

Comment on “*Scrutinizing the carbon cycle and CO₂ residence time in the atmosphere*” by H. Harde

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Abstract

Harde (2017) proposes an *alternative accounting scheme* for the modern carbon cycle and concludes that only 4.3% of today’s atmospheric CO₂ is a result of anthropogenic emissions. As we will show, this *alternative scheme* is too simple, is based on invalid assumptions, and does not address many of the key processes involved in the global carbon cycle that are important on the timescale of interest. Harde (2017) therefore reaches an incorrect conclusion about the role of anthropogenic CO₂ emissions. Harde (2017) tries to explain changes in atmospheric CO₂ concentration with a single equation, while the most simple model of the carbon cycle must at minimum contain equations of at least two reservoirs (the atmosphere and the surface ocean), which are solved simultaneously. A single equation is fundamentally at odds with basic theory and observations. In the following we will (i) clarify the difference between CO₂ atmospheric residence time and adjustment time, (ii) present recently published information about anthropogenic carbon, (iii) present details about the processes that are missing in Harde (2017), (iv) briefly discuss shortcoming in Harde’s generalization to paleo timescales, (v) and comment on deficiencies in some of the literature cited in Harde (2017).

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1. Residence time versus adjustment time

The global carbon cycle is currently not in a steady state as shown, for example, by measurements of atmospheric CO₂ concentration at Mauna Loa (Hawaii) and at the South Pole since 1958 (Dlugokencky et al., 2016). The main reason for this increase is the addition of ‘anthropogenic CO₂’ by burning of coal, oil, and gas, industrial processes and land use change (Le Quéré et al., 2016). In the case of non-steady state conditions one can ask the question: How long will the perturbation (here: higher atmospheric CO₂ concentration) stay? If one adds a certain amount of anthropogenic CO₂ to the atmosphere at time t_0 , the concentration will increase suddenly and then fall off following a complicated function that depends on the response of the various active carbon reservoirs (surface ocean, intermediate and deep ocean, marine sediments, terrestrial biosphere). The time connected to such a relaxation in atmospheric CO₂ concentration is the **adjustment (or equilibration) time** and the timescale of interest for the problem at hand. The function how CO₂ relaxes after such an initial perturbation can be approximated by the sum of a few exponential functions with different characteristic timescales (e.g. Archer et al., 1997; Lord et al., 2016). Simple one-box models suggest adjustment times of about 70 years, but these models ignore many relevant processes and consequently under-estimate this timescale (Cawley, 2011). More complex models suggest adjustment (equilibration) times of well over 100 years, and that it depends on total anthropogenic emissions (Archer et al., 2009; Joos et al., 2013; Lord et al., 2016). When anthropogenic CO₂ is added continuously one has to run a global carbon cycle model that takes into account the responses by the various reservoirs mentioned above (e.g. Friedlingstein et al., 2006; Jones et al., 2013).

The timescale determined in Equations (7) and (8) in Harde (2017) is actually an approximation of the **residence time**, i.e. the average length of time for which an individual molecule of CO₂ remains in the atmosphere before be-

ing taken up by the ocean or terrestrial biosphere. Given the fluxes into, and
30 out of, the atmosphere, we would expect a CO₂ molecule to only remain in the
atmosphere for a few years, before being replaced by a molecule from one of
the other reservoirs. The usual misunderstanding is that this is CO₂ leaving
the atmosphere, rather than mostly just being exchanged, leaving no change in
atmospheric CO₂ concentration. Even though the numbers presented in Harde
35 (2017) are reasonable approximations for the residence time, they are largely
irrelevant for what the paper later presents.

Changes in atmospheric CO₂ concentration following the initial perturbation
depend on the net CO₂ flux out of the atmosphere, rather than - as in the case
of the residence time - depending only on the flux into the natural sinks. Note
40 that the residence and adjustment times refer to different and distinct aspects of
the carbon cycle and have different definitions; a distinction clearly made in the
IPCC First Assessment Report (Houghton et al., 1990, §1.2.1) as well as in more
recent reports (Stocker et al., 2013, p. 1457). Thus to conflate residence time
and adjustment time is a fundamental misunderstanding of the carbon cycle.

45 Given this difference between the residence time (years) and adjustment
time (centuries to millennia) we would also not expect an enhancement in at-
mospheric CO₂ to be entirely composed of molecules of directly anthropogenic
origin, even if the cause for such an enhancement were entirely anthropogenic.
Therefore, the claim in Harde (2017) that the anthropogenic contribution makes
50 up only 15% of the increase since the industrial era - even if correct - is not an
indication that the increase is not entirely anthropogenic.

2. Most recent anthropogenic carbon inventory

Total anthropogenic CO₂ from fossil fuel and cement production emitted
between 1750 and 2010 has accumulated to 365 PgC (Le Quéré et al., 2016). A
55 further 153 PgC was emitted in the same time interval from land use changes
(Le Quéré et al., 2016). In 2010 the atmospheric CO₂ concentration was approx-
imately 390 ppm (Dlugokencky et al., 2016), a value that features prominently

in the calculations of Harde (2017).

Anthropogenic carbon in the ocean can be tracked by various methods, e.g. the ^{13}C Suess effect (Eide et al., 2017), ΔC^* method (Gruber et al., 1996), or anthropogenic produced substances, such as CFCs (Lauvset et al., 2016). Various approaches have shown that the oceanic sink accounts for 48% of the total fossil-fuel and cement-manufacturing CO_2 emissions of 118 PgC emitted between 1800 to 1994 (Sabine et al., 2004). Landschützer et al. (2016) calculated an increase in anthropogenic carbon in the ocean of about 60 PgC released by fossil-fuel and cement-manufacturing CO_2 emissions between 1982 and 2012. Taking the temporal overlay of both studies into account, we find an anthropogenic carbon inventory of the fossil-fuel and cement-manufacturing CO_2 emissions 1800–2012 in the ocean of about 150 PgC. This is 41% of the accumulated emission from fossil fuel and cement production, or 29% of the total emissions including land use change. In this scenario, the rise in atmospheric CO_2 from a preindustrial value of 278 ppm (= 589 PgC) before 1750, to 390 ppm (= 827 PgC) in 2010 is solely due to anthropogenic emissions. They overprint any potential natural CO_2 outgassing from the ocean (see the decomposition of anthropogenic and natural fluxes between ocean and atmosphere in Gruber et al. (2009)). The rise in the atmospheric carbon reservoir by 112 ppm, or 238 PgC, corresponds to an airborne fraction of 46% of the total anthropogenic emissions of 518 PgC. The missing residual of the anthropogenic emissions of 130 PgC is assigned to terrestrial carbon uptake.

According to Harde (2017), 4.3% of the actual atmospheric CO_2 concentration is of anthropogenic origin. With an atmospheric CO_2 concentration of 390 ppm used in Harde (2017), reached in ~ 2010 , this is similar to a proposed anthropogenic CO_2 concentration of about 17 ppm or 36 PgC. It would imply that only 7% of the total anthropogenic emissions remained airborne. The airborne fraction of Harde (2017) is therefore a factor of 6.6 smaller than in the inventory that is supported by observational-based studies. If the approach in Harde (2017) was correct, it would directly asked for evidence where this anthropogenic carbon has been stored. Unfortunately, no further evidence for

this storage has been given in the paper and as we have shown above, it cannot
90 reside in the ocean.

3. Why is the Harde model too simple?

The core argument in Harde (2017), section 3, is about the lifetime of anthropogenic CO_2 in the atmosphere, closely related to the airborne fraction that remains after a given time. A framework is then developed in which both natural
95 and anthropogenic carbon fluxes are analysed. In this framework one important part of the carbon cycle, which is of major relevance for the airborne fraction of CO_2 , is missing: the carbonate chemistry in the ocean. It is correctly stated that Henry's Law governs the net gas exchange of CO_2 between the surface ocean and the atmosphere, with higher temperatures leading to a higher net flux to the
100 atmosphere. However, within the ocean CO_2 molecules react with water to form carbonic acid (H_2CO_3) which subsequently dissociates into hydrogen ions (H^+) and bicarbonate ions (HCO_3^-). In a second step the HCO_3^- -ion dissociates into another H^+ -ion and a carbonate ion (CO_3^{2-}). The sum of all these carbon species is typically referred to as dissolved inorganic carbon (DIC). For present day conditions the fraction of carbonic acid is negligible; the majority of DIC ($\sim 90\%$)
105 is found as HCO_3^- , $\sim 9\%$ as CO_3^{2-} , and only about 1% is found as dissolved CO_2 (Zeebe & Wolf-Gladrow, 2001). Only this 1% of DIC in the surface ocean, found as dissolved CO_2 , can exchange with the atmosphere. Thus, the carbonate chemistry represents a bottleneck for the oceanic uptake of anthropogenic CO_2
110 emitted to the atmosphere. Note, that the basic knowledge on the marine carbonate system, which is completely neglected in Harde (2017), is at least 60 years old, e.g. see Revelle & Suess (1957) and references therein. Furthermore, different software packages to compute the marine carbonate chemistry have been published in the meantime (e.g. Orr et al., 2015), and are in most cases freely
115 available, e.g. see <http://cdiac.ornl.gov/ftp/oceans/co2sys/> for different versions of the package CO2SYS which was widely discussed in Orr et al. (e.g. 2015) or https://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csyst.html

for Matlab routines to Zeebe & Wolf-Gladrow (2001).

This effect of the carbonate chemistry on the carbon cycle is not a theoretical
120 concept, but an observed quantity also known as the Revelle (or buffer) factor R .
This is a fundamental property of the marine carbonate system and is implicitly
considered in marine carbon cycle models underlying the analyses summarized
in the IPCC-AR5, the 5th Assessment Report of the Intergovernmental Panel
on Climate Change (Stocker et al., 2013). The carbonate chemistry in seawater
125 describing these processes in detail is well known (compare, for example Dickson
et al., 2007; Zeebe & Wolf-Gladrow, 2001). The Revelle factor is defined as the
ratio of the relative change of dissolved CO_2 to the relative change of DIC and
can be readily calculated:

$$R = \frac{\Delta\text{CO}_2/\text{CO}_2}{\Delta\text{DIC}/\text{DIC}} \quad (1)$$

From open ocean data it is known that R varies between 8 and 15 (Sabine
130 et al., 2004). A Revelle factor of 8, for example, leads to a DIC increase by
only 12.5% for a doubling of dissolved CO_2 . A rise in atmospheric and oceanic
carbon content goes along with an increase in the Revelle factor, a phenomenon
which is already measurable (e.g. Hauck et al., 2010). This implies that the
oceanic uptake of anthropogenic carbon will become slower if we continue to
135 increase anthropogenic CO_2 emissions. This is already seen in all CMIP5 model
simulations (Jones et al., 2013). The scientific literature describing the ma-
rine carbonate chemistry, which, if complete, automatically includes the Revelle
effect, is based on decades of laboratory experiments, field observations and
theoretical understanding of the underlying chemical processes and is very well
140 established. The books by Dickson et al. (2007); Zeebe & Wolf-Gladrow (2001)
are only two examples of the state of knowledge in this field.

The carbonate chemistry is the most relevant part of the carbon cycle, which
is of importance on the timescale of interest, yet ignored in the erroneous ap-
proach of Harde (2017). The uptake of anthropogenic CO_2 by the terrestrial
145 part of the carbon cycle is also relevant (e.g. Joos et al., 2013), and nowadays
approximately of similar size as the marine carbon uptake (Le Quéré et al.,

2016). However, terrestrial carbon uptakes are in the global carbon budgets of Le Quéré et al. (2016) still estimated from the unexplained residual, after fossil fuels and emissions from industry and land-use change have been balanced by
150 constraints on changes in carbon pools in the atmosphere and the ocean. We therefore refrain from a more in-depth discussion of terrestrial carbon uptake processes here. Further processes with different impact on the airborne fraction of anthropogenic CO₂, which are of relevance if longer timescales are of interest (e.g. necessary for the generalization and application to the paleo data) are
155 ocean overturning, carbonate compensation and continental weathering rates (Lord et al., 2016). If implemented in a model this results in an airborne fraction of anthropogenic CO₂ emissions of around 40% on a 100-year timescale falling to ~18% on a 1000-year timescale (Joos et al., 2013) and down to 5% and 2% on timescales of 10⁵ and 10⁶ years, respectively (Lord et al., 2016).

160 Remark: Most of these details above on the role of the carbonate chemistry have been taken from another comment some of the authors published as part of the online discussion on another, overly simplistic, and therefore biased approach to explain the modern carbon cycle (<http://www.earth-syst-dynam-discuss.net/6/C813/2015/esdd-6-C813-2015.pdf>).

165 **Harde’s flawed 1-box carbon cycle:** One key element of Harde’s carbon cycle is the assumption of a simple absorption/decay process, which is unsuitable for the problem at hand. Harde’s Eq. (11) reads:

$$\frac{dC_{\text{CO}_2}}{dt} = e_T - \alpha \cdot C_{\text{CO}_2} , \quad (2)$$

where C_{CO_2} is the atmospheric CO₂ concentration, e_T is a total emission rate, $\alpha = 1/\tau$ is an absorption efficiency, and τ is Harde’s CO₂ “lifetime”. Thus,
170 Harde assumes that C_{CO_2} can be predicted by solving only a single rate equation of the carbon cycle (other reservoirs may exist but their time evolution is ignored). However, at any given time t , the CO₂ fluxes into and out of the atmosphere depend on, for instance, the atmosphere-ocean disequilibrium, which in turn depends on simultaneous changes in ocean carbon inventory and seawater chemistry, as explained above. Thus, even the simplest carbon cycle model
175

must at minimum comprise two boxes for atmosphere and ocean (including Revelle factor), whose equations are solved simultaneously. For investigations of timescales longer than centuries (e.g. in paleo applications as done in the generalization) processes which export carbon from the surface to the deep ocean (so-called carbon pumps, see Volk & Hoffert, 1985) also need to be taken into consideration, asking for at least another deep ocean box. Yet, Harde (2017) ignores this fact (and many others) that have been established in over 60 years of carbon-cycle research (a few examples include Revelle & Suess, 1957; Oeschger et al., 1975; Heimann & Maier-Reimer, 1996; Archer et al., 2009; Joos et al., 2013). As a result, the approach in Harde (2017) leads to fundamentally flawed mass balances, CO₂ “lifetimes”, and thus erroneous conclusions.

Note also that the posited analogy to radiocarbon and other isotopes is incorrect because changes in bulk inventory (total atmospheric CO₂) are confused with changes in tracers at minute concentration (strongly influenced by dilution). In detail, the concentration of CO₂ in the atmosphere, when perturbed by anthropogenic emissions, largely depends on the net oceanic CO₂ uptake rate, and therefore on the bottleneck of the carbonate chemistry as explained in section 3 above, while any changes in tracer concentrations such as atmospheric ¹⁴C does not depend on the net oceanic uptake, but on the gross gas exchange rates (e.g. see Joos et al., 1996; Naegler & Levin, 2006). Furthermore, the record of atmospheric radiocarbon is perturbed/depleted by the emission of ¹⁴C-free CO₂ from fossil fuels — the so-called ¹⁴C Suess effect (Suess, 1955; Köhler, 2016) — and points to much longer atmospheric adjustment time on the order of 100 years for 1985–2005 (LEVIN et al., 2010).

4. Harde’s generalization including approximations based on paleo reconstructions

Finally, Harde (2017) generalizes the results that incorrectly model the modern carbon cycle to draw, again, erroneous conclusions about the paleoclimate record (section 3.3 and Figure 3). Here, again, various shortcomings invalidate

205 the conclusions. The main ones are the following:

(a) **Glacial temperature:** The assumed surface temperature change for glacial times of -8 K is wrong, as the source cited (Petit et al., 1999) approximates not global temperature change, but that over East Antarctica. According to some recent studies the global temperature change at the last glacial maximum with respect to preindustrial times was -4.0 ± 0.8 K (Annan & Hargreaves, 210 2013). It is furthermore not clear to the reader how the data points in Figure 3 were generated with one data point for a temperature of 8, 10, 12, 14°C , while the underlying paleo data from the Vostok ice core contain several thousand data points of the last 420,000 years, also including periods which have been 215 warmer than the preindustrial climate.

(b) **Explaining paleo CO_2 :** Harde (2017) proposes that the complete glacial/interglacial change in CO_2 can be explained by a reduction in surface temperature. However, it is nowadays well established, that glacial/interglacial changes in atmospheric CO_2 can not be explained by one single process (e.g. 220 Köhler et al., 2005; Brovkin et al., 2007; Kohfeld & Ridgwell, 2009). Significant change in atmospheric CO_2 on glacial/interglacial timescales are expected from a rise in sea surface temperature, rising sea-level, reduced marine export production, and responses from carbonate compensation, together with changing land carbon storage (Kohfeld & Ridgwell, 2009). Although models still disagree 225 on the contribution of individual processes, the common consensus is, that the glacial/interglacial rise in temperature (more precisely sea surface temperature) might be responsible for a rise in atmospheric CO_2 mixing ratio of 20-30 ppm. The arguments in Harde (2017) are rather vague, but also seem to assume, that the temperature change might also trigger a change in terrestrial carbon stor- 230 age. This concept would therefore need to have higher terrestrial carbon storage in cold periods, that might then be released during deglacial warming. However, the glacial terrestrial carbon storage is nowadays found to be smaller (not larger) in glacial times than during the preindustrial period (Ciais et al., 2012). So, again evidence contradicts what is needed to support the concept set forth 235 in Harde (2017). One might now argue, that all mentioned processes vary syn-

chronously with temperature, and therefore the chosen temperature-dependency in Harde (2017) might be a possible simplification. However, this would largely ignore the complexity of the carbon cycle-climate system including the fact that the paleorecords also contain interglacial periods with higher than preindustrial
240 global surface temperature, but similar atmospheric CO₂ concentrations, such as the last interglacial about 130,000 years ago (e.g. Bakker et al., 2013; Past Interglacials Working Group of PAGES, 2016).

(c) **Paleo CO₂ data:** Furthermore, Harde (2017) argues that due to distortion and diffusion the CO₂ data from ice cores are rather imprecise leading
245 to large error bars for CO₂ shown in Figure 3 and to 20–30 ppm lower values than reconstructions based on fossil stomata. It must be clarified that ice core based CO₂ perfectly overlaps with the instrumental measurements of atmospheric CO₂ which started in 1958 and we therefore see no support for the contention that they might be biased to lower values (e.g. Ahn et al., 2012; Rubino et al., 2013; Köhler et al., 2017). Furthermore, short term variations
250 seen in stomata-based CO₂ during the Holocene have been heavily criticized, and when averaged for known enclosure characteristics of gas bubbles in ice cores have not been confirmed in ice core-based records (e.g. Ahn et al., 2014; Köhler et al., 2015). Together, the scientific arguments are in favour of the ice
255 core-based CO₂ records and not of that based on fossil stomata.

(d) **Impact of strong dependency of CO₂ on surface temperature:** Finally, the dependency of the atmospheric CO₂ concentration on the surface temperature, as depicted in Harde’s Figure 3 and his Equation 17 would imply — as also discussed in Harde (2017) — a large contribution of CO₂ from the
260 oceans for rising temperatures (but also some contributions from land). A large CO₂ outgassing contribution from the oceans, however, is at odds with the atmospheric oxygen records (e.g. see Keeling & Shertz, 1992).

5. Citations and some details on IPCC

Harde (2017) cites throughout various parts of the contribution of Working

265 Group 1 (physical science basis) to the IPCC-AR5 (Stocker et al., 2013) and
proposes *alternative views* on the impact of anthropogenic CO₂ emissions and
related global temperature increase. This approach is inappropriate because it
fails to address the actual underlying literature of the IPCC-AR5. The IPCC
summarizes the state of the art in the peer-reviewed literature. Hence neither
270 the residence time nor the adjustment time are assumptions or interpretations
of the IPCC-AR5, but robust outcomes of the underlying science, which is sum-
marized in the report. In presenting *alternative concepts* to the view presented
in the IPCC-AR5 the article of Harde (2017) ignores and is in contradiction to
the state of knowledge in the field, most obviously in the conflation of residence
275 and adjustment times.

Some of the citations in Harde (2017) are inappropriate, including video
presentations, and do not meet the standards of the peer-reviewed literature.

Further, Harde (2017) cites two papers (Essenhigh, 2009; Humlum et al.,
2013) that were subject to highly critical peer-reviewed comments (Cawley,
280 2011; Masters & Benestad, 2013; Richardson, 2013; Kern & Leuenberger, 2013),
none of which are referenced in Harde (2017). In fact, Harde (2017) repeats
many of the same arguments that have already been refuted.

6. Conclusion

In conclusion, Harde (2017) does not provide an *alternative view* of the
285 carbon cycle, but uses a too simplistic approach, that is based on invalid as-
sumptions, and which leads to flawed results for anthropogenic carbon in the
atmosphere. We suggest that the paper be withdrawn by the author, editor or
publisher due to fundamental errors in the understanding of the carbon cycle.

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References

- Ahn, J., Brook, E. J., & Buizert, C. (2014). Response of atmospheric CO₂ to the
295 abrupt cooling event 8200 years ago. *Geophysical Research Letters*, *41*, 604–609.
doi:10.1002/2013GL058177.
- Ahn, J., Brook, E. J., Mitchell, L., Rosen, J., McConnell, J. R., Taylor, K., Etheridge,
D., & Rubino, M. (2012). Atmospheric CO₂ over the last 1000 years: A high-
300 resolution record from the West Antarctic Ice Sheet (WAIS) Divide ice core. *Global
Biogeochemical Cycles*, *26*, GB2027. doi:10.1029/2011GB004247.
- Annan, J. D., & Hargreaves, J. C. (2013). A new global reconstruction of temperature
changes at the Last Glacial Maximum. *Climate of the Past*, *9*, 367–376. doi:10.
5194/cp-9-367-2013.
- Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K.,
305 Matsumoto, K., Munhoven, G., Montenegro, A., & Tokos, K. (2009). Atmospheric
Lifetime of Fossil Fuel Carbon Dioxide. *Annual Review of Earth and Planetary
Sciences*, *37*, 117–134. doi:10.1146/annurev.earth.031208.100206.
- Archer, D., Kheshgi, H., & Maier-Reimer, E. (1997). Multiple timescales for
neutralization of fossil fuel CO₂. *Geophysical Research Letters*, *24*, 405–408.
310 doi:10.1029/97GL00168.
- Bakker, P., Stone, E. J., Charbit, S., Gröger, M., Krebs-Kanzow, U., Ritz, S. P.,
Varma, V., Khon, V., Lunt, D. J., Mikolajewicz, U., Prange, M., Renssen,
H., Schneider, B., & Schulz, M. (2013). Last interglacial temperature evolu-
tion – a model inter-comparison. *Climate of the Past*, *9*, 605–619.
315 doi:10.5194/cp-9-605-2013.
- Brovkin, V., Ganopolski, A., Archer, D., & Rahmstorf, S. (2007). Lowering of glacial
atmospheric CO₂ in response to changes in oceanic circulation and marine biogeo-
chemistry. *Paleoceanography*, *22*, PA4202, doi: 10.1029/2006PA001380.
- Cawley, G. C. (2011). On the Atmospheric Residence Time of Anthropogenically
320 Sourced Carbon Dioxide. *Energy & Fuels*, *25*, 5503–5513. doi:10.1021/ef200914u.

- Ciais, P., Tagliabue, A., Cuntz, M., Bopp, L., Scholze, M., Hoffmann, G., Lourdantou, A., Harrison, S. P., Prentice, I. C., Kelley, D. I., Koven, C., & Piao, S. L. (2012). Large inert carbon pool in the terrestrial biosphere during the Last Glacial Maximum. *Nature Geoscience*, *5*, 74–79. doi:10.1038/ngeo1324.
- 325 Dickson, A. G., Sabine, C. L., & Christian, J. R. (Eds.) (2007). *Guide to Best Practices for Ocean CO₂ Measurements*. PICES Special Publication 3.
- Dlugokencky, E., Lang, P., Mund, J., Crotwell, A., Crotwell, M., & Thoning, K. (2016). Atmospheric Carbon Dioxide Dry Air Mole Fractions from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, 1968-2015, Version: 2016-08-30,
330 Path: ftp://aftp.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/ , .
- Eide, M., Olsen, A., Ninnemann, U. S., & Eldevik, T. (2017). A global estimate of the full oceanic ¹³C Suess effect since the preindustrial. *Global Biogeochemical Cycles*, *31*, 515–534. doi:10.1002/2016GB005472.
- Essenhigh, R. H. (2009). Potential Dependence of Global Warming on the Residence
335 Time (RT) in the Atmosphere of Anthropogenically Sourced Carbon Dioxide. *Energy & Fuels*, *23*, 2773–2784. doi:10.1021/ef800581r.
- Friedlingstein, P., Cox, P., Betts, R., Bopp, L., von Bloh, W., Brovkin, V., Cadule, P., Doney, S., Eby, F., Fung, I., Bala, G., John, J., Joos, F., Kato, T., Kawamiya, M., Knorr, W., Lindsay, K., Matthews, H. D., Raddatz, T., Rayner, P., Reick,
340 C., Roeckner, E., Schnitzler, K.-G., Schnur, R., Strassmann, K., Weaver, A. J., Yoshikawa, C., & Zeng, N. (2006). Climate-carbon cycle feedback analysis: results from the C⁴MIP model intercomparison. *Journal of Climate*, *19*, 3337–3353. doi:10.1175/JCLI3800.1.
- Gruber, N., Gloor, M., Mikaloff Fletcher, S. E., Doney, S. C., Dutkiewicz, S., Follows,
345 M. J., Gerber, M., Jacobson, A. R., Joos, F., Lindsay, K., Menemenlis, D., Mouchet, A., Müller, S. A., Sarmiento, J. L., & Takahashi, T. (2009). Oceanic sources, sinks, and transport of atmospheric CO₂. *Global Biogeochemical Cycles*, *23*, GB1005, doi: 10.1029/2008GB003349.
- Gruber, N., Sarmiento, J. L., & Stocker, T. F. (1996). An improved method for
350 detecting anthropogenic CO₂ in the oceans. *Global Biogeochemical Cycles*, *10*, 809–837. doi:10.1029/96GB01608.

- Harde, H. (2017). Scrutinizing the carbon cycle and CO₂ residence time in the atmosphere. *Global and Planetary Change*, 152, 19 – 26. doi:10.1016/j.gloplacha.2017.02.009.
- 355 Hauck, J., Hoppema, M., Bellerby, R. G. J., Völker, C., & Wolf-Gladrow, D. (2010). Data-based estimation of anthropogenic carbon and acidification in the Weddell Sea on a decadal timescale. *Journal of Geophysical Research*, 115, C03004. doi:10.1029/2009JC005479.
- Heimann, M., & Maier-Reimer, E. (1996). On the relations between the oceanic
360 uptake of CO₂ and its carbon isotops. *Global Biogeochemical Cycles*, 10, 89–110. doi:10.1029/95GB03191.
- Houghton, J. T., Jenkins, G. J., & Ephraums, J. J. (Eds.) (1990). *Climate Change - The IPCC Scientific Assessment*. Cambridge, U.K.: Cambridge University Press.
- Humlum, O., Stordahl, K., & Solheim, J.-E. (2013). The phase relation between
365 atmospheric carbon dioxide and global temperature. *Global and Planetary Change*, 100, 51 – 69. doi:10.1016/j.gloplacha.2012.08.008.
- Jones, C., Robertson, E., Arora, V., Friedlingstein, P., Shevliakova, E., Bopp, L., Brovkin, V., Hajima, T., Kato, E., Kawamiya, M., Liddicoat, S., Lindsay, K., Reick, C. H., Roelandt, C., Segsneider, J., & Tjiputra, J. (2013). Twenty-First-
370 Century Compatible CO₂ Emissions and Airborne Fraction Simulated by CMIP5 Earth System Models under Four Representative Concentration Pathways. *Journal of Climate*, 26, 4398–4413. doi:10.1175/JCLI-D-12-00554.1.
- Joos, F., Bruno, M., Fink, R., Siegenthaler, U., Stocker, T. F., Quéré, C. L., & Sarmiento, J. L. (1996). An efficient and accurate representation of complex oceanic
375 and biospheric models of anthropogenic carbon uptake. *Tellus*, 48B, 397–417. doi:10.1034/j.1600-0889.1996.t01-2-00006.x.
- Joos, F., Roth, R., Fuglestedt, J. S., Peters, G. P., Enting, I. G., von Bloh, W., Brovkin, V., Burke, E. J., Eby, M., Edwards, N. R., Friedrich, T., Frölicher, T. L., Halloran, P. R., Holden, P. B., Jones, C., Kleinen, T., Mackenzie, F. T., Matsumoto, K., Meinshausen, M., Plattner, G.-K., Reisinger, A., Segsneider, J., Shaffer, G.,
380 Steinacher, M., Strassmann, K., Tanaka, K., Timmermann, A., & Weaver, A. J.

- (2013). Carbon dioxide and climate impulse response functions for the computation of greenhouse gas metrics: a multi-model analysis. *Atmospheric Chemistry and Physics*, *13*, 2793–2825. doi:10.5194/acp-13-2793-2013.
- 385 Keeling, R. F., & Shertz, S. R. (1992). Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, *358*, 723–727. doi:10.1038/358723a0.
- Kern, Z., & Leuenberger, M. (2013). Comment on *The phase relation between atmospheric carbon dioxide and global temperature* Humlum et al. [Glob. Planet. Change 100: 51–69.]: Isotopes ignored. *Global and Planetary Change*, *109*, 1–2. 390 doi:10.1016/j.gloplacha.2013.07.002.
- Kohfeld, K. E., & Ridgwell, A. (2009). Glacial-interglacial variability in atmospheric CO₂. In E. Saltzman, & C. L. Quéré (Eds.), *Surface Ocean–Lower Atmospheres Processes* (pp. 251–286). Washington D.C.: AGU volume 187 of *Geophysical Monograph Series*. doi:10.1029/2008GM000845. 395
- Köhler, P. (2016). Using the Suess effect on the stable carbon isotope to distinguish the future from the past in radiocarbon. *Environmental Research Letters*, *11*, 124016. doi:10.1088/1748-9326/11/12/124016.
- Köhler, P., Fischer, H., Munhoven, G., & Zeebe, R. E. (2005). Quantitative interpretation of atmospheric carbon records over the last glacial termination. *Global Biogeochemical Cycles*, *19*, GB4020. doi:10.1029/2004GB002345. 400
- Köhler, P., Fischer, H., Schmitt, J., Brook, E. J., & Marcott, S. A. (2015). Comment on *Synchronous records of pCO₂ and Δ¹⁴C suggest rapid, ocean-derived pCO₂ fluctuations at the onset of the Younger Dryas* by Steinthorsdottir et al. *Quaternary Science Reviews*, *107*, 267–270. doi:10.1016/j.quascirev.2014.09.024. 405
- Köhler, P., Nehrbass-Ahles, C., Schmitt, J., Stocker, T. F., & Fischer, H. (2017). A 156 kyr smoothed history of the atmospheric greenhouse gases CO₂, CH₄, and N₂O and their radiative forcing. *Earth System Science Data*, *9*, 363–387. doi:10.5194/essd-9-363-2017.
- 410 Landschützer, P., Gruber, N., & Bakker, D. C. E. (2016). Decadal variations and

trends of the global ocean carbon sink. *Global Biogeochemical Cycles*, *30*, 1396–1417. doi:10.1002/2015GB005359.

Lauvset, S. K., Key, R. M., Olsen, A., van Heuven, S., Velo, A., Lin, X., Schirnack, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Perez, F. F., Suzuki, T., & Watelet, S. (2016). A new global interior ocean mapped climatology: the $1^\circ \times 1^\circ$ GLODAP version 2. *Earth System Science Data*, *8*, 325–340. doi:10.5194/essd-8-325-2016.

Le Quéré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P., Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S., Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Currie, K., Delire, C., Doney, S. C., Friedlingstein, P., Gkritzalis, T., Harris, I., Hauck, J., Haverd, V., Hoppema, M., Klein Goldewijk, K., Jain, A. K., Kato, E., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozi, D., Melton, J. R., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., O'Brien, K., Olsen, A., Omar, A. M., Ono, T., Pierrot, D., Poulter, B., Rödenbeck, C., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B. D., Sutton, A. J., Takahashi, T., Tian, H., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., Viovy, N., Walker, A. P., Wiltshire, A. J., & Zaehle, S. (2016). Global Carbon Budget 2016. *Earth System Science Data*, *8*, 605–649. doi:10.5194/essd-8-605-2016.

LEVIN, I., NAEGLER, T., KROMER, B., DIEHL, M., FRANCEY, R. J., GOMEZ-PELAEZ, A. J., STEELE, L. P., WAGENBACH, D., WELLER, R., & WORTHY, D. E. (2010). Observations and modelling of the global distribution and long-term trend of atmospheric $^{14}\text{CO}_2$. *Tellus B*, *62*, 26–46. doi:10.1111/j.1600-0889.2009.00446.x.

Lord, N. S., Ridgwell, A., Thorne, M. C., & Lunt, D. J. (2016). An impulse response function for the long tail of excess atmospheric CO₂ in an Earth system model. *Global Biogeochemical Cycles*, *30*, 2–17. doi:10.1002/2014GB005074.

Masters, T., & Benestad, R. (2013). Comment on *The phase relation between atmospheric carbon dioxide and global temperature*. *Global and Planetary Change*, *106*, 141 – 142. doi:10.1016/j.gloplacha.2013.03.010.

- Naegler, T., & Levin, I. (2006). Closing the global radiocarbon budget 1945-2005. *Journal of Geophysical Research*, *111*, D12311, doi: 10.1029/2005JD006758.
- Oeschger, H., Siegenthaler, U., Schotterer, U., & Gugelmann, A. (1975). A box diffusion model to study the carbon dioxide exchange in nature. *Tellus*, *27*, 168–192. doi:10.1111/j.2153-3490.1975.tb01671.x.
- Orr, J. C., Epitalon, J.-M., & Gattuso, J.-P. (2015). Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences*, *12*, 1483–1510. doi:10.5194/bg-12-1483-2015.
- 450 Past Interglacials Working Group of PAGES (2016). Interglacials of the last 800,000 years. *Reviews of Geophysics*, *54*, 162–219. doi:10.1002/2015RG000482.
- Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., Pépin, L., Ritz, C., Saltzman, E., & Stievenard, M. (1999). Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*, *399*, 429–436. doi:10.1038/20859.
- Revelle, R., & Suess, H. E. (1957). Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO₂ during the Past Decades. *Tellus*, *9*, 18–27. doi:10.1111/j.2153-3490.1957.tb01849.x.
- 460 Richardson, M. (2013). Comment on *The phase relation between atmospheric carbon dioxide and global temperature* by Humlum, Stordahl and Solheim. *Global and Planetary Change*, *107*, 226 – 228. doi:10.1016/j.gloplacha.2013.03.011.
- Rubino, M., Etheridge, D. M., Trudinger, C. M., Allison, C. E., Battle, M. O., Langenfelds, R. L., Steele, L. P., Curran, M., Bender, M., White, J. W. C., Jenk, 465 T. M., Blunier, T., & Francey, R. J. (2013). A revised 1000-year atmospheric $\delta^{13}\text{C}$ -CO₂ record from Law Dome and South Pole, Antarctica. *Journal of Geophysical Research: Atmospheres*, *118*, 8482–8499. doi:10.1002/jgrd.50668.
- Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, 470 T.-H., Kozyr, A., Ono, T., & Rios, A. F. (2004). The oceanic sink for anthropogenic CO₂. *Science*, *305*, 367–371. doi:10.1126/science.1097403.

- 475 Stocker, T. F., Qin, D., Tignor, G.-K. P. M., Allen, S., Boschung, J., Nauels, A., Xia, Y., Bex, V., & Midgley, P. (Eds.) (2013). *IPCC, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press.
- Suess, H. E. (1955). Radiocarbon Concentration in Modern Wood. *Science*, *122*, 415–417. doi:10.1126/science.122.3166.415-a.
- 480 Volk, T., & Hoffert, M. I. (1985). Ocean carbon pumps: analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂ changes. In E. T. Sundquist, & W. S. Broecker (Eds.), *The carbon cycle and atmospheric CO₂: Natural variations archean and present* (pp. 99–110). Washington, D.C., USA: American Geophysical Union volume 32 of *Geophysical Monograph*. doi:10.1029/GM032p0099.
- 485 Zeebe, R. E., & Wolf-Gladrow, D. A. (2001). *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes* volume 65 of *Elsevier Oceanography Book Series*. Amsterdam, The Netherlands: Elsevier Science Publishing.