Observation Based Budget and Lifetime of Excess Atmospheric Carbon Dioxide

Supporting Information

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S1. Abrupt cessation profiles shown in Figure 1 of main text.

The conditions of the studies yielding decay profiles of excess atmospheric CO2 subsequent to abrupt cessation shown in **Fig. 1** of main text are summarized in **Table S1.1**

**Table S1.1**. Prior model calculations examining mixing ratio of atmospheric CO2 following abrupt cessation of emissions, for which fractional decay profiles are shown in **Fig. 1** of the main text.

|  |  |
| --- | --- |
| Reference | Conditions and data sources |
| Allen et al., 2009 | 360 ppm.; Fig. S3 *b*. |
| Zickfeld et al ., 2013 | Ensemble average and range of 12 models; 750 ppm. Fig. 6 *b*. |
| Matthews and Caldeira, 2008 | Direct calculations, Fig. 2, and impulse response functions, Fig. 1, for cumulative or pulse emissions 2000 and 5000 Pg. |
| Plattner et al ., 2008 | 650 ppm; Fig. 5 *b*. |
| Cao and Caldeira, 2010 | 500 ppm; Fig. 1 *a*. |
| Zickfeld et al ., 2012 | 840 ppm; Fig. 1 *c*. |
| Solomon et al ., 2009 | 450 ppm; Fig. 1 *a*. |
| Knutti and Plattner, 2012 | 383 ppm; Fig. 1 *b*. |
| Gillett et al ., 2011 | 370 ppm; Fig. 1 *b*. |
| Frölicher and Joos, 2010 | 370 ppm; Fig. 1 *b*. |
| Raupach et al ., 2014 | 394 ppm; Fig. 4, col 1, row 2 |
| Hare and Meinshausen, 2006 | 382 ppm; Fig. 3 *a*. |
| Joos et al ., 2013 | 100 Pg pulse added to 389 ppm; Fig. 1 *a*, Table S1. |

References to material in Figure 1 and Table S1.

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S2. Relating stocks and concentrations.

As with many quantities pertinent to the CO2 budget, the precise conversion between stocks and concentrations is of secondary importance. However in taking differences it is necessary to use consistent conversions. For this reason the conversions employed here are stated explicitly.

For the conversion of CO2 mixing ratio in dry air *x*CO2 to atmospheric stock *S*a

. (S2.1)

where *N*air is the amount (moles) of air in the global atmosphere (excluding water vapor) and *M*C is the molar mass of carbon. AR5 gives the factor CO2 = 2.12 Pg ppm-1 (Ciais et al ., 2013, caption to Figure 6.1), with a citation to Prather et al . (2012). This conversion factor does not seem to be explicitly stated in Prather et al . (2012), but the conversion factor 0.1765 Tmol per ppb of dry air, equivalent to *N*air = 1.765 × 1020 mol) is given (Prather et al ., 2012, SI file grl29135-sup-0005-ts02.doc), which, together with *M*C 0.01201 kg mol-1, yields CO2 = 2.120 Pg ppm-1. This value is used throughout the present paper. By this conversion the stock of atmospheric CO2 at the preindustrial mixing ratio taken as 278 ppm is 589.4 Pg, and the stock corresponding to the current (2016) CO2 mixing ratio 405 ppm is 858.6 Pg, yielding for the anthropogenic increment 269.2 Pg. These quantities, which are presented in **Fig. 2** of main text are used in the analysis of the preindustrial and present budgets.

The concentration of dissolved inorganic carbon DIC or of one of the three constituent species carbonic acid H2CO3 and bicarbonate  and carbonate ions is commonly given as chemical amount per mass of seawater, mol. As the budget of CO2 is commonly expressed in terms of stocks, unit typically Pg of carbon, it is necessary to relate the concentration of DIC to the stock *S*, similarly to relating atmospheric mixing ratio to atmospheric stock. A principal difference is that the stock of DIC in the ML or in the DO compartment depends on (and is proportional to) the depth taken for the compartment, *zi* = *z*m or *z*d, respectively. Thus,

. (S2.2)

where *A*o denotes the area of the world ocean, 3.619 × 1014 m2 (Eakins and Sharman, 2012) and [DIC]vol*,i* denotes the volumetric concentration, mass per volume, here, kg m-3, in the respective compartment. [DIC]*m/v* is related to concentration in the more customary unit for this quantity, [DIC](mol) as

. (S2.3)

where **sw is the density of seawater (1025 kg m-3), and *m* denotes the DIC concentration in molality units  from which, for either compartment

, (S2.4)

or. (S2.5)

For the preindustrial burden of DIC in the mixed layer as calculated with the CO2SYS program (Lewis and Wallace, 1998) for CO2 mixing ratio taken as 278 ppm (and alkalinity 2349 µmol, temperature 18˚C, and salinity 35 as used throughout this paper), the corresponding equilibrium concentration of DIC is 2020 µmol, and the equilibrium stock of DIC in the ML is 900 Pg. Similarly for *z*d = 3583 m, (Eakins and Sharman, 2012) and preindustrial deep ocean DIC 2250 µmol, (Key et al ., 2004; McKinley et al ., 2017) *S*d = 36823 Pg, as given in **Fig. 2**.

S3. Equilibrium solubility of CO2 in ocean surface water.

The equilibrium solubility of CO2 in seawater directly affects the distribution of excess CO2 between the atmospheric and mixed–layer compartments. As noted in the main text **§2**, the equilibrium concentration of DIC in seawater exhibits a sublinear dependence on CO2 mixing ratio; *i.e*., solubility decreasing with increasing CO2 mixing ratio *x*CO2. For the analysis presented here the solubility of CO2 was calculated with the program CO2SYS (Lewis and Wallace, 1998) for temperature 18˚C, representative of the mean for the global ocean, and for alkalinity 2349 µmol, selected to obtain preindustrial stock of DIC equal to 900 Pg as given in previous analyses. Equilibrium DIC is shown in **Fig. S3.1** for the entire range of *x*CO2 and in **Fig. S3.2*a*** for the range of *x*CO2 pertinent to the Anthropocene. The sublinearity of the dependence of DIC on *x*CO2, which is manifested in the relative increase of *S*m over the Anthropocene being much less than that of *S*a, **Fig. 2** of main text, has the effect of distributing anthropogenic CO2 increasingly into the atmosphere versus the ocean.

The equilibrium ratio of the stocks in the atmosphere and the ML, of interest in the interpretation of the results obtained here, is obtained from **Eqs S2.1 and S2.4** as

 (S3.1)

f3

fS3.1TCO2 vs pCO2 0909.pxpG0\_18.eps

**Figure S3.1**. Dependence of the equilibrium aqueous concentration [DIC], left axis, and mixed-layer stock *S*m, right axis, of dissolved inorganic carbon, *i.e.*, total CO2, on the atmospheric dry-air mixing ratio *x*CO2 or stock *S*a of CO2. *S*m is calculated for mixed layer depth *z*m = 100 m, ocean temperature, 18 ˚C and total alkalinity, 2349 µmol. SI data table, sheet 2.

More pertinent to changes over the Anthropocene is an equilibrium constant defined for the anthropogenic enhancement of these quantities as

, (S3.2)

where  denotes the anthropogenic enhancement of the molal concentration of DIC, as a function of CO2 mixing ratio, and similarly for, shown in **Fig. S3.2*b***. ispertinent to the dependence of the turnover time of stocks in the combined atmosphere–ML compartment  on the stocks and on depth of the ML **SI Text §S7**, the small magnitude of this ratio relative to unity leading to the insensitivity of the turnover time to choice of these parameters. Also shown, **Fig. 3.2*c*** is the equilibrium fraction of the stocks in the AC and the ML present in the AC, a = *S*a/(*S*a + *S*m), a quantity used in solution of the differential equations describing the temporal evolution of the stocks in the several compartments (**Eq 11**), and the equilibrium ratio of the anthropogenic stocks in the two phases.

fS3

fS3.2 TCO2 vs pCO2 0909.pxpLayo.eps

**Figure S3.2**. *a*, Dependence of the equilibrium aqueous concentration [DIC], left axis, and mixed-layer stock *S*m, right axis, of dissolved inorganic carbon, *i.e.*, total CO2, on the atmospheric dry-air mixing ratio *x*CO2 or stock *S*a of CO2, as in **Fig. S3.1**, but limited to range of *x*CO2 pertinent to the Anthropocene. Open circles denote 20-year intervals of atmospheric *x*CO2, 1750-2010; points are also shown corresponding to preindustrial PI, 1750; the beginning of contemporaneous measurements, 1959; the present, 2016; and twice preindustrial, 2 × PI. *b*, Equilibrium ratio of anthropogenic stocks (i.e., stocks in excess of preindustrial) in ML to AC, left axis, or of anthropogenic increase of concentration in ML to anthropogenic mixing ratio in AC, right axis. *c*, Equilibrium fraction of stock in AC, a = *S*a/(*S*a + *S*m). SI data table, sheet 2.

S4. Anthropogenic emissions of CO2

Emissions employed in this study, **Fig. S4.1**, are taken mainly from the tabulation of Le Quéré et al . (2018*a*). Estimates of LUC emission are not available for years 1750–1850. Although emission prior to 1850 was small relative to cumulative emission over the Anthropocene, it is not negligible with respect to the present examination of anthropogenic perturbation to the CO2 budget, the estimate for *Q*lu for year 1850 being 0.67 Pg yr-1. In order not to bias the present analysis by setting *Q*lu prior to 1850 equal to zero, this emission was estimated as a linear ramp from 0 in 1750 to 0.67 Pg yr-1 in 1850. LUC emission estimated this way comprises virtually all of the emissions prior to 1850; however the cumulative LUC emission (1750-1849) estimated in this way, 33 Pg, comprises only about 5% of cumulative anthropogenic emission of CO2 over the period 1750 - 2016. Emission data are presented in SI data table, sheet 3.

fS4

fS4.1 Emissions.eps

**Figure S4.1** Annual (*a*) and cumulative (*b*) CO2 emission over the Anthropocene. Data source: Le Quéré et al . (2018*a*), based for *Q*ff on Boden et al . (2017) and for *Q*lu on Houghton and Nassikas (2017) and Hansis et al . (2015), extended from 1750 to 1850 by a linear ramp; *Q*tot= *Q*ff + *Q*lu. SI data table, sheet 3.

As shown in **Fig. S4.1** emissions from land-use change *Q*lu exceeded emissions from fossil fuel production and cement production *Q*ff until as recently as about 1950, but subsequently *Q*ff increased rapidly and is now the dominant contribution, ~89%, to total emissions. Cumulative emissions from land-use change exceeded those from fossil fuel combustion and cement production until the mid 1980's. These cumulative emissions are shown in **Fig. 2** of main text as decreases in the boxes denoting the stocks of the terrestrial biosphere and fossil fuel reserves.

S.5 Annual increment in atmospheric stock

The annual increment in the atmospheric stock *S*a, , is central to observational determination of the anthropogenic CO2 budget. This annual increment, shown in **Fig. S5.1** for the entire period of contemporaneous measurements of CO2 in air as tabulated by Le Quéré et al . (2018*a*), is based on measurements of Keeling and colleagues initially at Mauna Loa and Antarctica (Keeling et al ., 1976; 2001 as updated), subsequently extended to a global network (Ballantyne et al ., 2012, as updated by Dlugokencky and Tans, 2018), from which the present annual increment is estimated as 5.17 ± 0.42 Pg yr-1, where the uncertainty reflects the uncertainty associated with the intercept at year 2016 of least squares fits to the data over two periods, 1998–2016, and 2001–2016, yielding estimates of present (2016) value of *dS*a/*dt* and associated uncertainty, 5.14 ± 0.45, and 5.21 ± 0.40 Pg yr-1, respectively. The scatter in the data arises from fluctuations in the rates of removal processes and/or annual emission. The annual increment represents about half of current emissions (46 ± 5%), where the uncertainty takes into account uncertainty in  and *Q*tot. The annual uptake of current emissions by dissolution into the ocean and by the terrestrial biosphere, obtained by difference, is 6.07 ± 0.96 Pg yr-1, or 54 ± 5% of annual emissions. Results from the present model closely track the observations but exhibit much less year-to-year variation than the observation-derived growth rate because of constant transfer coefficients employed in the model.

fS5

fS5.1 dSa\_dt.eps

**Figure S5.1**. Annual rate of increase in atmospheric stock of CO2 *dS*a/*dt* based on differences in annual mean atmospheric mixing ratio of CO2. Data from Le Quéré et al . (2918*a*). Line segments represent linear fits to data; error bars represent uncertainties in present (2016) value of *dS*a/*dt* for the two fits. Also shown are results from present model for (, *b*) = (500 Pg, 0.3). **SI data table, sheets 4, 6.**

S6. Dependence of adjustment time on functional form of CO2 emission rate.

Because of concern (Joos, 2013; also, O'Neill et al ., 1994; Raupach, 2013) that the adjustment time might be influenced by the emissions of CO2 being approximately exponential with time and the constant ratios of eigenvectors in the solution of the differential equations that would result from such an exponential forcing term, the adjustment time of excess CO2 was examined for the model run with emissions approximated by a linear function of time from 1925 to 2016, shown by the dashed lines in **Fig. S6.1*a***. The resulting adjustment time was determined as a fit to decay of excess atmospheric CO2 following abrupt cessation of emissions, as in **Fig. 12*a*** of main text, shown in **Fig. S6.1*b***, and also as the equivalent 1/*e* lifetime **E, **Eq 2.6** of main text, and compared in **Fig. S6.1*c*** with the result for the historical emissions. Both means of determining the lifetime for this very different emission profile yield values that are in essential agreement each other and with the values determined for historical emissions, demonstrating that the value of the lifetime is not a consequence of the approximately exponential growth of historical emissions.

fS6

**Figure S6.1**. Linear approximation to anthropogenic emissions. *a*, Historical emissions and linear approximation. *b*, Mixing ratio of atmospheric CO2 as calculated with present model for historical emissions and for linear approximation from 1750 to 2016 and with emissions reduced to 0 in 2017; both calculations are for (, *b*) = (400 Pg, 0.6). Also shown is observed CO2 mixing ratio as in **Fig. 8** of main text. Magenta and cyan dashed curves are fits of excess CO2 to exponential decay to 278 ppm for historical emissions and linear approximation, respectively, over the initial 100 years subsequent to cessation, with indicated time constants. *c*, Equivalent 1/*e* lifetime **E of excess atmospheric CO2 for historical emissions and for linear approximation. SI data table, sheet 6.

Also of note in **Fig. S6.1*b*** is the close approach of the model results with the linear emissions profile to the observations subsequent to about 50 years after initiation of the linear emissions. This result suggests that under conditions of increasing emissions, at any given time there is little memory of emissions history prior to about one adjustment time before the time of interest.

S7. Numerical modeling

As noted in the text (**§5**) the differential equations (**Eq 6.1-6.5**) consist of expressions for the rates of change of the stocks in the several compartments *S*i that are functions of the present values of these stocks, with transfer coefficients *k*ij, as well as of external forcings, *Q*ff and *Q*lu, that are functions of secular time, where the stocks at the time of evaluation are obtained from the previous time step in the solution of the equations. For the most part the transfer coefficients are constants, independent of time (or of the stocks) except for the coefficient describing the transfer of CO2 from the ML to the atmosphere, which, through detailed balance considerations, depends on the equilibrium solubility of CO2 at the time of evaluation, being dependent on the concentration in the surface water, and hence the stock in the ML. The rates of transfer between the AC and the ML in **Eqs 6.1 and 6.2** are thus evaluated in terms of the departure of the actual stock *Si* and the stock that would be in equilibrium between the two phases for the sum of the two stocks at the time of evaluation. This local equilibrium distribution depends on the amount of *S*am, or equivalently on equilibrium CO2 mixing ratio, and can (and can only) be evaluated numerically from the equilibrium constants, total alkalinity, temperature and other controlling variables. The transfer coefficient *k*am denotes the global mean transfer coefficient of CO2 from the AC to the ML. The coefficient describing the rate of transport from the ML to the AC  is evaluated as, where  is the differential equilibrium constant between *S*m and *S*a (**Eq 2**; **Appendix B** of main text, **Eq B15, Fig. B1**).

 (6.1)

 (6.2)

 (6.3)

. (6.4)

 (6.5)

The function IntegrateS(tt, S, dSdt) listed below evaluates the derivatives of the stocks dS[i]/dt required by the ODE solver (here in the Igor Pro software package; www.wavemetrics.com). The function is called by the ODE solver at variable time step to achieve specified convergence of solution. Input to function is current values of the stocks S[i] at the time tt of the call, together with other variables: emissions Qtot and Qlu, functions of secular time; differential equilibrium constant  (variable name KKpma), function of *S*am; equilibrium distribution fraction aq (variable name Phi\_aeq), function of *S*am; riverine flux Ftm\_pi, and particulate flux from ML to DO Fpc. Phi\_aeq and KKpma are evaluated at run time by interpolation in tables of Phi\_aeq and KKpma versus *S*am calculated offline using CO2SYS (Lewis and Wallace, 1998; Pierrot et al ., 2006); attempts to solve the differential equations using regression fits failed, necessitating the interpolation.

Function IntegrateS(tt, S, dSdt)

// Denotes comments

// tt, time since initiation of run

// S[i] = Sa, Sm, Sd, Sl, So for i = 0 ... 4; //Stocks to be calculated

// dSdt[i] = dSa/dt, etc. //Derivatives to be calculated

//---Constant variables (may depend on parameters Sl\_pi and bexp)

Variable /G bexp // Fertilization exponent b

Variable /G Fom\_pi // Riverine flux

Variable /G Fpc // Particulate flux ML to DO

Variable /G FGPPpi //PI GPP

Variable /G Sa\_pi, Sm\_pi, Sd\_pi, Sl\_pi, So\_pi //PI stocks

Variable /G Sa\_pd, So\_pd, SoAntpd //PD stocks

Variable /G FGPPpd = FGPPpi\*(Sa\_pd/Sa\_pi)^bexp //power law dependence of GPP on Sa

Variable /G dSapddt //PD rate of increase in Sa

Variable /G Upsilon = bexp\*(Sa\_pd/Sa\_pi)^bexp \* dSapddt/Sa\_pd //intermediate variable

Variable /G dSlpddt = Upsilon\*Sl\_pi // derivative; chain rule; calculated for specified Sl\_pi and bexp

Variable /G dSbpddt //PD rate of increase in TB due to transfer to/from from other compartments; does not include emissions from OB

Variable /G dSopddt = dSbpddt- dSlpddt //by difference; does not include emissions from OB

Variable /G kmd, kdm //transfer coefficients

Variable /G kla = FGPPpi/Sl\_pi

Variable /G Faopi = (dSopddt - Fom\_pi\*SoAntpd/So\_pi)/((Sa\_pd/Sa\_pi)^bexp - So\_pd/So\_pi)

Variable /G koa = (Faopi - Fom\_pi)/So\_pi

//---Time-dependent variables

Variable yeartt= tt+1740   
//secular time variable. Integration starts at 1740

Variable Sam = S[0] + S[1]   
//Value at the beginning of time step;

Variable Phi\_a = Interp(Sam, Sameq, Phi\_aeq)   
//Phi\_aeq = Saeq/(Saeq + Smeq) (calculated offline)

Variable Phi\_m= 1-Phi\_a   
// complement of Phi\_a

Variable V\_Saeq = Sam\*Phi\_a   
// Equilibrium amount of Sa for specified Sam

Variable V\_Smeq = Sam\*Phi\_m   
// Equilibrium amount of Sm for specified Sam

Variable V\_KKpma = Interp (Sam, SameqPgC, KKpma)   
//local value of KKpma, the differential eq constant between Sm and Sa as fn of amount of CO2, here Sam

Variable QQQ = Qtot[floor(yeartt-1740)]  
// Total annual emission as fn of time, from table; = Qff + Qlu

Variable QQlu = Qlu[floor(yeartt-1740)]  
// LUC Emission as fn of time, from table

//---Expressions for derivatives

dSdt[0] = QQQ -kam\*(S[0] -V\_Saeq) +kam\*V\_KKpma\*(S[1] -V\_Smeq) - FGPPpi\*(S[0]/Sa\_pi)^bexp + kla\*S[3] - Faopi\*(S[0]/Sa\_pi)^bexp + koa\*S[4]//Sa

dSdt[1] = kam\*(S[0] -V\_Saeq) -kam\*V\_KKpma\*(S[1] -V\_Smeq) -kmd\*S[1] +kdm\*S[2] +Fom\_pi -Fpc //Sm; Adding preindustrial Fom\_pi flux here; loss of Fpc

dSdt[2] = kmd\*S[1] -kdm\*S[2] + Fpc //Sd; Only exchanges are with Sm

dSdt[3] = FGPPpi\*(S[0]/Sa\_pi)^bexp -kla\*(S[3]) //Sl

dSdt[4] = Faopi\*(S[0]/Sa\_pi)^bexp -koa\*(S[4]) - Fom\_pi -QQlu //So

Return //returns values of stocks S[i] and derivatives dSdt[i] at times tt

End