Reply to Reviewer Reports

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Title: Reply to Comment on "Scrutinizing the carbon cycle and CO2 residence time in the atmosphere"
Journal: Global and Planetary Change

Prof. Cloetingh as responsible Editor of GloPlaCha excluded my Reply to the Comment of Köhler et al. and justified his decision with the recommendation of two reviewers not to publish the Reply. With this rejection I have been deprived of any fair opportunity to respond on Köhler et al's Comments as well as on the Reviewer Reports.

As already mentioned in my letter to the Editor and Publisher from 14 October, 2017, much of the reviewer’s remarks do not even concern the Reply to Köhler et al’s Comment. Rather, they introduced new material which was not developed in the Comment, and therefore was not considered in the Reply. The untimely introduction of such claims would be tantamount to a new Comment on Harde (2017).

Although with the rejection any further review process or publication in GloPlaCha is terminated, the many misinterpretations, unacceptable claims and imputations in the reviewer reports cannot remain unanswered. At the same time this Reply documents the strongly prejudiced review process in a highly-polarized debate between two scientific positions, in which the nominated reviewers exclusively advocated the fundamentally restricted view of the IPCC's interpretation of the carbon cycle.

In what follows are the Reviewer Reports presented in black typeface, my comments in between in blue. Incidentally some comments required some longer excurses to exhibit the different concepts and to clarify some obviously intended misinterpretations.

Comments of Reviewer 1

I commend the editor of Global and Planetary Change for accepting for publication the manuscript by Köhler et al., which provides a fundamental, solid and scholarly critique of the paper by Harde, 2017, which was published previously in Global and Planetary Change. All three reviewers unanimously stated that the original Harde paper contains serious scientific flaws, errors and misconceptions, and ignores of a whole body of scientific literature. I fully support the statement in the concluding section of Köhler et al.: “In conclusion, Harde (2017) does not provide an alternative view of the carbon cycle, but uses a too simplistic approach, that is based on invalid assumptions, 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.”

Apparently, Global and Planetary Change has now offered Harde to submit a reply to the Köhler et al. paper which I have been asked to review. As shown below in my comments, the reply repeats and even amplifies the erroneous arguments presented in the original Harde 2017 paper.

Harde and colleagues, not named as formal coauthors, argue in the original article and in the present comment manuscript that they present an “alternative concept” of how the global carbon cycle works. In principle, “alternative concepts” or new views of how a particular component in the Earth System works, are very welcome. To be accepted, however, requires that the alternative concept is consistent with all the available observational evidence, and, if claimed to be superior to previous work, requires a thorough confrontation with the existing body of knowledge amassed by scholars during the past. Unfortunately, neither the original publication by Harde 2017 nor the present comment manuscript provide this evidence.

In the following I denote with H0 the original paper by Harde, 2017, and with H1 the reply comment reviewed here. The reply comment H1 contains so many blatant errors and misconceptions, that I can only comment on a few major flaws.
The alternative concept is consistent with all available observations, in particular it satisfies the Conservation Law, different to the Bern Model and its derivatives. The contemporary observations of the CO$_2$ increase at Mauna Loa since 1958 can very well be explained, based on Eq.(11) of H0 and using the CDIAC-data for fossil fuel emissions as well as the global GISS temperature measurements (see Fig. 3 of Reply).

Reviewer 1 should remember: Evidence cannot prove a theory right, it can only prove a theory wrong. Different to our evidence in the Reply that different decay times violate the Conservation Law, the reviewer fails to disprove our alternative approach.

Comments to Claim 1: Residence time differs from adjustment time.

The fundamentally contrasting imagination of a real absorption is to consider natural emission and absorption fluxes as virtual phenomena; apparently this view is also captured by the reviewer. In this case a real exchange of CO$_2$ between the atmosphere and extraneous reservoirs does not exist. Instead, this could better be described as a turn-over process of CO$_2$ in an almost closed atmosphere, which has not to be accounted for in any balance but is considered to be the same over the last 270 years.

In this picture it is further considered that the atmosphere is placed above saturated extraneous reservoirs with very limited buffer capacities. Blocking of these reservoirs only gets slightly relieved, when anthropogenic emissions increase the partial pressure in the atmosphere. Based on this imagination a limited uptake (~55%) of CO$_2$ by the external reservoirs takes place, the rest (~45%) known as Airborne Fraction (AF) is assumed to accumulate in the atmosphere. In other words: It exists a fractional absorption for anthropogenic emissions, whereas variations in the natural fluxes or additional native emissions and also temperature induced changes have no influence on the atmospheric CO$_2$ concentration.

Such interpretation - essentially hypothesized in the Bern Model - is indeed in direct contradiction to real absorption and emission processes, which obey the Conservation Law and which are effective in the same way for native as well as for human emissions.

To describe the absorption as a first order process is by far not identical with the assumption that absorbed molecules are completely removed from a further excitation-absorption cycle. In molecular or laser physics, e.g., it is standard to express the absorption or emission processes of photons by rate equations, where the population densities of involved molecular states are changing proportional to their actual populations. So, the spontaneous emission rate of an excited molecular state is given by the product of the excited state population density and the transition probability to all lower states, the latter equivalent to the inverse lifetime of the upper state. The more molecules are excited, the more can decay. With each transition the population of the upper state is reduced and at the same time a lower level filled. When an appropriate broadband excitation is available, the molecules can again take part in a new excitation-decay cycle; when a selective excitation only from one specific lower level is possible, only molecules which decayed to this state, can again be pumped up with a net transition rate proportional to the population difference between lower and upper state. This is the Conservation Law.

An analogue situation is found for the CO$_2$ molecules in the atmosphere, which 'decay' to one of the reservoirs. From there, dependent on the concentration and emissivity rate a new emission to the atmosphere is possible. These and also additional fluxes from volcanic activities, natural variations and from human emissions have to be considered. In the Conservation Law they are summarized as total emissions, evidently including all 'return fluxes' from the different reservoirs.
Only when one of the directly coupled reservoirs is saturating, a feedback can be expected as assumed in the Bern Model. But a saturation is not observed (see Reply, Appendix A.3). Would this be the case, natural variations from year to year or the seasonal changes, which are comparable or even larger than the anthropogenic emissions, could not be counterbalanced within shorter intervals. Such fluctuations are typically equalized within one residence time or shorter. When we would trust the Bern Model, not only anthropogenic emissions but also all seasonal variations, volcanic eruptions or El Niños have to be summed up, like an electric rectifier is operating, and at least 20% of all these shorter emission pulses would stay in the atmosphere for ever. Observations show that this is not the case.

The total emission and uptake rate together define the equilibrium concentration in the atmosphere, to which the system tries to return after a perturbation. This is directly controlled by the deviation of the instantaneous concentration from equilibrium, not by changes of the decay time, which is always identical for naturally or anthropogenically emitted molecules and would only change at saturation of the extraneous reservoirs.

The in- and out-fluxes react much more sensitively on direct temperature changes than on indirect feedbacks via return fluxes from previous absorptions. Therefore, the equilibrium concentration is by far no universal constant but also changes slightly with the average environmental conditions. This is a continuous adaptation process, which is dictated by the response of the emission and absorption rates to temperature, to photosynthesis, the bio-cycle and additional emission sources or absorption sinks.

When temperature, radiation and photosynthesis changes over shorter or longer periods this has nothing to do with the so called 'adjustment time' as outlined in the IPCC reports. In the alternative concept, satisfying the Conservation Law, an additional emission from fossil fuel combustion or land change - and in the same way a reduced emission - perturbs the equilibrium state, and the system tries to adjust to this balance with the residence time. This is the fundamental difference to the Bern Model and an airborne fraction (AF), where almost nothing is adjusting, only accumulating.

This view is described in H1 with the bathtub analogue on page 4: water that leaves the bathtub through the different leaks is removed completely from the bathtub. Such an analogue is approximately correct in the case of atmospheric methane, which is chemically destroyed by its sinks and where the methane sinks do not feed back on the methane sources. However, the atmospheric CO2 cycle is not a bathtub: On land, enhanced photosynthesis leads to enhanced respiration, since there is more biomass that can be decomposed.

Reference to the bathtub is misguided. The analogue discussed had a completely different background to show that it gives no sense to introduce different decay times. Without influx indeed the bathtub gets dry, with a constant influx the equilibrium concentration is adjusting.

Similarly enhancing the gross ocean CO2 uptake by increasing of the partial pressure of atmospheric CO2 increases the carbon content in the sur ocean, which, through changes in the carbonate chemistry increases the partial pressure of CO2 in the sur ocean and which in turn then increases the gross outgassing CO2 flux. These feedbacks of atmospheric CO2 absorption on the return fluxes to the atmosphere are observed: 100’000s of sur ocean pCO2 measurements worldwide show that pCO2 in the sur ocean increases over time in response to the atmospheric CO2 perturbation. Similarly on land 100’s of fluxtowers and also in FACE experiments show that most of the CO2 absorbed is released later through respiration back to the atmosphere and that an increase of photosynthesis inevitably fosters an increase in respiration.

At best pCO2 can be determined with an accuracy of a few % (see Takahashi et al., 1993). This is more than any anthropogenic contribution. Synoptic observations necessary to evaluate global emission or absorption do not exist. It is also not proved that pCO2 only increases in response to atmospheric CO2 or this is caused at least to some extent by the temperature.

How fast these return fluxes respond to an increase in atmospheric CO2 depends on the speed of carbon cycling within the land biosphere and the ocean. It is through these processes that the decay of an
atmospheric perturbation does not follow a single exponential, but includes multiple time scales. To address this, one needs to represent the global carbon cycle at least as a coupled three-reservoir system in which carbon is a conserved quantity.

Reviewer 1 seems to have another understanding of sources and sinks for CO\textsubscript{2}. An increase of \((pCO_2)_{sw}\), which more likely results from the rising sea surface temperature (SST) than from anthropogenic absorption, as already mentioned above, is made responsible for the feedback of CO\textsubscript{2} on the return flux to the atmosphere. And this is made responsible for the different decay times! Indeed, one possible interpretation could be that a feedback is changing the influx (excitation rate). This influx depends on the adaptation of the extraneous reservoirs to environmental conditions like temperature or biochemical processes, but all this has nothing to do with an introduction of different time scales, one even lasting for ever. A fast or slowly changing influx, from natural or anthropogenic emissions, cannot generate different decay times, it only shifts the equilibrium concentration, to which the atmosphere tries to adjust with the residence time.

Another interpretation of possible feedbacks of atmospheric CO\textsubscript{2} absorption on the return fluxes to the atmosphere is to directly consider this absorption. For the oceans in steady state it scales with the difference of the CO\textsubscript{2} partial pressures of sea water and the air: \(\Delta pCO_2 = (pCO_2)_{sw} - (pCO_2)_{air}\). When the sea water term increases faster than the atmospheric partial pressure and this due to the additional atmospheric CO\textsubscript{2} and not the temperature, we call this a saturation, which for the oceans up to now cannot be observed (for details see Appendix A.3 and references therein). Since all uptake processes act parallel and not in series, the unique absorptivity rate is the sum of the individual processes, and the resulting absorption time, equivalent to the residence time, is the reciprocal of the total absorptivity rate. From this it follows: It gives only one unique decay time, which can increase at stronger saturations, but only as a collective effect of all directly absorbing reservoirs. Again, an increasing absorption time changes the ouflux and thus, the equilibrium concentration in the atmosphere. On any deviations from this balance the atmosphere reacts with the residence time.

A saturation with its consequences is several times discussed in the Reply, also together with the bathtub analogy. This analogy also holds with a continuous influx, e.g. from a water tap representing the natural emissions, but then with even more dramatic consequences. When in this case the larger tubes pluck up and the influx is not stopped, this quickly causes a flood.

In contrast to any saturation effects the CO\textsubscript{2} partial pressure in sea water changes with temperature as \((pCO_2)_{sw} = (pCO_2)_{sw}(T_0) \times \exp[0.0433*(T-T_0)]\). An increase of 1°C causes a pressure change of 17.7 µatm ≈ 18 ppm, which amplifies the influx and attenuates the outflux. Sarmiento and Sundquist (Revised budget for the oceanic uptake of anthropogenic carbon dioxide, Nature 356, 589–593, 1992) and Robertson and Watson (Thermal skin effect of the surface ocean and its implications for CO\textsubscript{2} uptake, Nature 358, 738–740, 1992) discuss that a lower skin than bulk temperature of 0.17°C due to wind speeds reduces \((pCO_2)_{sw}\) by 1%. This should increase the CO\textsubscript{2} air-to-sea (net) flux by 30% (~0.5 PgC/yr). Conversely, only assuming linear response to warming, 1°C would change the net flux by 6*30% or about 3 PgC/yr. This has to be compared with an average anthropogenic emission rate from 1750 to 2010 of 518 PgC/260 yr = 2 PgC/yr (see Köhler).

The second fundamental flaw in Hardes arguments is the contention that the atmospheric response to a pulse input of CO2 is the same as to a pulse of 14C. This is wrong as has been shown many times before (Köhler et al. provide some references). Assume for the sake of argument a hypothetical carbon cycle with just atmosphere and land biosphere, but in which the photosynthesis of the land biosphere is limited by available nutrients. In this system, a pulse input into the atmosphere will remain there since the photosynthesis flux due to the nutrient limitation cannot increase with higher CO2. Conversely, a pulse of 14C will be redistributed between the two reservoirs, since some of the carbon atoms in the steady state flux between atmosphere and biosphere will be replaced by 14C atoms. Ultimately, the 14C atoms will be uniformly distributed between the two reservoirs. This simple thought experiment shows that the dynamics of a CO2 perturbation is not the same as for 14C. The atmospheric decrease of the bomb 14C
input indeed poses some constraint on the global carbon cycle dynamics, but it needs to be addressed properly as has been done in the literature many times over the last 50 years. A good start of how to calculate it mathematically is given e.g. by Oeschger et al., 1975. In the present manuscript appendix B only addresses the additional complication through the dilution effect by 14C free fossil fuel CO2, but it ignores the basic 14C dynamics.

With this hypothetical carbon-cycle example the reviewer tries to demonstrate that $^{14}\text{CO}_2$ is furthermore regularly sucked up by plants, but an additional CO2 pulse will remain in the atmosphere, therefore, $^{14}\text{CO}_2$ would fail to act as a tracer. The reviewer’s claim is fanciful. This would require that plants violate the equivalence principle, and also different residence times of the isotopologues in the atmosphere are presupposed. $^{14}$C concentration differs between the atmosphere and Earth's surface by only a couple of percent (because the two are only weakly out of equilibrium, see http://www.c14dating.com/isotope.html). Therefore, re-emission from the Earth's surface cannot sharply modify the decay of $^{14}$C. The effect is analogous to the so-called Suess effect, which the Reply (Appendix B) shows is inconsequential.

Indeed shows the photosynthesis a smaller preference for heavier molecules to be uptaken, as we know from the $^{13}$C/$^{12}$C ratio with the consequence that the absorption efficiency of these molecules is slightly smaller and their residence time marginally larger. Additionally considering the re-emission of $^{14}$C that was already absorbed from the atmosphere (see Reply, Section 3, last paragraph and Appendix B), an even slower decay than in the presence of absorption alone has to be expected.

What the reviewer designates as steady state flux between atmosphere and biosphere is not really clear. Therefore, we may distinguish between three cases:

(i) When he/she understands this as a simple turn-over process (see above), a real exchange of CO2 between the atmosphere and the extraneous reservoir does not exist. In this case indeed an additional pulse would stay in the atmosphere, even the identical molecules would be shelved there. But then also no transfer of $^{14}$CO2 to the biosphere takes place.

(ii) When real fluxes are presupposed, this is identical with a direct exchange of CO2 between the reservoirs with an atmospheric residence time given by the ratio of the atmospheric CO2 concentration to the absorption or emission rate. With a concentration of 400 ppm and an absorption/emission rate of 100 ppm/yr the atmospheric CO2 molecules as an average are exchanged every 4 yr. In this exchange process additionally injected molecules take part in the same way as those molecules which are already in the atmosphere, and of course, this is also valid for the $^{14}$CO2 molecules, only with a few ‰ reduced probability. As long as no saturation is given, after the pulse input the system returns to its steady state concentration (before perturbation) with the residence time.

(iii) When the photosynthesis of the land biosphere is limited, an additional CO2 pulse e.g. of 100 ppm increases the concentration to 500 ppm. At complete saturation this concentration stays in the atmosphere and the residence time for all molecules rises to 5 yr. With a fractionation of a few ‰ it is identical for all CO2 molecules.

In all cases $^{14}$CO2 molecules are part of the same exchange process, only with the difference that a direct re-emission of the radioactive molecules results in a slower decay of the observed radioactivity than the residence time. Therefore, the measured decay of $^{14}$CO2 as a tracer reflects an upper limit of the apparent CO2 lifetime in the atmosphere. This has several times been mentioned in the Reply.

It would be an absolutely strange physical imagination to assume a regular absorption and emission exchange between atmosphere and biosphere like 1750 or 1850, in which $^{14}$CO2 is integrated as part of a steady state flux with well observable uptake rates, but for an additional pulse to request zero absorption. When the photosynthesis flux due to the nutrient limitation is restricted, this acts back on all molecules in the atmosphere in the same way (with the small preference for lighter molecules). Thus, molecules from a CO2 pulse cannot be shelved in the atmosphere, while only the radioactive molecules would be distributed between the two reservoirs. They take part in the general steady state flux
between the reservoirs, which is not switched off for the additionally injected molecules. A system with a limited or saturated absorption for CO$_2$ has to be described by an increasing absorption time that is identical for all molecules, those which are already in the cycle or which are later added to this cycle. The increased absorption time only affects the steady state level which is shifted to a new equilibrium concentration.

Applying the model of H1 with the 14C based adjustment time leads to a very small atmospheric increase (15% of the observed increase) caused by the anthropogenic emissions. We don't use any adjustment time, only the residence time, which is derived from the IPCC specified in- and out-fluxes and which is the same for all CO$_2$ molecules. What the Reply shows is that adjustment and residence time are equivalent. Distinction is a major error in IPCC and an equally important contribution - which GPC has chosen to censor. In order to reconcile this with the atmospheric CO$_2$ increase, H1 invokes ad hoc a temperature driven CO$_2$ source. Where would this CO$_2$ come from? It comes from the same sources as always, which supply the atmosphere. The total in- and out-fluxes, natural and anthropogenic together, determine the balance equation. This balance with its equilibrium concentration is shifted with temperature (see also below).

If the ocean were outgassing CO$_2$ by warming, it would also outgas oxygen leading to an increasing trend in atmospheric oxygen - contrary to what is observed. If it came from land, it would imply less carbon stored on land in a warmer world - contrary to what is observed in vegetation warming experiments but also from numerous paleo studies. Even when at increasing temperature more oxygen can be released to the atmosphere, in the photosynthesis and respiration cycle CO$_2$ and O$_2$ are just anti-cyclic. Also the biochemical reactions in the atmosphere are completely different. CO$_2$ is an almost inert gas, while O$_2$ preferentially oxidizes other materials and is tied in chemical compounds. All these reactions are directly controlled by the temperature. So O$_2$ gives little evidence that the decline in atmospheric oxygen proves human emissions, as claimed by the IPCC, or it would contradict a temperature influenced shift of the steady-state CO$_2$ level in the atmosphere.

Reviewer 1 should also look to the paper of Huntingford et al. (Implications of improved representations of plant respiration in a changing climate, 2017, NATURE COMMUNICATIONS 8, 1602, DOI: 10.1038/s41467-017-01774-z), where actual results are presented about the release of CO$_2$ from dark respiration and how this contribution strongly increases with rising temperature.

An increase of atmospheric CO$_2$ is not only the result of additional emissions, e.g., from oceans but also the consequence of a reduced uptake of the oceans at increased temperatures.

Comments to Claim 2: Anthropogenic CO$_2$ is not absorbed by other reservoirs
The text in H1 is very much misleading: We know (1) the cumulative anthropogenic emissions from statistics of fossil fuel use, (2) the atmospheric CO$_2$ increase from ice core and atmospheric measurements, and (3) the change in ocean carbon since preindustrial from 100’000s of in situ oceanographic observations. Harde disputes the estimates of (3) as “preposterous” but provides no evidence. He is welcome to study the relevant literature starting e.g. by Sabine et al., 2004. H1 states: “Without global observations necessary to quantify those properties, the purported inventory of changes that could be associated with absorption of anthropogenic CO2 is fanciful.” This statement shows the ignorance of Harde regarding knowledge of the global carbon cycle: We do have global observations: one alternative method is based on concurrent atmospheric oxygen and CO2 measurements. Analysing the trends of both gases allows to quantify the global ocean CO2 sink (e.g. Keeling et al., 1996), which nicely confirms (3). A third method for quantifying the ocean uptake is based on observations of changes of the 13C/12C stable isotope ratio, which also confirms (3). Any “alternative concept” needs to explain also this hard observational evidence.
Not the number of in situ probes on the main ship routes but a more homogeneous coverage of ocean and land observations and their accuracy determines the reliability of an inventory. Synoptic global observations of these quantities do not exist.

As long as parameters like sea and air temperature, the local air pressure and partial CO₂ pressure in the atmosphere, the salinity or humidity - all quantities which are required to determine the partial pressure \((p\text{CO}_2)_{sw}\) of a sample in sea water - add up to an inaccuracy larger than any anthropogenic contributions, and as long as other sources like underwater volcanic activities or permafrost are not really known, any conclusions of exclusively human initiated changes are indeed fanciful.

And: Dividing (2) by (1) provides the “airborne fraction” - this is not an assumption to calculate CO₂ absorption as claimed by H1, but simply an observational number.

Köhler et al. and the IPCC presume that natural fluxes are constant. We show that they cannot be constant. This central failure invalidates Köhler et al’s analysis, as well as the reviewer’s claims (see also comments to Reviewer 3).

H1 also claims that ocean acidification is based only on models: “Climate models are even invoked to claim in which layers of the ocean carbon will accumulate and, thereby, lead to acidification. Such claims are little more than hypothetical.” Well, ocean acidification is observed at several long-term oceanic observation stations, a further observational evidence that is ignored by H1.

Comments to Claim 3: Treatment is too simple
See above my comments to claim 1.

Comments to Claim 4: Application of paleoclimate record is incorrect
This section contains again old material on the fallacy of ice core measurements by Jaworovsky that has been disproved long time ago.

I also concur with Köhler et al., that paleo-CO2 determination from stomata density on plant material has been disproved. H1 ignores any literature of these disprovals - see also comment below.

Unfortunately the reviewer only gives a general statement and does not explain what he/she believe to be incorrect in our Reply about paleoclimate records. Therefore, here we cannot respond on any further details.

Comments to Claim 5:
It is up to the scientific journal to which extent it accepts references to non-refereed literature. What is up to the author, however, is a fair assessment of the existing refereed literature and not selectively cite literature that supports his own claims as done here. I strongly concur with Köhler et al. that H0 and even more so H1 both cite publications (some in the gray literature) that have been proved to be wrong. Also one of the main claims regarding the 14C vs CO₂ absorption is referenced to Salby (2016), which is not even a gray literature document but a link to scientifically unrefereed videos of two lectures given by M. Salby.

Is Köhler citing literature which contradicts his scientific understanding? When developing a concept different to the mainstream, it is not appropriate to list the literature everyone knows and to repeat this in each article again. It is much more close-by and gives more sense to cite papers which confirm and support a modified approach.

Reviewer 1 should have listed and explained which of our cited publications have been proved to be wrong. Only to write a comment, as this is obviously a habit of Köhler and others, when they do not agree with the results or conclusions of a paper, is by far no proof for a flawed publication, particularly when a Reply to such Comment is suppressed. A serious rebuttal requires a detailed evidence where an approach or a theory fails, not only a simple statement in a Comment.

-Reviewer 2 - no comments
The reply by Harde et al is erroneous, misleading and in conflict with many different observations. It must not be published.

The main argument by Harde is that the removal flux of CO$_2$ from the atmosphere, $a$, is proportional to the atmospheric CO$_2$ concentration, $C$, and, thus, is governed by the equation $a=-C/t$. The time scale of removal $t$ is estimated by Harde to be about 4 years only.

Harde states: “we considered a fundamental physical constraint that must be obeyed. Atmospheric CO$_2$ is governed by the balance equation, the conservation law wherein the uptake of CO$_2$ is proportional to the instantaneous concentration of CO$_2$”. While many fluxes in physical, biological and chemical systems are governed by first order kinetics, this is not a universal physical law as claimed by the author. For example, a diffusion flux is driven by the concentration gradient (Einstein, 1905) and a net flux of a soluble gas between water and air is not proportional to the concentration in the air. The net flux is proportional to the difference in partial pressure or concentration between the water and air (Wanninkhof, 2014). First order kinetics fails to represent the exchange of CO$_2$ between the atmosphere and the ocean.

It is unphysical to neglect the flux of CO$_2$ from the sur ocean to the atmosphere as done by Harde.

See our comment to Reviewer 1. It should further be clear that the Bern Model as well as any of its modifications are also based on first order kinetics. The difference to our approach, however, is that not the actual atmospheric CO$_2$ concentration but only deviations from an assumed equilibrium CO$_2$ concentration in 1750 are considered. Such procedure neglects natural variations and exclusively focuses on human emissions. The existing discrepancy to observations is simply compensated by significantly increasing the absorption time, this with the argument that any additional uptake of extraneous reservoirs is strongly restricted. The fatal flaw of those models is to suppose a strong stepwise saturation of sequentially positioned reservoirs, each characterized by different decay times, although neither ocean nor land uptake indicate any significant saturation effects (see also Reply, Appendix A.3). The failure of such a description is twofold:

1. It does not obey the conservation law, as shown in the Reply and
2. Prevalence of a single absorption time is an empirical fact: documented in $^{14}$C(t).

Reviewer 3 misses that a net flux can also be expressed as the difference of all emissions and all uptake. This is particularly necessary, when different and independent emission sources have to be taken into account. For an exchange between the atmosphere and oceans the net flux, which is proportional to the difference in partial pressures between water and air $\Delta p_{CO_2} = (p_{CO_2})_{sw} - (p_{CO_2})_{air}$ or proportional to the concentration difference $\Delta C = C_{sw} - C_{air}$, can also be expressed by the respective rates $e_{sw} - a_{air} = \varepsilon C_{sw} - \alpha C_{air}$ with $\varepsilon$ as emissivity and $\alpha$ as absorptivity rate.

There are numerous measurements of the partial pressure of CO$_2$ in the atmosphere and the sur ocean that show an increase in sur water and atmospheric CO$_2$. For example, the latest version of the Sur Ocean CO$_2$ Atlas (SOCAT; version 5; https://www.socat.info/) has 21.5 million quality-controlled observations from 1957 to 2017 for the global oceans and coastal seas (Bakker et al., 2016) and demonstrate an increase in CO$_2$ both in the air and the water.

We do not refute any increase of CO$_2$ neither in air nor in water. But such increase must not exclusively be the result of a saturated uptake of anthropogenic emissions, instead it can also result from a rising sea surface temperature. This is considered in the "alternative concept".

Harde states: “Common to many physical processes, this feature of CO$_2$ absorption is an empirical fact: It is observed in the decay of carbon 14. $^{14}$C is a tracer of atmospheric CO$_2$. It was elevated by nuclear bomb testing during the 1950s and 1960s. As seen in Fig. 1 (circles), the decay of $^{14}$C after nuclear testing ended is almost perfectly exponential. .., and Harde provides an estimate of the decay time scale of 8.7 yr in Figure 1.

This estimate of the removal time scale is based on a misinterpretation of observations of the $^{14}$C/C ratio
of atmospheric CO$_2$. Radiocarbon data are given in D$^{14}$C units ("D" stands here for the Greek Delta) and the background air radiocarbon data, mentioned by Harde in Fig. 1, are reported by (Levin et al., 2013) as fractionation-corrected permil-deviations from Oxalic Acid standard activity corrected for decay. It holds: D$^{14}$C = (14R$_N$/14R$_{Std}$ – 1) 1000 permil, where 14R$_N$ is the 13C normalized activity and 14R$_{Std}$ the Oxalic Acid standard activity. The later corresponds to an isotopic 14C/C ratio of 1.7 10$^{-12}$ (see (Orr et al., 2017; Siegenthaler, 1989; Bé et al., 2013). Setting an isotopic ratio equal to a concentration as done by Harde to infer the CO$_2$ removal time scale is simply wrong.

It is not clear what Reviewer 3 designates as misinterpretation of observations of the $^{14}$C/C ratio and where in our Reply an isotopic ratio is set equal to a concentration. To emphasize this again, an accurate determination of the $^{14}$C/C ratio or an absolute $^{14}$CO$_2$ concentration in air is of no relevance for our considerations. Different to radiocarbon dating only their relative change with time after some perturbation is of interest. From this it is derived an upper limit of the CO$_2$ residence time in the atmosphere. What is shown in Fig. 1 is the perturbation of the $^{14}$CO$_2$ radioactivity in the atmosphere due to the bomb tests with its subsequent decline after the stop of these tests, this in relative units. This figure indeed uses data of Levin et al. (1994, http://cdiac.ess-dive.lbl.gov/ftp/trends/co2/vermunt.c14), but not the data reported in 2013.

It is well known that the observed radioactivity $^{14}$R of $^{14}$CO$_2$ is a direct indicator of the instantaneous number of $^{14}$CO$_2$ molecules in a sample and, thus, a measure of their concentration, since the radioactive decays per time and volume are directly proportional to the number of radioactive molecules in a volume and thereby proportional to their concentration in air. With a half-life of 5700 yr, much larger than the residence time of CO$_2$ molecules in the atmosphere, the decline of radioactive decays per time is a direct indication, how long $^{14}$CO$_2$ molecules and in good approximation (with a small correction due to fractionation) also the other isotopologues in average are staying in the atmosphere, before they are exchanged.

A perturbation P(t) in the activity rate $^{14}$R(t) which may be defined as

$$P(t) = \frac{^{14}R(t) - ^{14}R_B}{^{14}R(0) - ^{14}R_B} = \frac{D^{14}C(t) - D^{14}C_B}{D^{14}C(0) - D^{14}C_B} \cdot 10^3 = \frac{\Delta^{14}C(t) - \Delta^{14}C_B}{D^{14}C(0) - D^{14}C_B} \cdot 10^3,$$

(1)

describes the difference between the observed rate $^{14}$R(t) after the stop of bomb tests and a background activity $^{14}$R$_B$ caused by cosmic ray activation of CO$_2$ and measured before the tests. The approximate symbol expresses the lack of knowledge that from the web-site http://cdiac.ess-dive.lbl.gov/ftp/trends/co2/vermunt.c14 it is not clear, if the tabulated values D$^{14}$C(t) are already fractionation corrected or not.

The normalized perturbation as plotted in Fig. 1 of the Reply is:

$$P_N(t) = \frac{^{14}R(t) - ^{14}R_B}{^{14}R(0) - ^{14}R_B} = \frac{D^{14}C(t) - D^{14}C_B}{D^{14}C(0) - D^{14}C_B}$$

(2)

with $D^{14}$C$_B$ as an average D-value before the bomb tests and $D^{14}$C(0) as the maximum in 1964. $P_N(t)$ is again displayed in Fig. A on a magnified scale together with the original data $D^{14}$C(t). The only consideration of relevance is that the reference ($^{12}$C) is changing. We can show that, like the Suess effect, it’s influence on the decay of $D^{14}$C is inconsequential.

Both plots proceed absolutely identical and can be fitted with identical exponentials. Two examples for a residence time of 8.7 yr (green line) and a time of 15 yr (blue line) are also shown. The reader may decide, what fits better. This strongly depends on how the very first part of the decline is weighted and how the background is defined. Because of this insecurity and smaller discrepancies between observations on the Northern and Southern Hemisphere in the Reply we always talk about an absorption time of only a "decade", where the apparent absorption is actually an upper bound on true absorption.

We are aware that the meanwhile extended observations of Levin et al. (2013) together with data from their homepage may allow an improved definition of the background. A plot for the fractionation corrected $\Delta^{14}$C values in relative units is displayed in Fig. B. These data give a slightly larger upper limit
for the residence time of $\tau \approx 15 \text{ yr}$, but a longer time scale may also follow from inter-calibration errors between two different sites. Whatever, the fatal discrepancy to the Bern Model remains. This is the main aspect which has been discussed in the Reply. It has also been mentioned several times that due to re-emissions of $^{14}$CO$_2$ from extraneous reservoirs the real residence time of $^{14}$CO$_2$ in the atmosphere as well as the other isotopologues of CO$_2$ can only be shorter.

The CO$_2$ and $^{14}$C data for tropospheric air show that the amount of radiocarbon in the troposphere remained almost constant in the past decades. $^{14}$CO$_2$ decreased from about 150 permil in 1990 (http://www.iup.uni-heidelberg.de/institut/forschung/groups/kk/Data_html) to about 40 permil in 2010 (Levin et al., 2013). This corresponds to a drop in the isotopic ratio 14R$_N$ of about 9.5%. At the same time atmospheric CO$_2$ increased by 9.6% from 354 to 388 ppm.
Thus, tropospheric radiocarbon inventory changed little over the past decades and the claim that radiocarbon concentrations, and by analogy CO2 concentrations, decrease with an exponential removal time of less than 10 years is in conflict with the atmospheric D14C and CO2 observations.

This is no conflict, see above. An almost exponential decay of 14CO2 as explicitly mentioned in the paper of Levin et al. can be observed much more sensitively directly after the stop of the bomb tests. 55 yr later (several residence times) a surplus of radioactive molecules indeed should have disappeared and the concentration is mostly determined by the background activity.

Levin et al. write: "The Δ14CO2 decline today is driven primarily by the ongoing input of 14C-free fossil fuel CO2 into the global atmosphere, as the atmospheric bomb 14C perturbation of the early 1960s has been almost fully equilibrated with surface ocean water and the terrestrial biosphere." But the upper plot from their own data shows no obvious deviations from an exponential which fits the data over the last 53 yr and doesn't need any additional 14C-free emissions which in any case can only contribute to a small correction of the decline. Nevertheless, besides any fossil fuel emissions a decreasing background can also be explained due to stronger upwelling waters of the deep ocean, melting glaciers, partially thousands of years frozen, and of course by geo- and solar-magnetic influences.

But it would be a fatal error when reviewer 3 believes we infer from the 14CO2 decay also a general CO2 decrease in the atmosphere. 14C goes where 12C goes. If it didn't, we wouldn't be looking at it. The 14CO2 decline allows to deduce an upper limit of the residence time, it is not a tracer for the atmospheric CO2 concentration, which depends on the in- and out-fluxes.

This difficulties by the author to correctly convert units demonstrates a lack of a sound physical and biogeochemical understanding of the carbon cycle.

Before reviewer 3 expresses such denunciating statement he/she should explain, which units are incorrectly converted and what other time scale would be derived, when D14C-data (corrected or not corrected) are analyzed in comparison to a relative activity rate!

A distinction leaped upon by the reviewer is as important as the Suess effect, which is shown in the Reply to be inconsequential. What matters is the relative change of 14C, irrespective of normalization. Changes in the reference, 12C, can be shown to have only a minor influence. And what can be wrong to plot rates in relative units which refer to an initial rate in 1964 and to compare the 14C decline with the prognosticated decline of a standardized input pulse as this is discussed in the Bern Model? Or does the reviewer seriously question that a changing radioactive decay rate is no measure for the changing number density of 14CO2 molecules in air?

Harde states: “The observational vacuum must be compensated for by models, which are intertwined with the scarce observations. “ and that “Human emissions only contribute 15 % to the CO2 increase over the Industrial Era”. The fact that Harde is not aware of the existing observations and measurements does not mean that these measurements do not exist. Two globally representative records are formed by observations/measurements of the atmospheric 13CO2/12CO2 isotopic ratio (Francey et al., 1999) and of the atmospheric oxygen content (or O2/N2 ratio) (Keeling et al., 1996). The atmospheric isotopic record is complemented by a wealth of isotopic data from the ocean (Eide et al., 2017b;Eide et al., 2017a;Key et al., 2004) and the land biosphere (Cornwell et al., 2016). These geochemical records are in conflict with the claim that the atmospheric CO2 increase is largely driven by a response of natural carbon fluxes to warming.

Huntingford et al. (2017) report that dark respiration is underestimated and apparently contributes about 30% more than derived from previous studies. This respiration increases exponentially with leaf temperature.

The 13C data show that the ocean is enriched in 13C relative to the atmosphere and the atmosphere is enriched relative to the land biosphere. A net addition of carbon from the ocean to the atmosphere is
inconsistent with the observed decline in atmospheric 13C/12C ratio (it is also inconsistent with marine measurements of total carbon and of superficial CO2). Similarly, the O2 measurements show that the land biosphere is a carbon sink, not a source. Only a source that is depleted in 13C/12C and linked to consumption of oxygen, i.e., the release of CO2 from fossil fuel burning, can explain the decrease in atmospheric 13C/12C ratio and in atmospheric O2.

The 13C/12C ratio in the atmosphere or its normalized difference (δ13C)atm is measured at Mauna Loa and at the South Pole atmospheric station (see AR5, Fig. 6.3). At Mauna Loa, e.g., it shows an average decrease of 0.7‰ from -7.6‰ in 1980 to -8.3‰ in 2010. Over these 30 years was the anthropogenic emission rate increasing by 1.8 ppm/yr from 2.5 ppm/yr in 1980 to 4.3 ppm/yr in 2010 (CDIAC). With respect to the total emission rate this corresponds to an increase of 1.8 %.

It should be absolutely clear that with real in- and out-fluxes the fossil fuel emissions cannot cumulate in the atmosphere but will be absorbed with the same probability as naturally emitted CO2 molecules (equivalence principle). Thus, in first order the 13C/12C ratio in the atmosphere can only be reduced by a leaner 13C concentration as the result of its fraction and concentration difference to the total flux. Smaller corrections will result from the fractionation for lighter molecules and a slightly higher emission probability for molecules, which were just uptaken (re-emission).

Since the fossil fuel emissions have a leaner (δ13C)fuel = -18 ‰ compared to the atmosphere or (δ13C)fuel = -25 ‰ with respect to the PDB standard, the rising human emissions over the 30 yr interval can only have contributed to a decline of Δ = (δ13C)fuel×1.8% = -18‰×1.8% = -0.32 ‰ or a (δ13C)atm = -7.92‰ in 2010. Thus, the difference to -8.3‰, which is more than 50%, in any case must be explained by other effects.

One possible explanation for a faster decline of (δ13C)atm to -8.3‰ can be - even with the oceans as source and an 13C/12C ratio in sea water greater than in air (particularly in the surface layer) - that the lighter 12CO2 molecules are easier emitted at the bound than 13CO2 with the result of a leaner 13C concentration in air and higher concentration in the upper water layer (see also, Siegenthaler, U. & Münich, K.O., 1981: 13C/12C fractionation during CO2 transfer from air to sea. In: Bolin, B. (Ed.): Carbon cycle modelling (SCOPE 16). John Wiley & Sons, 249-257). From water we also know that its isotopologues are evaporated with slightly different rates.

Such behaviour coincides with the observation that with higher temperatures the total CO2 concentration in the atmosphere increases, but the relative 13CO2 concentration decreases. This can be observed, e.g., at El Niño events (see M. L. Salby, 2012, Fig. 1.14; Etheridge et al., 1996: Natural and anthropogenic changes in atmospheric CO2 over the last 1000 years from air in Antarctic ice and firn, J. Geophys. Res. 101, 4115-4128; Friedli et al., 1986: Ice core record of the 13C/12C ratio of atmospheric CO2 in the past two centuries, Nature 324,237-238).

We also remind at the Mauna Loa curves which show for the total emissions a seasonal variation with an increasing CO2 concentration from about October till May and a decline from June to September. The increase is driven by respiration and decomposition mainly on the Northern Hemisphere (NH), and the temperature on the Southern Hemisphere (SH). The (δ13C)atm value is just anti-cyclic to the total CO2 concentration (AR5, Fig. 6.3) with a minimum at maximum CO2 concentration and with seasonal variations of 0.3 - 0.4‰, the same order of magnitude as the fossil fuel effect.

An increase of 13C in the upper strata of oceans also results from an increased efficiency of photosynthesis for lighter CO2. Plankton accumulates this form and sinks to lower layers, where it decomposes and after longer times is emitted in higher concentrations with stronger upwelling waters particularly in the Eastern Tropic Pacific.

It is also known that the 13C concentrations are by far not equally distributed over the Earth's surface. So, it can be expected that with volcanic and tectonic activities different ratios can be released.

Another fact is that the CO2 gradient between the Northern and Southern Hemisphere is increasing since the start of atmospheric CO2 measurements in the late 1950ies. This increase scales linearly with anthropogenic emissions as these emissions are predominantly located in the northern hemisphere.
ruling out a major role for ocean outgassing of CO2 as most of the ocean is in the Southern Hemisphere. The strongest terrestrial emissions result from tropical forests, not industrial areas. The strongest oceanic emissions can be seen from the map of Takahashi et al. (2009) They are between 10°N and 10°S in the Eastern Tropic Pacific. Nevertheless, there is no doubt that industrial emissions endow their fingerprints in the atmosphere; this was never questioned, neither in Harde (2017) nor in the Reply. The influence and size of these emissions has already been discussed above, and their different impact on the two hemispheres can be estimated from Fig. 6.3c of AR5-WG1, indicating a slightly faster decline of \((\delta^{13}C)_{atm}\) for the NH in agreement with predominantly located industrial emissions in this hemisphere. But this impact is still significantly less than the seasonal variations, and it doesn't rule out the validity of the Conservation Law.

Independent of the size and location of "oceanic outgassing" or not the crucial point is another: From Takahashi et al. (Global Biogeochemical Cycles 7, pp. 843-878, 1993) and similar studies it follows that oceans are net sinks. According to the IPCC the oceans account for 40% of overall absorption of CO2 (AR5, 2013, Fig.6.1), from which over the Industrial Era the human contribution in average was less than 1% and actually accounts for about 2.4% (0.55x4.3%).

Further following the IPCC, with an anthropogenic emission of \(e_A = 8.9 \text{ PgC/yr} \) (32.7 Pg/yr \(CO_2 = 4.2 \text{ ppm/yr}\)) in 2012 and an AF of 45% the oceans absorb 55% of 40%, which gives 2 PgC/yr, and including the land uptake the total anthropogenic absorption is \(a_A = 8.9 \text{ PgC/yr} \times 55% = 4.9 \text{ PgC/yr} = 18 \text{ Pg/yr} CO_2 = 2.3 \text{ ppm CO}_2\). This calculation is the result of an extremely simplified balance equation

\[
dC/dt - e_A = -a_A
\]

with the measured atmospheric carbon or \(CO_2\) increase of \(dC/dt = 4 \text{ Pg/yr} C = 14.7 \text{ Pg/yr} CO_2 = 1.9 \text{ ppm/yr} CO_2\). From Eq.(3) the ever repeated argument is deduced: "the left side of this balance equation is negative, thus, nature (oceans and land) is a net absorber and cannot be an emitter". Why this absorption is still a constant fraction of the continuously increasing anthropogenic emissions, although the uptake is assumed to be strongly saturated, is not further explained.

In the alternative concept based on the Conservation Law the oceans and land together absorb the same amount; they are still net absorbers, only based on another accounting scheme. To emphasize the most important differences to the IPCC, we again summarize here the main deviations, although in a slightly different form already mentioned above for Reviewer 1:

(i) Natural fluxes cannot be assumed to be the same over 270 years. We observe a continuous temperature increase over recent years (the IPCC says: as fast as never before), and already seasonal changes modify significantly the in- and out-fluxes, comparable or even stronger than the anthropogenic emissions. Thus, in any realistic consideration also changes of these fluxes have to be included. A balance exclusively focussing on anthropogenic emissions as done above (Eq.(3)) and deducing an absorbed fraction only from the observed \(CO_2\) increase is incomplete and erroneous.

(ii) As elaborately outlined in the Reply and also above, a complete balance equation has to consider the full emission and absorption rates and not only deviations from an artificial equilibrium assumed in 1750. In a balance which considers the full fluxes, the absorption scales also with the total\(CO_2\) concentration and not with deviations from an assumed equilibrium.

(iii) The total in- and out-fluxes with all their environmental influences just define the equilibrium concentration, not an arbitrary definition for the year 1750. After a perturbation the system tries to return to its equilibrium position with a typical time constant known as residence time.

(iv) With (i) - (iii) and an anthropogenic carbon emission rate \(e_A = 8.9 \text{ PgC/yr} \), resp 4.2 ppm/yr \(CO_2 \) (4.3% of the total emission rate 97.2 ppm/yr) fossil fuel emissions contribute not more than 17 ppm to the \(CO_2\) concentration of 390 ppm in 2012.

(v) At a further constant natural and anthropogenic emission rate the atmospheric \(CO_2\) concentration no longer increases, the system stabilizes at a level, e.g., of 390 ppm. Emissions not exceeding the previous years are again fully absorbed, also anthropogenic emissions over the running year.
At increasing natural and/or anthropogenic emission rates together with a reduced uptake rate the equilibrium level rises up and the system tries to stabilize at a new higher \( \text{CO}_2 \) concentration.

A realistic balance equation satisfying the Conservation Law, takes the form:

\[
\frac{dC}{dt} - e_A(t) = e_N(T(t)) - C / \tau(T(t))
\]

with \( e_N(T) \) as the time and temperature dependent natural emission rate and \( \tau(T) \) as the time and temperature dependent absorption or residence time. The left side is the same as above, and the right side represents a net absorption rate, in its size the same as above. But this absorption is no longer exclusively led back to a fractional uptake of only anthropogenic emissions, but it is the result of the native in- and out-fluxes with their temperature and time dependence.

It must be clear that an additional process like outgassing of the oceans is not simply switched on, but that the anyway active natural sources and sinks which absolutely dominate the balance, are slightly changing in their emission and absorption rates. This is expressed by Eq.(4) and Eq.(13) of the Reply by the temperature dependent rates, including the increasing anthropogenic emissions. And Fig. 3 of the Reply shows that with this alternative approach the measured \( \text{CO}_2 \) concentration over the last 60 years can be well explained.

Harde invokes a temperature sensitivity of a natural CO2 flux to explain most of the atmospheric \( \text{CO}_2 \) increase. As far as the temperature sensitivity of the marine carbon is concerned, an increase in sur water temperature of 1K leads to an increase in pCO2 of about 4 percent. Taken at value, a warming by 10K would be required to explain the atmospheric CO2 increase of 40% (280 ppm to 400 ppm) over the industrial period.

Indeed, 1°C gives 4.4% pressure increase. Incline from 280 to 390 ppm (in 2012) is 110 ppm, from which 17 ppm result from anthropogenic emissions. The remaining 93 ppm are 33% from 280 ppm and not more than 25% from 373 ppm. 33%/4.4% gives a necessary temperature increase of 7.5 °C to explain the \( \text{CO}_2 \) growth exclusively by oceanic emissions. But this would require steady state conditions, which do not exist. Although local seasonal variations of this size with intense emission pulses are observable, in average the oceans are \( \text{CO}_2 \) sinks, whose uptake is declining with increasing temperature.

So, a rising atmospheric \( \text{CO}_2 \) concentration must not necessarily result from a \(^{13}\text{C}\) enriched emission of the oceans, but it is also the consequence of a reduced uptake at growing (pCO2)sw. This continues until a new equilibrium level between in- and out-fluxes is established. This has been explained again above. But also other temperature dependent sources like land decomposition, permafrost or emissions, which are stimulated by internal oscillations like ENSO or AMO, have to be considered.

It is not the question from where the additional \( \text{CO}_2 \) would come from or that the oceans are net sinks, the important point is that with all emissions, natural and anthropogenic, and the respective uptake the steady state conditions for the atmospheric \( \text{CO}_2 \) concentration are changing with temperature, radiation and other environmental influences.

Carbon is conserved in the climate system. The model by Harde assumes a balance equation (eq. 2) for atmospheric carbon which is built on wrong assumptions and is in conflict with measurements. In addition, the model fails to consider where this carbon and carbon isotopes are going. It is build on equations which are not supported by physics and chemistry and yields results in conflict with many different types of observations. The reply by Harde to the comment by Köhler et al. contains many wrong statements, some of which are discussed above, and many wrong claims and concepts. It should therefore not be published.

Apparently the reviewer impeaches the Conservation Law. Our analysis of the carbon cycle, which exclusively uses data for the \( \text{CO}_2 \) concentrations and fluxes as published in AR5, shows complete conformity with all observations, measurements and natural causalities. Different to the Bern Model it is in full agreement with the fundamental physical laws and, of course, it fully accounts for carbon
entering and leaving the atmosphere. Obviously reviewer 3 missed to read Appendix A.3 of our Reply where several references are listed explaining the uptake and sequestration of CO₂.

References of Reviewer 3:


Levin, L., Kromer, B., and Hammer, S.: Atmospheric ∆ 14 CO 2 trend in Western European background
