based on GENIE-1. In the dynamical ocean model, there are 16 vertical levels on a 36 x 36 equal area horizontal grid. In addition, there are energy-moisture balance model of the atmosphere and dynamic-thermodynamic model of sea ice. Ocean production occurs in the two layers within the top 100m and has dependence on, among other factores, the diagnosed mixed layer depth.

MPI-UW (Mikolajewicz et al 2007) consists of a coupled coarse-resolution atmospheric general circulation model ECHAM3 (Roeckner et al 1992), an updated version of the Large Scale Geostrophic ocean model (LSG) (Maier-Reimer et al 1993) which drives HAMOCC3 ocean biogeochemistry (Winguth et al 1994). The land biosphere is simulated using the dynamic vegetation model LPJ (Sitch et al 2003). In order to reduce the amount of computer time required the model has been run in periodically-synchronous mode (Mikolajewicz et al 2007) for the periods without rapid changes in atmospheric CO2 concentration. Ensemble simulations have been performed for some experiments to average out the effect of natural variability.

The simulations have been initialized with different states (1000 years apart) of the control simulation.

UVIC2.8 is the University of Victoria Earth System Climate Model, consisting of a vertically integrated, energy/moisture balance, atmospheric model with dynamic feedbacks, coupled to the MOM2 ocean general circulation model and a dynamic/thermodynamic sea-ice model (Weaver et al 2001). The horizontal resolution is 1.8x3.6 degrees and the ocean model has 19 vertical levels. The terrestrial carbon model is a modified version of the MOSES2 land surface model and the TRIFFID dynamic vegetation model (Meissner et al 2003). Ocean carbon is simulated by means of an OCMIP-type inorganic carbon-cycle model and a marine ecosystem model solving prognostic equations for nutrients, phytoplankton, zooplankton and detritus (Schmittner et al 2008). Sediment processes are represented using an oxic-only model of sediment respiration (Archer 1996). Isopycnal mixing and flux corrected transport were used in the ocean model with diapycnal diffusion specified as a horizontally constant profile. The sea-ice model is a simple, single layer, thermodynamic version, with elastic-viscous-plastic dynamics.

Methodology

The heart of the intercomparison is a series of fossil-fuel neutralization experiments. The CO_2 release is instantaneous, to simplify the analysis of the resulting atmospheric CO_2 trajectory. Pulses of 1000 and 5000 Pg C are considered, round numbers that have been used in the past. The base case calls for invasion into the ocean with no feedbacks or sediments. This provides a baseline against which the impacts of various feedbacks can be evaluated and could be regarded as a control experiment. The chemistry of the

ocean responds to the CO_2 invasion, limiting the amount of the released CO_2 slug that the ocean ultimately holds. The CO_2 drawdown trajectories tend to follow quasi-exponential decay functions toward new long-term values within the first millennium of the simulations, representing equilibration between the ocean and sediments (but not with the minerals). This response time and final state are well resolved by our simulations. We also drove the models with the historical rate of atmospheric CO_2 rise (designated Hist), to obtain a snapshot of CO_2 invasion pathway and to compare the present-day uptake rate of fossil fuel CO_2 with observations.

When possible in each model, we included the impacts of various feedbacks to the CO_2 system, including feedbacks from climate, from sediment dissolution, from enhanced weathering, and from uptake by vegetation and release by soils. The feedbacks were added cumulatively in that order, and the impact of each feedback is gauged as the difference in the drawdown of atmospheric CO_2 that results. Our definitions of feedback strength are thus experiment-dependent; we might have gotten different answers if we had layered the feedbacks in a different order. The order we chose to some extent reflects the relative certainties of the feedbacks as well as their expected magnitudes. Not all of the models in our pool have the capacity to do all of the simulations.

First, the climate feedback is added in the 'C' case. The chief impact of changing climate is via the solubility of CO_2 gas in seawater, which decreases with warming. There may also be changes in ocean circulation or ventilation patterns and rates that impact CO_2 invasion.

Sediment feedbacks are neglected in the base case, but they are added in 'S' and 'CS'. The sediment response is composed of two components, a fast pH-neutralizing reaction

of CO_2 with $CaCO_3$ on the sea floor (a process called chemical erosion) followed by a longer time-scale reaction of CO2 with carbonates on land (weathering) (Archer et al 1997, Ridgwell & Hargreaves 2007). The amount of $CaCO_3$ on the sea floor available to dissolve is limited by the formation of a clay layer on the sea floor, the nonreactive leftover material after $CaCO_3$ dissolves which impedes further $CaCO_3$ dissolution (Archer et al 1997, Broecker & Takahashi 1978). The 5000 Pg C CO_2 release is close to enough to deplete the available $CaCO_3$ stock of the ocean, leaving excess weathering over $CaCO_3$ burial to drive the CO_2 neutralization.

A weathering feedback 'W' is included in the 'CSW' case, reflecting a climate impact on the rate of chemical weathering on land, driven by excess runoff in a wetter high-CO_2 world as well as faster rates of dissolution in a warmer more acidic environment (Berner et al 1983). The weathering feedback pertains to $CaCO_3$ dissolution, as well as the dissolution of igneous rocks that ultimately controls atmospheric CO_2: the silicate weathering thermostat with its CO_2-regulating time constant of hundreds of thousands of years (Walker et al 1981).

Vegetation feedbacks are indicated by the 'V' in the simulation 'CSWV'. The impact of vegetation is to absorb carbon into biomass and soil organic matter in response to changes in atmospheric CO_2 concentration or climate.

Results

In the first millennium after the instantaneous CO_2 release the trajectory of atmospheric CO_2 is dominated by CO_2 dissolution into the ocean and transport to depth. Figure 1 illustrates this for the ocean-only base case, and together with the climate and sediment feedbacks. The equilibration time scale for ocean invasion, calculated by by a least

squares fit of an exponential to the CO_2 concentration trajectory, is about 250 ± 90 years for the 1000 Pg C release spike, and 450 ± 200 years for the 5000 Pg C release (Figure 2a). These equilibration times are conceptually the same as what IPCC called their "atmospheric lifetime" which they found to be 50-200 years, based on the modoel response to an instantaneous doubling of atmospheric CO_2 (590 Pg C). Our results here show that the equilibration time scale depends on the magnitude of the CO_2 slug, and is longer for larger slugs. The climate feedback (grey bars) increases the diagnosed equilibration time in the 5000 Pg C release cases, but had mixed impact on the 1000 Pg C model runs. In general there is less model agreement for the base case when the emission slug is large (5000 Pg C) than when it is small (1000 Pg C). The impact of the climate sensitivity however is more consistent between models when the emission slug is large.

One check on the predicted rate of CO_2 uptake in the future is to compare the historical forcing (Hist) model runs with the present-day CO_2 uptake rate of around 2.2 Pg C / year observations (Denman 2006). These are presented in Figure 2d, showing reasonable values for all models except GEOCYC, which assumes a homogeneous ocean and therefore misses nonlinearity in CO_2 uptake into a more realistic ocean.

The final equilibrium airborne fraction of the released CO_2 is shown for the ocean-only base model and for the climate feedback C model runs in Figure 2b. Without the climate feedback, the 1000 Pg C release experiments asymptote to an airborne fraction of about 20%, while the 5000 Pg C experiments equilibrate with about 35% of the CO_2 released remaining in the atmosphere. For large CO_2 release of 5000 Pg C, the airborne fraction is therefore considerably higher than the 20% claimed in the 2007 IPCC Summary for Policymakers. Primarily because CO_2 is less soluble in warmer seawater, the climate

feedback increases the airborne fraction by about 15%. Since the climate impact of the CO_2 persists as long as the CO_2 does, the climate feedback affects atmospheric CO_2 for the entire duration of the long tail.

The magnitude of the climate feedback is presented as the difference in atmospheric CO_2 concentration with the feedback and without it, in Figures 3a and 4a. The climate feedback generally diminishes after the atmosphere equilibrates with the ocean in the first millennium, but persists at a lower level for the entire 10,000 year duration of the runs. The magnitude of the climate feedback varies greatly, with the UVic2.8 model showing by far the largest feedback. Much of this appears to be due to the complex ocean biological response in this model (Ridgwell & Hargreaves 2007), with as much as half of the climate feedback attributed to changes in ocean biology (results not shown). The UVic2.8 model also shows abrupt changes in CO2 for the 1000 Pg C experiment. Abrupt warming, and accompanying increase in CO_2, is caused by flushing events in the Southern Ocean, which in this model have been shown to be dependent on the level of atmospheric CO_2 (Ridgwell & Hargreaves 2007)

The sediment feedback is primarily driven by excess dissolution of $CaCO_3$ on the time scales of these model simulations, although imbalance between the dissolution (weathering) of CaCO3 on land and burial in marine sediments is equally important on slightly longer time-scales (Lenton & Britton 2006, Ridgwell & Hargreaves 2007). The impact of the sediment feedback is generally small over the first thousand years, but grows over the 10,000 years of the simulations to result in generally more drawdown to the equilibrium state than we saw from the climate feedback (Figure 3b and 4b). The CO_2 drawdown from $CaCO_3$ dissolution follows a trajectory which is similar to an

exponential decay, with time constants derived by regression shown in Figure 2c. The Lenton and Britton model (2006) had a much faster neutralization response than this, of just 500 years, but none of our models do that. Other previous studies (Archer et al 1997, Ridgwell & Hargreaves 2007, Tyrrell et al 2007) predicted $CaCO_3$ neutralization time scales of millennia and longer, consistent with our results. It should be noted that because of the computational constraints that some of the LTMIP ensemble models are subject to, the experiments presented here are not ideal for determining the equilibrium airborne fraction after $CaCO_3$ compensation from these runs, because the ocean burial of $CaCO_3$ has not yet reached steady state with respect to weathering after 10,000 years.

The weathering feedback, an acceleration of the dissolution on land of $CaCO_3$ and calcium-bearing silicate minerals resulting from the warmer climate (Berner et al 1983, Ridgwell & Zeebe 2005), generally increases its impact on atmospheric CO_2 with time in our model runs, although the CC_SED model shows a strong peak in CO_2 drawdown in the first millennium, the time when atmospheric CO_2 is highest. By the end of the simulations, the weathering feedback has decreased atmospheric CO_2 by about half as much as the sediment feedback alone did. The global $CaCO_3$ burial rates are plotted in Figure 5, showing considerable disparity in the model results.

The vegetation feedback operates on annual to century time scales - substantially faster than the ocean feedbacks. The productivity of terrestrial plants increases instantaneously with elevated atmospheric CO_2 concentration because a physiological response of the plant stomata leads to higher water use efficiency and consequent increase in plant biomass (Denman 2006). Enhanced respiration of plant tissues and accelerated decomposition of soil organic matter due to elevated temperatures counteract this effect,

but a net result of projected changes in CO_2 and climate is an increase of the land carbon storage in most of vegetation models (Cramer et al 2001, Friedlingstein et al 2006). This is reflected in the Figure 3 and 4: a presence of vegetation feedback in the simulations substantially reduces an airborne CO2 fraction especially during the first hundred years. After this period, the ocean carbon uptake gains control over the atmospheric CO_2 concentration because of much larger buffering capacity of the ocean in comparison with the land.

While these results are in line with expected long-term vegetation feedback (Bala et al 2005, Plattner et al 2008), many uncertainties in the representation of long-term land biogeochemistry make the land feedback story more comprehensive. Modeling of soil carbon dynamics is still in its infancy: many important mechanisms, for example the priming effect of addition of fresh organic material to the soils (Fontaine 2003) or processes of anaerobic decomposition of organic matter (Frolking et al 2001) are not yet accounted for in the coupled global models. Nitrogen and phosphorus balance is ignored in most of the models (Reich et al 2006), and changes in carbonate storages in dryland soils are neglected (Lal et al 2000). Models of vegetation (forest) dynamics on a global scale are extremely simplified and difficult to validate because of long time scale involved (Purves & Pacala 2008). Finally, changes in the land carbon uptake due to future alteration of land use by humans are almost impossible to foresee. All these limitations of the land model assumptions make the simulations of the land carbon response to the CO_2 pulse presented here rather illustrative than predictive.

The mean lifetime, or CO_2 transit time back to the solid earth, depends strongly on the assumption of the time scale for the silicate weathering feedback, which is not resolved

by the duration of these model experiments or the primary focus of the modeling exercise. If we assume however that 10% of the fossil fuel remains in the atmosphere until it is neutralized by silicate weathering on a time scale of 100,000 years, then the mean lifetime of fossil fuel CO_2 for both CO_2 release scenarios, 1000 and 5000 Pg C, is about 12 - 14 kyr. Assuming a 400,000 year time constant for the silicate weathering feedback would result in mean CO_2 lifetimes of about 45 kyr. These exceed the IPCC-quoted "atmospheric lifetime" by a factor of 50 or 100, and would change the Global Warming Potentials of the other greenhouse gases by this factor. We do not argue that other greenhouse gases are unimportant by their lack of a comparable geological-time scale tail to their atmospheric residence. It makes sense to base the calculation of GWP on the time scale of the human lifetime. However, the calculation should be transparent and based on the true behavior of CO_2 in the Earth system, rather than on a misunderstanding.

Conclusions

The models presented here present a broadly coherent picture of the fate of fossil fuel CO_2 released to the atmosphere. Equilibration with the ocean will absorb most of it on a time scale of 2-20 centuries. Even if this equilibration were allowed to run to completion, a substantial fraction of the CO_2, 20-40%, would remain in the atmosphere awaiting slower chemical reactions with $CaCO_3$ and igneous rocks. The remaining CO_2 is abundant enough to continue to have a substantial impact of climate for thousands of years. The changes in climate amplify themselves somewhat by driving CO_2 out of the warmer ocean. The CO_2 invasion has acidified the ocean, the pH of which is largely restored by excess dissolution of $CaCO_3$, from the sea floor and on land, and ultimately

be silicate weathering on land. The recovery of ocean pH restores its buffer capacity to absorb CO_2, tending to pull CO_2 toward lower concentrations over the next 10,000 years. The land biosphere has its greatest impact within the first few centuries, the time of the CO_2 peak. Nowhere in these model results or in the published literature is there any reason to conclude that the effects of CO_2 release will be substantially confined to just a few centuries. In contrast, generally accepted modern understanding of the global carbon cycle indicates that climate effects of CO_2 releases to the atmosphere will persist for tens, if not hundreds, of thousands of years into the future.

Figure Captions

Figure 1. Atmospheric CO_2 trajectories for the 10,000 year duration of the model simulations. Note the split scale, expanding the action in the first 1000 years. Different line types designate the base (ocean only) simulation, the climate feedback (C), the climate + sediment feedback (CS), the climate + sediment + weathering feedback (CSW), and the climate + sediment +weathering +vegetation feedback (CSWV) cases.

Figure 2. a) Equilibration time for CO_2 invasion into the ocean. b) Equilibrium airborne fraction of CO_2 after ocean invasion, for cases with no sediment interaction. c) $CaCO_3$ dissolution response time. d) Predicted present-day CO_2 uptake rates when the models are subjected to historical (Hist) atmospheric CO_2 concentration trajectories. The real ocean took up about 2.2 Pg C / year between the comparable time interval, 1990-2000.

Figure 3. Impacts of feedbacks to atmospheric CO_2 concentration, expressed in terms of atmospheric CO_2 difference when the feedback is applied. Results from 1000 Pg C release experiments. The physically impossible positive weathering feedback for CC_SED in the first millennium is an artifact of different initial conditions for the two versions of the model.

Figure 4. As Figure 3 but for 5000 Pg C release experiments.

Figure 5. Global rates of $CaCO_3$ burial from the models.

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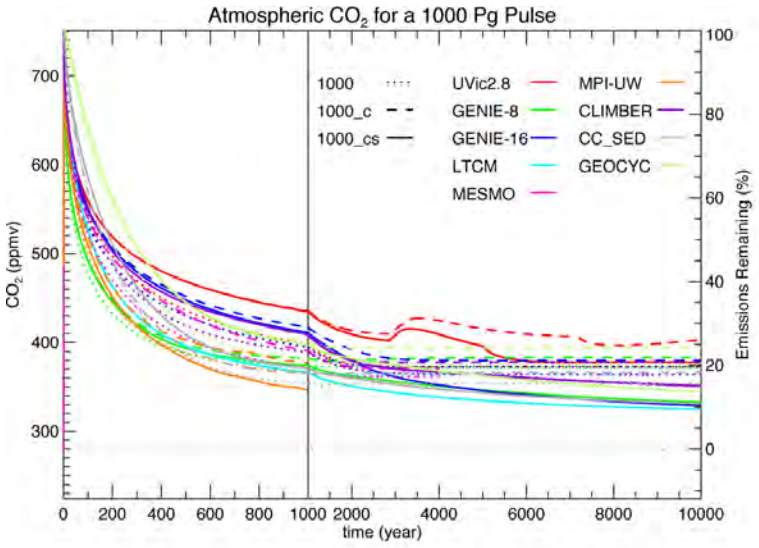
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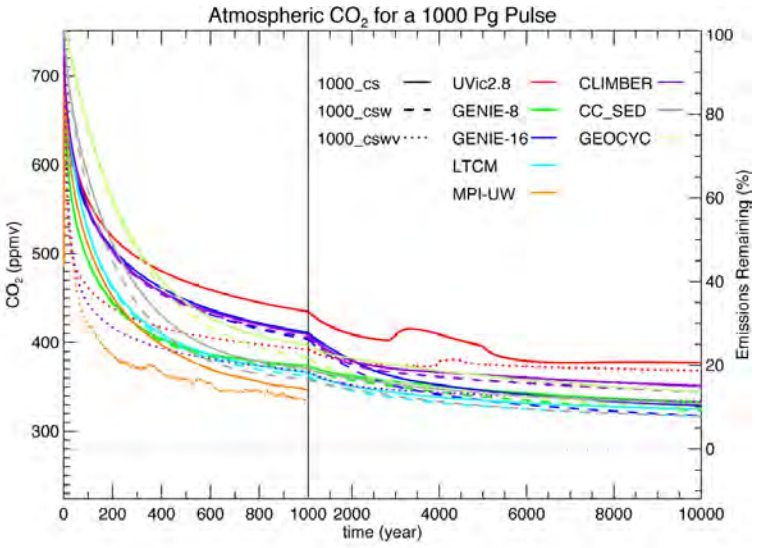
GEOCYC
CO_2 (ppmv)
Emissions Remaining (%)
time (year)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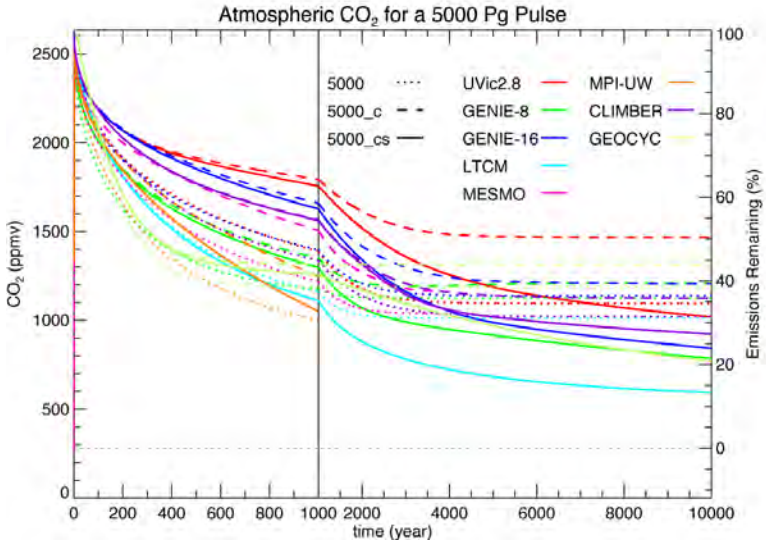
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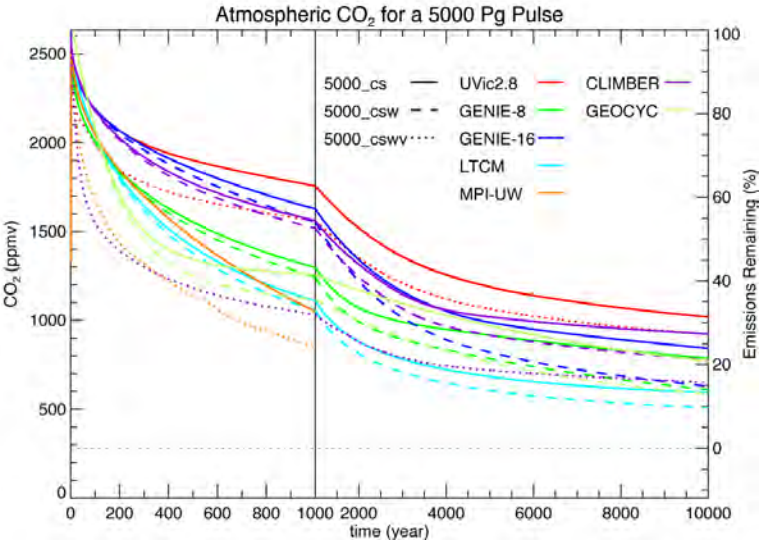
time (year)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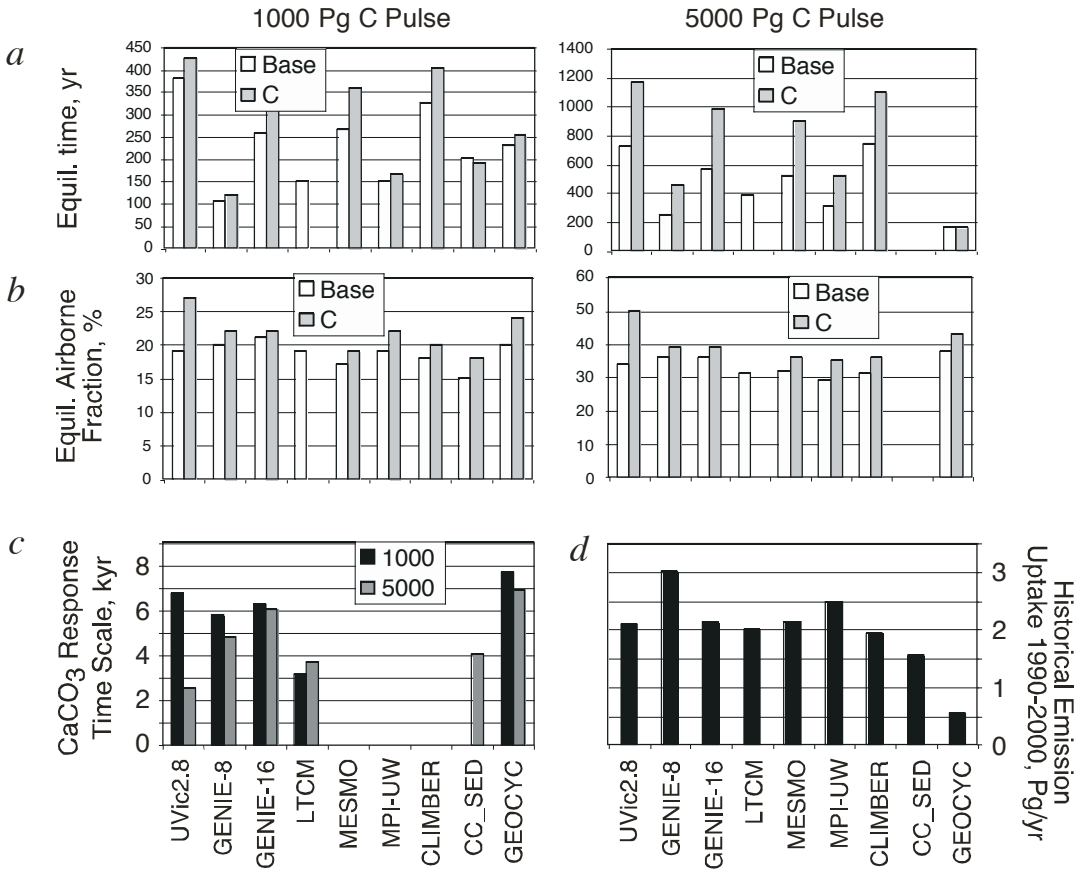
Emissions Remaining (%)
time (year)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5000 Pg C Pulse
a
Equil. time, yr
Base
C
b
Equil. Airborne Fraction, %
c
CaCO3 Response Time Scale, kyr
1000
5000
d
Historical Emission Uptake 1990-2000, Pg/yr
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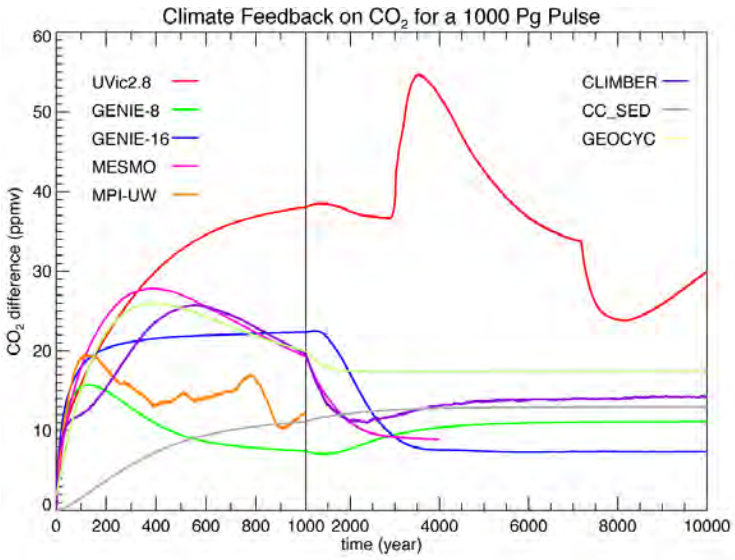
MPI-UW
CLIMBER
CC_SED
GEOCYC

Figure 2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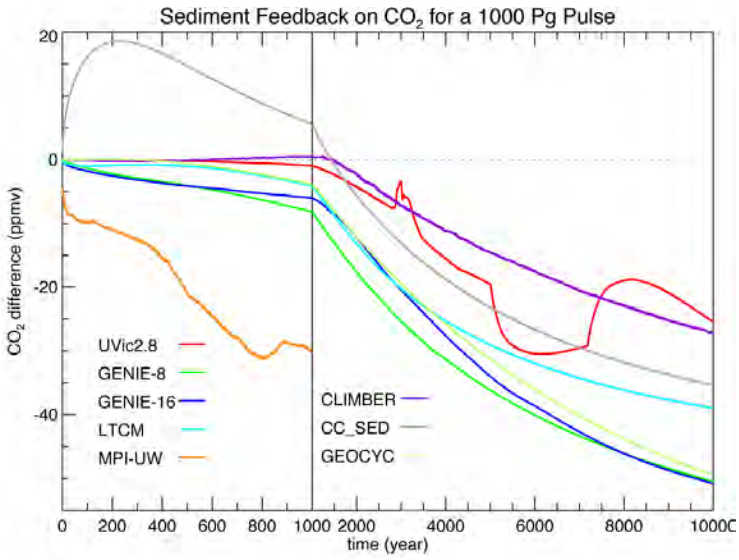
time (year)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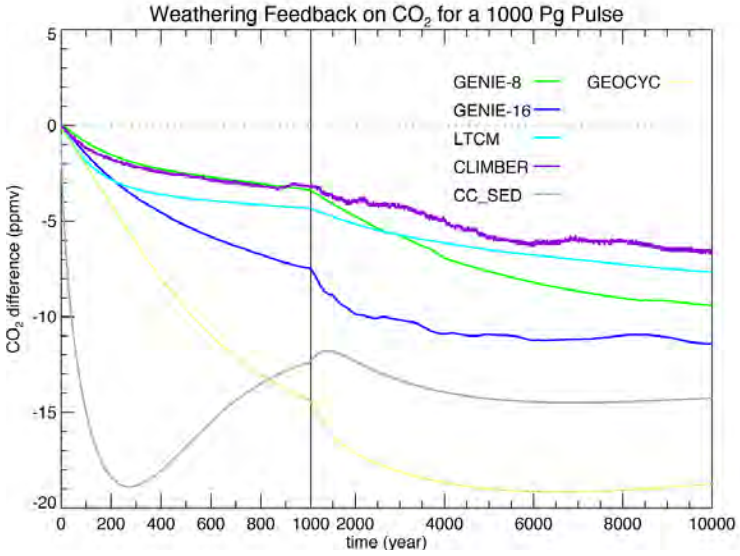
time (year)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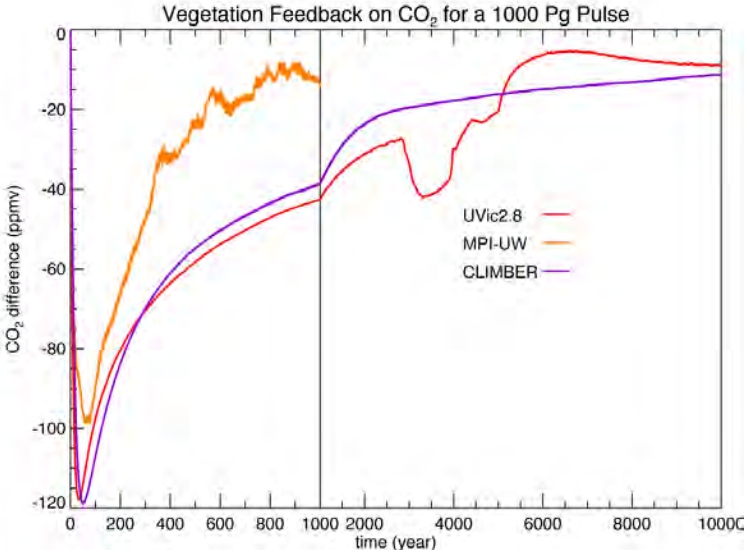
time (year)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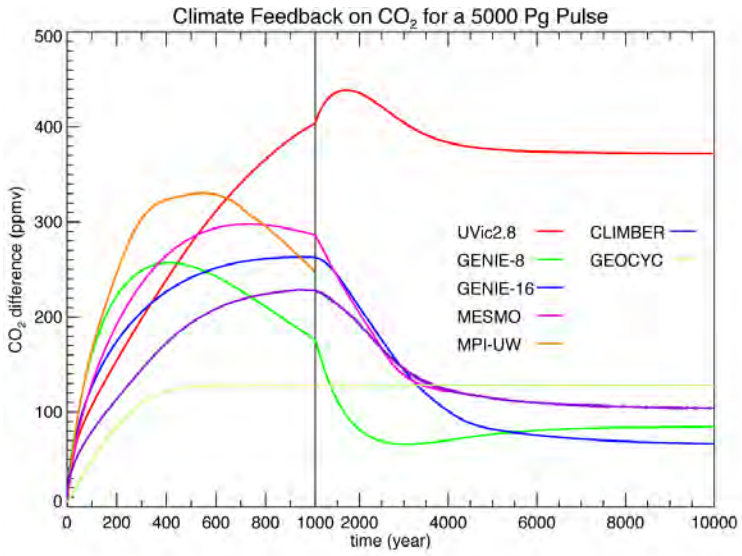
CO_2 difference (ppmv)
time (year)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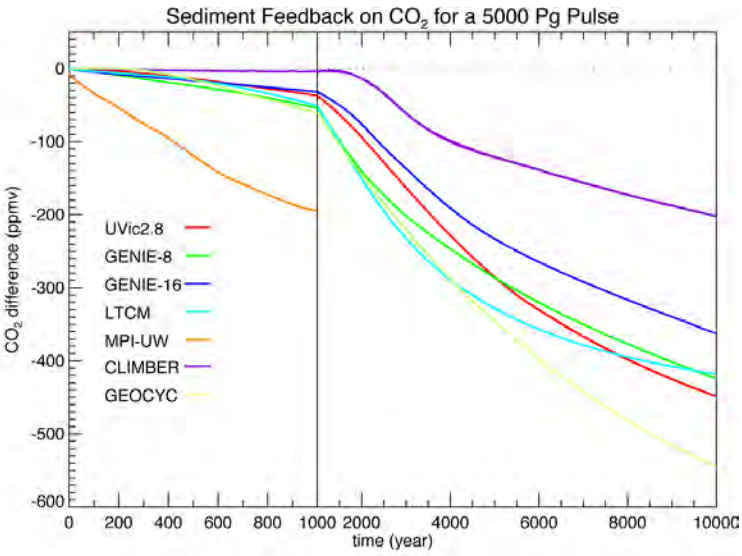
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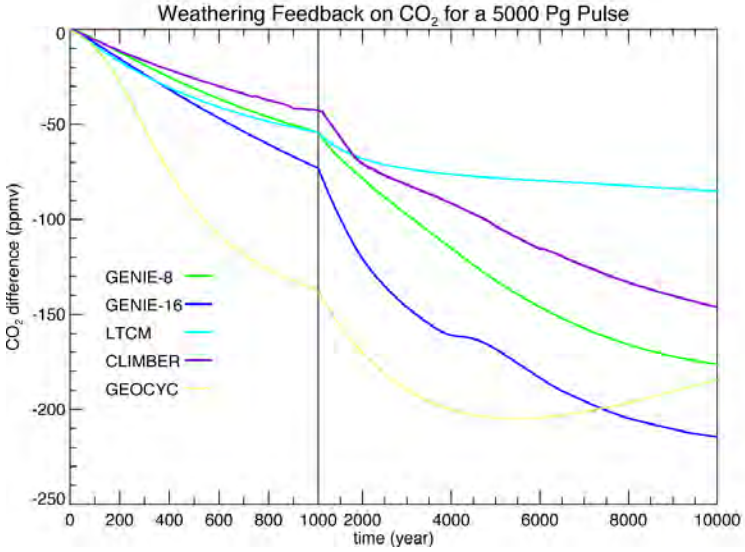
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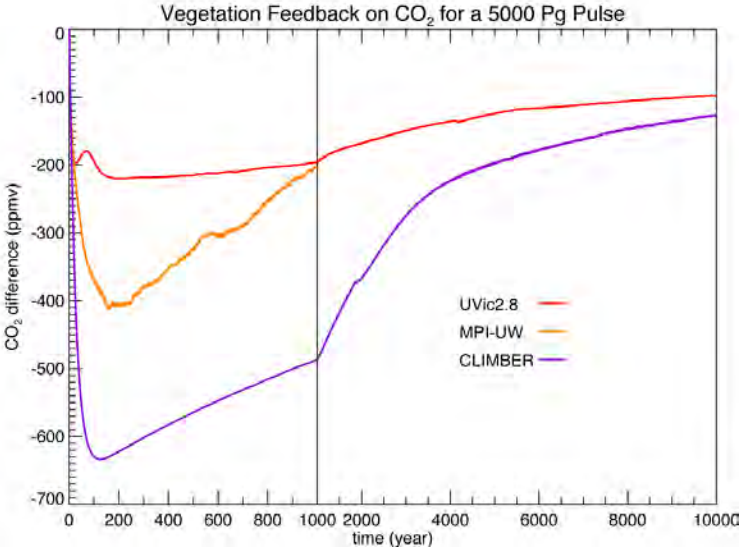
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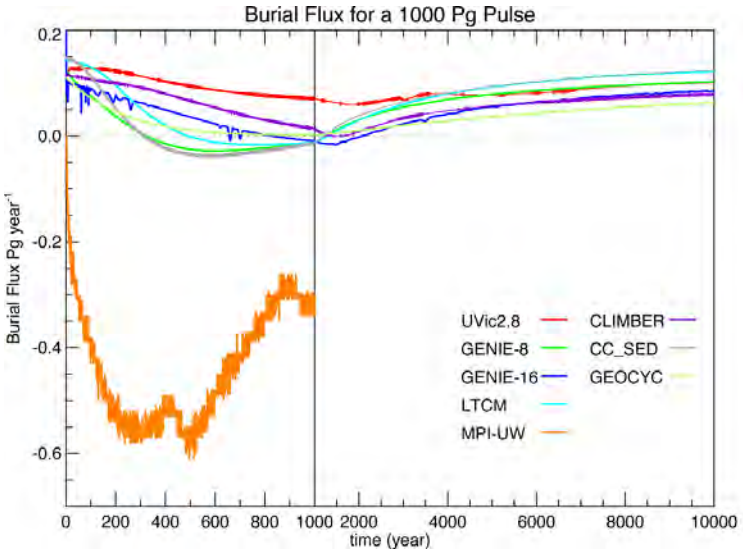
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Burial Flux Pg year-1
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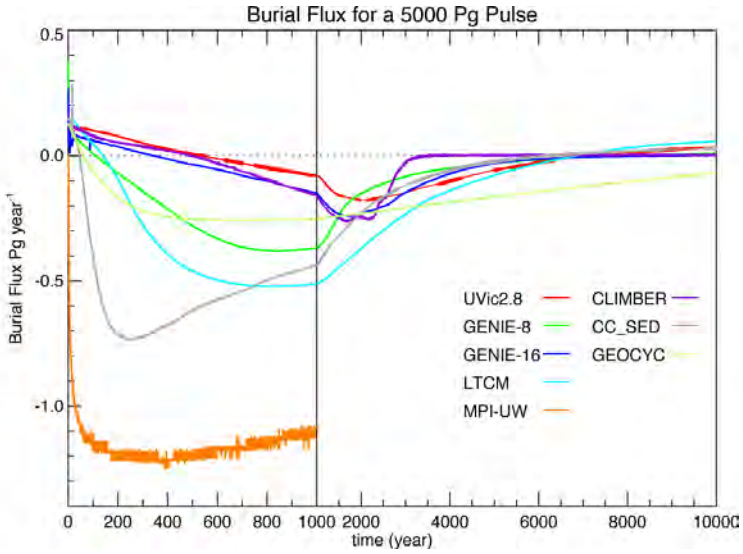
CC_SED
GEOCYC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