

# ESD Ideas: Photoelectrochemical carbon removal as negative emission technology

## Author's response

Matthias M. May & Kira Rehfeld

December 4, 2018

Dear Prof. Zeng,

thank you for the evaluation of our manuscript. We would also like to thank the Referees for their valuable comments.

In addition to our point-by-point answers to the Referees in the Author comments (attached below), we have also introduced an additional brief discussion on the storage itself (page 4):

*“Requirements for the safe storage will vary significantly with the choice of the sink product. Formic acid would certainly be problematic due to its corrosiveness, also in the case of spilling events. Acetic acid and the alcohols are inflammable at high concentrations and would have to be diluted with water, increasing the water and volume footprint. For oxalate, the sink product with the highest STC efficiency, mineral trapping by reaction with a suitable calcium source, such as calcium chloride, to the stable mineral whewellite could be anticipated. The 10 Gt CO<sub>2</sub> goal would result in roughly 17 Gt of the mineral. As a solid product, this – or other organic minerals – would not require underground injection and hence at this stage appears to be the most attractive option, with similar requirements as biomass storage. However, post-processing will increase the energy footprint and hereby also the costs.”*

To the best of our knowledge, there is currently no literature on storage issues for the geological injection of high-value hydrocarbons into underground reservoirs. This is most probably due economic boundary conditions, which, at this stage, strongly favour their extraction.

A version of our manuscript with all changes highlighted in colour is attached at the end of this document.

Yours sincerely on behalf of the Authors,

Matthias May

## ***Interactive comment on “Ideas: Photoelectrochemical carbon removal as negative emission technology” by Matthias M. May and Kira Rehfeld***

**Matthias M. May and Kira Rehfeld**

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We thank Prof. Parkinson for his valuable comments. In the following, we address them on a point-to-point basis.

**Referee:** 1. “I do find it unlikely that anyone who is investing substantial energy in a CO<sub>2</sub> reduction product, that also has fuel value, can be persuaded to sequester the product. Even the first reduced product, formate, that has the highest potential for efficiency is essentially a hydrogen carrier.”

**Authors:** This concern is also valid for other negative emission approaches such as

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biomass production. Therefore, the creation of incentives to actually sequester the products of negative emission technologies is certainly an issue that has to be addressed in future climate treaties. We will add a general statement to the manuscript.

**Referee:** 2. "On page 2 line 19 they suggest that the reduced products could be used as precursors to "organic construction materials". Given the scale of what would be needed it would be unlikely that such a huge market for such a material would exist. And if so it would have to be something much cheaper than could be justified from the cost of the electrons needed to reduce the CO<sub>2</sub>. Large subsidies might be needed to make this possible."

**Authors:** It is true that the market for organic construction materials or other plastics will probably be smaller than the volume of products generated by negative emission technologies in the anticipated scenarios, i.e. 10 Gt CO<sub>2</sub> per year by 2050. We see this rather as an added benefit since energy and money will have to be invested anyway for the achievement of a (sub) 2°C target limit for global warming with the aid of negative emissions. To what extent the further use of the carbon-rich products (such as for organic plastics) will make sense economically, will depend on the costs of sequestration as well as the future costs for the extraction of the remaining fossil oil resources.

**Referee:** 3. "I would like to see the authors include oxalate in their analysis since this requires only one electron per CO<sub>2</sub> and could be stored as solid oxalic acid dihydrate by concentrating the reduced brine or as precipitated calcium oxalate if a calcium source other than CaCO<sub>3</sub> or limestone could be used such as CaCl<sub>2</sub> from the ocean or other natural brines."

**Authors:** We appreciate this suggestion. Oxalate is indeed a highly interesting product which we had not included. Oxalate production from CO<sub>2</sub> comes with an electrochemical load of 1.82 eV [e.g. Qiao et al, Chem. Soc. Rev., 2014, 43, 631] and one electron per CO<sub>2</sub> molecule. The overall resulting solar-to-carbon efficiency in our model (with its idealised catalysis), would be with system loss about 15%, which is significantly higher

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than formate (see Fig. 1, update to Fig. 1c,d in the manuscript). With respect to point 1, one could argue that oxalate is a lower-value molecule, which results in a higher incentive to actually sequester the product.

We will include the dicussion above and the updated figure in the revised version of our manuscript.

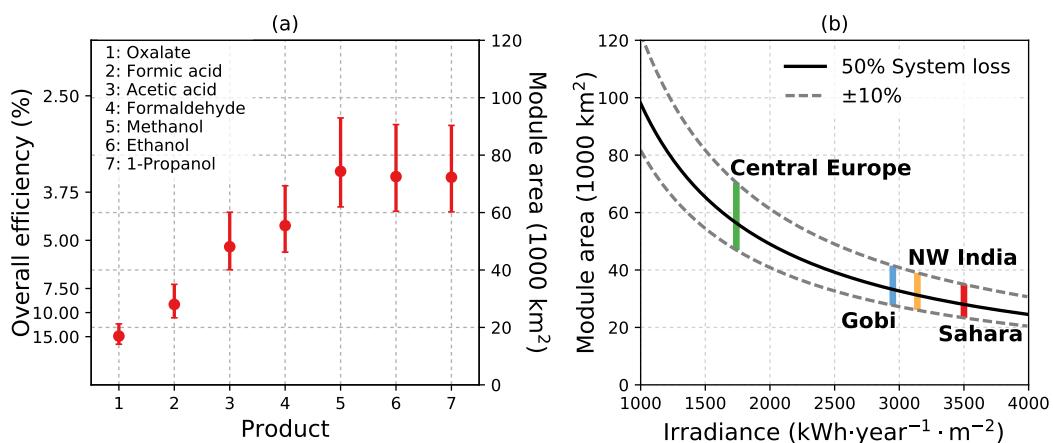
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Interactive comment on *Earth Syst. Dynam. Discuss.*, <https://doi.org/10.5194/esd-2018-53>, 2018.

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**Fig. 1.** Efficiency and module area for the -10 Gt CO<sub>2</sub>/year scenario. (a) STC efficiency and module area required under Sahara irradiance at 50% system loss. (b) Module area for formic acid production.

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## ***Interactive comment on “Ideas: Photoelectrochemical carbon removal as negative emission technology” by Matthias M. May and Kira Rehfeld***

**Matthias M. May and Kira Rehfeld**

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We thank the referee for the detailed and constructive criticism. In the following, we address the comments on a point-to-point basis. We also indicate the changes to be implemented in our manuscript.

**Referee:** 1. “The last sentence of the abstract (and some associated text in the introduction) contains some assertions that are not supported by the literature. These detract from the paper overall. Specifically:

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First "should (i) rely on an unlimited source of energy (solar)", contains a number of implicit assumptions. "unlimited" implies that negative emissions should be maintained indefinitely. If taken literally this would eventually decrease CO<sub>2</sub> concentrations below preindustrial levels! Not a goal I suspect the authors intend nor has this been proposed. If we posit an eventual goal of a zero carbon energy system, then the role of negative emissions is a finite one whose role is to "draw down" atmospheric CO<sub>2</sub> levels until a "safe" level is reached (e.g. UNFCCC). Therefore, an unlimited source of energy is not required, just a source that is sufficient for the amount of negative emissions that might be needed."

**Authors:** *We agree that a reduction of CO<sub>2</sub> concentrations below preindustrial levels is most probably not desirable. The length of time, for which negative emissions will be required, depends on the pace and the completeness of the transition towards a low- or zero-carbon economy and is hitherto unclear. By "unlimited" we did, however, not want to express "infinite", but rather "non-limiting" in a sense that the energy source should scale up to the required level and not deplete over the anticipated timeframe in the order of at least several decades or a century (as also mentioned by the Referee in point 12). The decarbonisation of the electricity sector, the fuels sector, a growing world population, increased standards of living, and finally negative emission technologies will all add to the demand for sustainable energy sources. Consequently, it is important that there are at least no physical limits that might arise from the sheer scale of the undertaking. This does, however, not exclude economic barriers.*

**Changes to the manuscript:** To avoid this misunderstanding, we will change the wording to "[...](i) rely on a scalable and sustainable source [...]" . We will furthermore correct "(iv) be [...]" to "(iv) feature [...]" .

**Referee:** 2. "While of course it is important that any such process "result in a safely storable product", there is no evidence for the second portion of this statement, that this needs to be liquid or solid, not gaseous. There is a related misstatement later

about geologic CO<sub>2</sub> storage since, in fact, at the depths where CO<sub>2</sub> is injected for storage pressures are high enough that CO<sub>2</sub> is liquid. A substantial body of literature has verified that CO<sub>2</sub> injection at a number of sites around the world, the most well known of which is likely the Norwegian Schipner natural gas field, has shown that CO<sub>2</sub> injection results in stable, trapped CO<sub>2</sub>. Again, this does not detract from the idea proposed by the authors, but statements in a scientific paper do need to be scientifically accurate! There is also a rather long history of CO<sub>2</sub> injection for enhanced oil recovery, which has also provided substantial information on sub-surface behavior of CO<sub>2</sub> (albeit in a condition not designed for 100% long-term storage)."

**Authors:** *Gaseous products are, by their intrinsically more volatile nature, more challenging to contain over long periods of time than solids or liquids. The trapped CO<sub>2</sub> mentioned by the referee is in this "product" state also not gaseous, but might, upon change of the conditions (e.g. a variation in pressure) return to the gaseous state. We do, however, agree that without further elaboration, this short statement does not improve clarity.*

**Changes to the manuscript:** We will remove "(e.g. liquid or solid, not gaseous)".

**Referee:** 3. "Line 15. 'therefore, the currently most feasible option appears to be the use of natural photosynthesis to generate biomass through afforestation or ocean fertilization.'

The authors do not appear to be aware of the literature here. First, it is not clear if ocean fertilization is feasible (experiments have not always provided support for this idea), nor are the side effects of ocean fertilization well enough understood."

**Authors:** *We are aware of the literature. The compactness of the "ESD Idea" does, however, only allow us to refer the reader to select review articles, where the different technologies are discussed in more detail, e.g. the reference [Smith et al., *Nature Climate Change* 6, 42 (2016).] We agree that each technology has its specific advantages*

*and risks and/or limits. Consequently, at the current level of negative technologies, the judgement, which technology is most promising, depends to a large degree on the relative weight of the parameters. We rephrase some of our statements to clearly indicate that this is a lively and ongoing discussion in the community and emphasize that there is indeed abundant literature.*

**Changes to the manuscript:** We will add “[...] are explored] and there is an active discussion on costs and scalability of the various technologies, see (Smith et al., 2016) and references cited therein.”. Furthermore, we will repeat the Smith et al. reference at the end of our statement “[...] ocean fertilization.”.

**Referee:** 4. “The authors are deliberately ignoring geologic Carbon Capture and Storage (CCS), which is the leading option, along with reforestation, and related strategies, examined in scenarios to date. This is already being practiced today at a number of sites and there are no known technical barriers to large-scale application. While there may be legitimate concerns with this option, some of those concerns are also likely to apply to the option proposed by the authors. A more balanced discussion is needed (particularly since the authors later suggest geologic injection of the carbon-based liquids produced by their methods, which is inconsistent with the neglect of geologic CCS). A discussion of CCS and, presumably, contrast with the author’s proposal needs to be added.”

**Authors:** *With “primarily direct air capture” in “At present, primarily direct air capture and biomass production are explored” on page one, we had geological storage of the captured CO<sub>2</sub> in mind, referring – for the sake of brevity – to the comparative review paper of Smith et al. (2016). In doing so, we followed the terminology of the aforementioned paper, where ‘CCS’ refers to the capture of emissions from fossil fuels, which does not lead to net negative emissions.*

**Changes to the manuscript:** We will add “followed by geologic injection” to “[...] direct

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air capture (followed by geologic injection) [...]" (For further amendments, see our comments to related point 7.)

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**Referee:** 5. "Page 1 Line 22. I am aware of course of the Heck et al. (2018) estimate, however much other literature does not come to the same conclusion (for example see the SSP scenarios, which are produced by models that integrate energy land and economics into a consistent projection framework). This not to discount the issue, but note that this is not a settled issue scientifically, and there are many nuances that prohibit such a blanket statement. For example, there is not one hard and fast estimate for the amount of negative emissions that are needed, this depends on the specific target and the rate that the world energy system is decarbonized. However even taking the author's statement that 10 Gt/year of CO<sub>2</sub> is needed, residue biomass sources (e.g. rice straw, corn stover, etc.), which do not require any additional land, could supply this amount by mid-century as crop production expands globally to support growing population and affluence levels. There is abundant literature on this point."

**Authors:** *This discussion is reflected in the review papers, we refer to (e.g. Smith et al., 2016; Anderson and Peters, 2016), and for the sake of brevity, we cannot dive more deeply into it. We reformulate our statement to put more emphasis on the discussion status.*

**Changes to the manuscript:** We will change this to "There is an ongoing discussion whether scaling biomass production to the required 10 Gt/year is at all compatible with planetary constraints.(Heck et al., 2018)".

**Referee:** 6. "Page 2 line 10. "These could be stored in underground reservoirs such as depleted oil fields, but also used as precursors for organic construction materials." The problem with using these liquids as precursors for organic construction materials is that these materials will eventually oxidize and return carbon to the atmosphere. It is

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possible that this could still result in a long-term sink, but at only a fraction of the initial flow. (There are a number of papers that examine the substitution of wood for concrete as a building material that can be used for references and guidance here and should be cited.)

Further, if the authors are proposing use as construction materials, than the energetic cost of converting liquids to solids should be discussed."

**Authors:** *We would expect the lifetime of the organic construction material to be similar to conventional plastic, i.e. decades to centuries. Due to the compactness of the 'ESD Ideas' format, we can, unfortunately, not go into a deeper discussion at this point. Also, as Referee B. Parkinson pointed out, this pathway will probably not be very relevant, as the market will be too small for the required scale.*

**Referee:** 7. "Page 2 Line 17. As noted above this statement is not correct. First CO<sub>2</sub> is not a gas at the relevant pressures, and there is abundant literature and data that indicate that CO<sub>2</sub> can be safely injected into formations where it appears to be trapped on a long-term basis. (Some of these statements may indicate a misunderstanding of how deep CO<sub>2</sub> injection works. Injected CO<sub>2</sub> does not form some sort of large "bubble", but instead moves into rock pore spaces where chemical and physical reactions then occur.) "

**Authors:** *Again, we would like to refer to the review paper, which we are citing. The trapping mechanisms, as well as the probability of their failure, are discussed in the work of Damen et al. Interestingly, they consider the mechanism of mineral trapping as most secure, an approach that would also be feasible with the sink product oxalate (see below).*

**Changes to the manuscript:** We will rephrase "this leaves us with liquids or solids, since gases, such as CO<sub>2</sub> itself, can leak back to the atmosphere" to "Therefore, liquids or solids appear preferable, as gaseous products could leak back to the atmosphere,

depending on the trapping mechanism.(Damen et al., 2006)"

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**Referee:** 8. "Page 3 Line 6. Reference needed for what "previously largest project for solar electricity production in the Sahara desert" since this is a moving target!"

**Authors:** *We had the – currently stalled – DESERTEC project in mind, but agree with the referee that the scale is a moving target and therefore omit this argument in the revised manuscript for the sake of brevity.*

**Changes to the manuscript:** We will delete "[...]" and about one order of magnitude larger than the previously largest project for solar electricity production in the Sahara desert."

**Referee:** 9. "Page 4, line 10. This "Unlike solar energy, however, large-scale mechanical wind extraction from the atmosphere might be limited. (Miller et al., 2011)" is another strawman that is irrelevant. We do not need unlimited energy for this process, just sufficient, affordable energy. In some locations that might best be supplied by wind, some solar, and in others biomass."

**Authors:** *We do not believe that this is a "strawman" because it is important to consider the whole transformation process towards a carbon-free economy. That includes renewable electricity and fuels production. At the same time, agricultural production is to be maintained for a growing (both in numbers and affluence, as pointed out by the referee above) world population, and, finally, negative emissions are required to stabilize climate. All these transformations depend on energy and, ultimately, land. Consequently, efficiency and scalability are crucial for the success of the process and it is therefore important to acknowledge or discuss potential limitations of the two main "renewable energy" technologies with the currently highest growth rates, i.e. direct solar and wind power.*

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**Changes to the manuscript:** We will replace the sentence with "For the scales required, it appears that the potential of solar energy will, unlike wind, not be a limiting factor.[Kleidon et al. in *Solar Energy for Fuels* (2016)]", changing the reference to a later publication of the authors, where they directly compare wind and solar energy.

**Referee:** 10. "Page 4 line 16 - "While we estimate the costs for photoelectrochemical CO<sub>2</sub> removal to roughly 65 Eur per ton" (add reference to the appendix where the details are given)."

**Authors:** We agree.

**Changes to the manuscript:** We will add a reference to the appendix.

**Referee:** 11. "page 4. What is missing here are a discussion of transportation and storage costs. For any system that is sufficiently large scale, pipelines would likely be the most efficient mechanism for transport. Costs of pipeline transport of CO<sub>2</sub> are well known (this is already a common practice) as also, of course, petroleum products, so a direct comparison of costs per km per tonne of C should be feasible and would be very useful. There are unlikely to be that many suitable storage locations in the places with the highest solar irradiance. So long-distance transport would likely be necessary. This is not necessarily a huge barrier (current scenarios with CO<sub>2</sub> with CCS envision long-distance transport of CO<sub>2</sub>, and the world currently transports large quantities of petroleum across the globe - this would actually be a useful comparison. Are we talking about a volumetric transport rate per year that is on the order, much less than, or greater than current international shipments of oil by tanker? See the data in the "Review of Maritime Transport" series by the UNCTAD)."

**Authors:** We appreciate this suggestion. This is a good point. We added this consideration in Appendix B.

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**Changes to the manuscript:** We will add “Transport costs to the storage location will vary with the chosen product and the vicinity between production and storage facility. If we assume, as a very rough estimate, similar transport costs of formic acid as for crude oil over a distance of 2000 km,[Verma et al., Energy 124 (2017).] this would result in additional 24 Eur per ton CO<sub>2</sub>. The overall volume to be transported would be in the same order of magnitude as the present day oil production.” to the end of Appendix B.

**Referee:** 12. “The volume needed for storage is a significant potential issue for this proposed negative emissions mechanism and needs to have more discussion and some order of magnitude estimates. The total storage volume over, say a 50 to 100 year period should be estimated by the authors and compared with potentially available storage locations. The authors mentioned depleted oil fields - the problem here is the same one mentioned by the authors as an issue for CCS with CO<sub>2</sub>, liquids injected into the oil fields may come to the surface (given that oil already comes to the surface in production wells).”

**Authors:** *We agree that both a substantial storage volume will be required, and that this volume has to be sealed off from the surface. However, the volume depends to a large degree on the product and its further processing. A detailed estimate of this volume is beyond the scope of this manuscript. We can, however, expect that the volume is not significantly larger than that required for the application of direct air capture followed by geological injection. Some products (such as oxalate-derived minerals) could also be stable enough to be stored above-ground.*

**Changes to the manuscript:** See reply to point 13 directly below.

**Referee:** 13. “There will also be some cost for storage. Injection into geologic formations (such as old oil wells) requires compression and pumping. The cost of this is well known and should be added to the cost estimates in Appendix B.”

**Authors:** *The costs for storage will vary significantly with the chosen sink product, especially if it is further processed. Cost estimates for all the different options is beyond the scope of this manuscript.*

**Changes to the manuscript:** We will add “The costs for storage will vary with the sink product, the product volume, and the required post-processing.”

**Referee:** 14. “One advantage of CO<sub>2</sub> sequestration is that CO<sub>2</sub> is harmless, although it does pose a danger at concentrations large enough to exclude oxygen (e.g. this is the sort of low probability high consequence event considered by regulators in developing CO<sub>2</sub> pipeline, and ultimately CCS, regulations). The potential health and environmental issues associated with the proposal should also be mentioned. One would presume that there could be environmental damage due to spills of these hydrocarbons from pipelines and/or leakage into groundwater or to the surface from storage sites. Are there likely to be tradeoffs between carbon density, transportation issues (e.g. low enough viscosity to be transported by pipeline), and low toxicity or other environmental impacts?”

**Authors:** *This is indeed an interesting point that we can only briefly cover here as again, it varies significantly with the chosen product and its post-processing. We will add a short discussion on this.*

**Changes to the manuscript:** We will add “Related to storage are also environmental issues from potential spilling events. Here, formic acid could be problematic due to its corrosiveness. Oxalate, on the other hand, could be processed further with calcite to the stable mineral weddellite.” to Appendix A after “[...] because of its high melting point.”

**Referee:** 15. “Page 5 the statement “these idealised assumptions result in a maximum electronic photocurrent density of  $je$  mAcm<sup>-2</sup>” needs support. How was this value

obtained. What assumptions were used to obtain this specific value.

Similarly here: “It follows that ideally ca. 19% of the incoming solar photons transform a CO<sub>2</sub> molecule to the liquid,” as the percent value does not seem obvious or related to the above values.

The values seem reasonable, but it is important to state one’s assumptions so that readers know exactly what is being referred to here.”

**Authors:** *We expand our description of the calculation. The full calculations are accessible by inspecting the publicly available source code of the solar fuel calculator YaSoFo and the Python notebook, we will make both accessible as asset with our manuscript.*

**Changes to the manuscript:** In the appendix A, we will insert “total” to “[...] over the total incoming photon flux,  $j_{ph}$ , given by the integrated solar spectrum.” and will add thereafter the sentence “The electronic current corresponding to this total photon flux would be the photocurrent that could be extracted from an ideal absorber with an infinitesimally small bandgap, where each photon contributes to one electron in the photocurrent.” Furthermore, we added “under air mass 1.5 global illumination” to “The current density of an ideal tandem absorber under air mass 1.5 global illumination with [...]” and thereafter “Under the assumption of unity absorption above the bandgap, the top cell absorbs photons  $n(\lambda)$  between  $\lambda \rightarrow 0$  nm and the wavelength corresponding to its bandgap, the bottom cell experiences the photon flux filtered by the top cell and therefore absorbs between the respective bandgaps of top and bottom cell. The smaller of the two values then gives the maximum photocurrent at zero load. The operational photocurrent is then obtained by intersecting the overall current-voltage curve of the solar cell with the curve of its load, given by the Gibb’s Free energy of the redox couple and the catalyst characteristics described by exchange current density and Tafel slope. [See asset].”.

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**Referee:** 16. “It is also important to note that these values are ideal cases. This

needs to be emphasized in the main paper. This is fine, and is a reasonable starting point for bounding the possibilities, but it needs to be made clear that this is just the theoretical limit, which is unlikely to be approached commercially. (If we could approach the efficiency of nature, it would be a great starting point.)"

**Authors:** *We already stated in the introduction that 'more than half of the theoretical limits' have been achieved for the similar processes water splitting and CO<sub>2</sub> reduction for solar fuels and "highly idealised" on page 2. We acknowledge that we should make this clearer in the discussion.*

**Changes to the manuscript:** We will change "Taking into account photoconversion, Faradaic, and system losses, values of 10% STC or more appear feasible." (Appendix A) to "[... or more appear feasible] as for the similar process of photoelectrochemical water splitting, 85% of the material-specific and ca. 2/3 of the overall theoretical efficiency limit were already demonstrated on a lab-scale.[Cheng et al.]" and removed "conservative [assumption]" on page three.

**Referee:** 17. "This " $\eta_e = 0.5$ " seem backwards, as the variable is described as "how many electrons are consumed for the formation of one product molecule from CO<sub>2</sub> and water", which would suggest the value should be 2, not 0.5. But perhaps the definition was not written correctly?"

**Authors:** *This was indeed stated ambiguously. For two electrons, the electron efficiency should be 0.5, for four 0.25.*

**Changes to the manuscript:** We will change "[...i.e. how many electrons [...]" to "[...i.e. the inverse of how many electrons".

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Interactive comment on Earth Syst. Dynam. Discuss., <https://doi.org/10.5194/esd-2018-53>, 2018.

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# ESD Ideas: Photoelectrochemical carbon removal as negative emission technology

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**Abstract.** The pace of the transition to a low-carbon economy – especially in the fuels sector – is not high enough to achieve the 2°C target limit for global warming by only cutting emissions. Most political roadmaps to tackle global warming implicitly rely on the timely availability of mature negative emission technologies, which actively invest energy to remove CO<sub>2</sub> from the atmosphere and store it permanently. The models used as a basis for decarbonisation policies typically assume an implementation of such large-scale negative emission technologies starting around the year 2030, ramped up to cause net negative emissions in the second half of the century and balancing earlier CO<sub>2</sub> release. On average, a contribution of -10 Gt CO<sub>2</sub>/year is expected by 2050. (Anderson and Peters, 2016) 2050 (Anderson and Peters, 2016). A viable approach for negative emissions should (i) rely on an unlimited a scalable and sustainable source of energy (solar), (ii) result in a safely storable product (e.g. liquid or solid, not gaseous), (iii) be highly efficient in terms of water and energy use, to reduce the required land area and competition with water and food demands of a growing world population and (iv) be feature large-scale feasibility and affordability.

Processes for the extraction of CO<sub>2</sub> from the atmosphere are energy-intensive. This energy has to be supplied by low- or zero-carbon sources. At present, primarily direct air capture (followed by geologic injection) and biomass production are explored (Smith et al., 2016) and there is an active discussion on costs and scalability of the various technologies, see (Smith et al., 2016) and references cited therein. Renewably driven direct air capture is believed to be expensive and has not yet demonstrated scalability. Therefore, the currently most feasible option appears to be the use of natural photosynthesis to generate biomass through afforestation or ocean fertilization (Smith et al., 2016). Grown plants are then permanently stored, building a new stock of fossil fuels. Alternatively, the plant material can be combusted with carbon capture and storage to act as a low-carbon fuel. However, the efficiency of natural photosynthesis drops at high light conditions and because a significant fraction of the energy is used for the metabolism (Melis, 2012), the storage of solar energy in biomass is limited to 2-3% efficiency. Therefore large areas of agricultural land would be required for the achievement of the negative emission goals: The removal of one Gt CO<sub>2</sub>/year can demand more than 1 million km<sup>2</sup>, the combined area of Germany and France (Smith et al.,

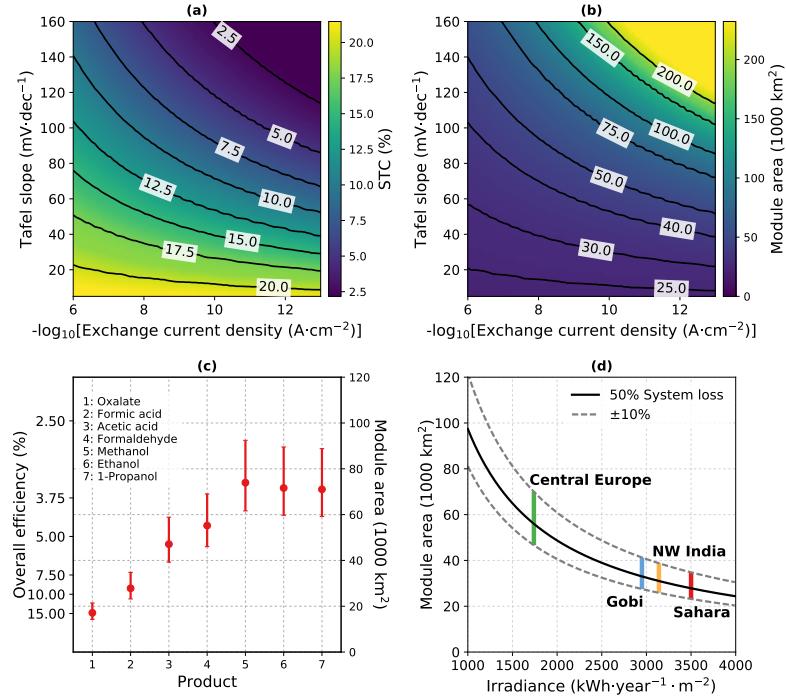
2016). ~~Sealing~~ There is an ongoing discussion whether scaling biomass production to the required 10 Gt CO<sub>2</sub>/year is hence ~~unlikely to be at all~~ compatible with planetary constraints (Heck et al., 2018).

We suggest to employ photoelectrochemical CO<sub>2</sub> reduction, also called *artificial photosynthesis*, ~~to this end~~. As in its natural counterpart occurring in plants, photons in the artificial photosynthesis process excite charge-carriers, which then reduce (and 5 oxidise) reactants in a liquid electrolyte to solar fuels. The photon energy is only briefly converted to electron energy, and then stored in molecular bonds. Light is absorbed in synthetic materials such as semiconductors or dyes and the chemical conversion typically takes place at (co)catalysts at the interface between electrolyte and light absorber. We primarily focus on tightly integrated photoelectrochemical systems, where the absorber is immersed into the electrolyte. While this approach imposes restrictions on the light absorber design, the tight integration also promises cost benefits (Kirner et al., 2016).

10 Artificial photosynthesis already delivers fivefold higher efficiencies than natural photosynthesis, as 13% for CO<sub>2</sub> reduction and 19% for solar water splitting have recently been demonstrated, ~~(Schreier et al., 2017; Cheng et al., 2018)~~ ~~(Schreier et al., 2017; Cheng et al., 2018)~~ more than half of the theoretical limits. Using solar fuels, either hydrogen or carbon-based from CO<sub>2</sub> reduction, would cut greenhouse gas emissions. However, while the combustion product of hydrogen is water, using renewably generated carbon-based fuels releases the captured greenhouse gas back into the atmosphere. Recapturing the CO<sub>2</sub> from the atmosphere would 15 be energy-intensive and hereby lower the overall carbon reduction efficiency, which is why solar energy-driven water splitting may be the preferable fuel, eliminating carbon completely from the energy system (Parkinson, 2016). Photoelectrochemical CO<sub>2</sub> reduction could, therefore, be better placed to generate carbon-rich products that can safely and permanently store carbon extracted from the atmosphere. The electrochemical reactions have to be chosen to generate products that can be stored safely below-ground over thousands of years. ~~This leaves us with liquids or solids, since gases, such as CO<sub>2</sub> itself, can leak back into the atmosphere~~ ~~Liquids or solids appear preferable, as gaseous products could leak back to the atmosphere, depending on the trapping mechanism~~ (Damen et al., 2006). The handling of a solid product in an efficient flow-cell reactor is not practical. ~~Therefore~~ ~~Although a large variety of products is in principle feasible~~, the production of carbon-rich liquids, such as alcohols or (fatty) acids, ~~is appears~~ most promising. These could be stored in underground reservoirs such as depleted oil fields, ~~be sequestered in the form of organic minerals~~, but also used as precursors for organic construction materials.

25 Any competitive artificial approach should provide a significantly higher turnover than natural photosynthesis. To assess the technologies, their efficiency for carbon removal has to be estimated and compared. The typically used solar-to-fuel efficiency (May et al., 2017) is not suitable, as it only describes the relative fraction of incident solar radiation that is converted to chemical energy. Instead, negative emission technologies based on solar energy are better assessed by the *solar-to-carbon* (STC) efficiency, which we define as the ratio of converted CO<sub>2</sub> molecules to the incoming photon flux (Appendix A).

30 Our calculations in the following were performed under the – highly idealised – assumption that the overpotential is dominated by the oxygen evolution reaction for a very good catalyst, which can be justified for water splitting. CO<sub>2</sub> reduction with the currently available catalysts, on the other hand, is associated with significantly higher overpotentials. The direct impact of catalysis performance on achievable efficiencies can be seen in Figure 1(a-b), where obtainable STC efficiencies and resulting module areas are plotted as a function of Tafel slope and exchange current density.



**Figure 1.** Theoretical efficiency limits and module area for the -10 Gt CO<sub>2</sub>/year scenario. (a) STC efficiency limit of a dual-junction absorber for formic acid (without system loss) as a function of exchange current density and Tafel slope. (b) Resulting module area at Sahara irradiance and 50% system loss. (c) STC efficiency and module area required under Sahara irradiance for [different a selection of](#) products at 50% system loss. Error bars indicate 40 and 60% loss, respectively. (d) Module area for formic acid production over the yearly irradiance at 50% (solid line), as well as 40 and 60% (dashed lines) system loss. Vertical lines mark typical irradiances accessible to a 2-axis tracker.

Artificial solar energy conversion does – unlike natural photosynthesis – not suffer from an efficiency decrease due to high light conditions, as beneficial effects of light concentration on the solar cell and higher temperatures on catalysis can over-compensate the detrimental effect of temperature on the absorber. Hence, near-equatorial regions with high solar irradiation are viable target areas for its deployment. Under the assumption of 3500 kWh/m<sup>2</sup> available per year for a 2-axis tracker in the 5 Sahara desert region (Amillo et al., 2014), we can estimate the required module area for the 2050 negative emission target of 10 Gt CO<sub>2</sub>/year. At a maximum STC efficiency of ca. 19% ([for formic acid, see Appendix A](#)), this would be approximately 13,500 km<sup>2</sup>. Under the [conservative](#) assumption that for a mature technology the overall system efficiency is half of the theoretical efficiency, this translates to an areal requirement of about 27,000 km<sup>2</sup> (Fig. 1a). The typical space factor for tracking photovoltaics of 0.2 ([Araki et al., 2016](#)) finally leads to a land footprint of ca. 135,000 km<sup>2</sup>. Other desert areas such as the Gobi 10 desert, or the Thar desert in north-western India, would also be interesting regions. In areas such as central Europe, a lower irradiance translates to larger footprints (Fig. 1b). The scale of such an effort, if one tried to realize it in a single project, would [considerable and about one order of magnitude larger than the previously largest project for solar electricity production in the](#)

~~Sahara desert~~ be considerable. However, it could be realized alongside with biomass approaches in other world regions, as it does not rely on agriculturally usable land. With the 2°C target, there is a truly global incentive to realise such an undertaking. Especially if spread over several projects, the economic added value would be created in the regions that suffer most under global warming.

5 Carbon removal by artificial photosynthesis is water-efficient, compared to its natural counterpart, as water is only used as chemical precursor and not evaporated from the closed system. Considering formic acid as product to be stored, and the target of 10 Gt CO<sub>2</sub>/year to be removed, the water demand is about 4.1 Gt/year. This would be a substantial amount in dry regions. Desalination of seawater would be possible, albeit energetically inconvenient. However, the direct use of seawater was already demonstrated for electrochemical hydrogen production (Fukuzumi et al., 2017), and might therefore also be possible for  
10 CO<sub>2</sub> reduction. Another challenge is that high-efficiency carbon sinks concentrated in large-scale facilities could, in principle, suffer from mass transport limitations of dilute CO<sub>2</sub> in the atmosphere. This could be alleviated by selecting sites with high atmospheric convection rates, by spacing facilities sufficiently widely apart, or to combine them with solar updraft towers for electricity generation.

15 Requirements for the safe storage will vary significantly with the choice of the sink product. Formic acid would certainly be problematic due to its corrosiveness, also in the case of spilling events. Acetic acid and the alcohols are inflammable at high concentrations and would have to be diluted with water, increasing the water and volume footprint. For oxalate, the sink product with the highest STC efficiency, mineral trapping by reaction with a suitable calcium source, such as calcium chloride, to the stable mineral whewellite could be anticipated. The 10 Gt CO<sub>2</sub> goal would result in roughly 17 Gt of the mineral. As a solid product, this – or other organic minerals – would not require underground injection and hence at this stage appears to  
20 be the most attractive option, with similar requirements as biomass storage. However, post-processing will increase the energy footprint and hereby also the costs.

In principle, electrochemical reduction of CO<sub>2</sub> would also be possible using photovoltaics or wind power to first generate electricity, and then drive electrolysis and the chemical conversion. This introduces the intermediate step of converting solar to electrical energy. ~~Unlike solar energy, however, large-scale mechanical wind extraction from the atmosphere might be limited.~~  
25 ~~(Miller et al., 2011) For the scales required, it appears that the potential of solar energy will, unlike wind, not be a limiting factor (Kleidon et al., 2016).~~ Hybrid approaches, where inorganic solar cells are combined with bacteria, are also possible ~~(Liu et al., 2015)~~  
~~(Liu et al., 2015)~~, but efficiencies are currently low and it is unclear how the drop in production rate under high illumination conditions can be overcome.

30 Artificial photosynthesis in the form of CO<sub>2</sub> reduction represents ~~consequently~~ an interesting technological option for negative emissions due to its high efficiency. This would greatly reduce land use for the anticipated 2050 negative emission target compared to so far considered – mainly biomass-based – technologies. The installation of the required minimum module area of about 30,000 km<sup>2</sup> would, however, still be an enormous undertaking. While we estimate the costs for photoelectrochemical CO<sub>2</sub> ~~removal conversion to the sink product~~ to roughly 65 Eur per ton ~~(see appendix B)~~, we emphasize that the development stage of highly efficient photoelectrochemical CO<sub>2</sub> conversion does not yet allow a robust estimate of the costs, rendering this  
35 value rather speculative. ~~Furthermore, some of the anticipated sink products have an economic value as energy carriers and~~

therefore require the creation of incentives to actually sequester and not combust the product. Physical feasibility and technological challenges can, however, already be anticipated. The greatest challenges to overcome towards the application are, for now, to develop and implement systems that are stable under operating conditions, as well as the derivation of earth-abundant, efficient catalysts (Schreier et al., 2017; Cheng et al., 2018).

5 *Code availability.* Calculations were performed with YaSoFo, the source code is available under <https://bitbucket.org/YaSoFo/>. The python source code to reproduce the calculations is available under DOI:10.5281/zenodo.1489158.

## Appendix A: Solar-to-carbon efficiency measure

Given a PEC device and a target sink product, we define the STC efficiency by the ratio of carbon atoms, which are chemically fixed, over the total incoming photon flux,  $j_{ph}$ , given by the integrated solar spectrum. The electronic current corresponding to this total photon flux would be the photocurrent that could be extracted from an ideal absorber with an infinitesimally small bandgap, where each photon contributes to one electron in the photocurrent. The STC efficiency limit for an ideal photoelectrochemical solar cell can then be calculated as follows: The Gibbs free energy difference per electron,  $\Delta G$ , constitutes the electrochemical load of the cell. It limits, together with the terrestrial solar spectrum,  $n(\lambda)$ , the electronic current density,  $j_e$ . Tandem solar cells are required for high efficiencies in photoelectrochemical energy conversion as they provide high currents and sufficient voltage to drive the reaction. The current density of an ideal tandem absorber under air mass 1.5 global illumination with very good catalysts can be calculated in the detailed-balance-scheme (May et al., 2017)(May et al., 2017). Under the assumption of unity absorption above the bandgap, the top cell absorbs photons  $n(\lambda)$  in the range between the far UV ( $\lambda \rightarrow 0$  nm) and the wavelength corresponding to its bandgap, the bottom cell experiences the photon flux filtered by the top cell and therefore absorbs between the respective bandgaps of top and bottom cell. The smaller of the two values then gives the maximum photocurrent at zero load. The operational photocurrent is then obtained by intersecting the overall current-voltage curve of the solar cell with the curve of its load, given by the Gibb's Free energy of the redox couple and the catalyst characteristics described by exchange current density and Tafel slope (see Asset). The selected product then defines the electron efficiency,  $\eta_e$ , i.e. the inverse of how many electrons are consumed for the formation of one product molecule from  $\text{CO}_2$  and water. With the Faradaic efficiency  $\eta_F$ , describing the efficiency of the conversion from current to desired product, the STC can be formulated as:

$$\text{STC} = \eta_F \eta_e \min_i \left[ \frac{\int_{\lambda_i}^{\lambda_{i+1}} n(\lambda) d\lambda}{\int_0^{\infty} n(\lambda) d\lambda} \right] = \frac{\eta_F \eta_e j_e}{j_{ph}} \quad (\text{A1})$$

For formic acid ( $\text{HCOOH}$ ,  $\Delta G = 1.4 \text{ eV}$ ,  $\eta_e = 0.5$ ), these idealised assumptions result in a maximum electronic photocurrent density of  $j_e \simeq 26 \text{ mA cm}^{-2}$ . For unity Faradaic efficiency, we obtain a product current density equivalent of  $\eta_e j_e = 13 \text{ mA cm}^{-2}$ . It follows that ideally ca. 19% of the incoming solar photons transform a  $\text{CO}_2$  molecule to the liquid – and

hence storable – product. The STC efficiency would therefore be 19%. Taking into account photoconversion, Faradaic, and system losses, values of 10% STC or more appear feasible as for the similar process of photoelectrochemical water splitting, 85% of the material-specific and ca. 2/3 of the overall theoretical efficiency limit were already demonstrated on a lab-scale (Cheng et al., 2018). This is high compared to the currently achieved energetic efficiencies for natural photosynthesis of 2-3%,  
5 which translate to roughly 1.5-2% STC efficiency.

STC efficiencies are a function of the reaction path, similar to CO<sub>2</sub> reduction for fuel generation, where the obtainable efficiency depends on the Gibbs free energy (May et al., 2017)(May et al., 2017). The distribution of energy over the chemical bonds varies for different products, yet for CO<sub>2</sub> removal, we are primarily interested in the number of converted CO<sub>2</sub> molecules. Therefore, the STC efficiencies can deviate significantly for products that have a similar energetic efficiency (Fig. 1ac). Feasible  
10 products are associated with distinct storage requirements, but also different catalysts. Acetic acid, for instance, could be an interesting option for long-term storage because of its high melting point. Though the electronic photocurrent could be higher than for for acetic acid compared to formic acid due to a reduced electrochemical load, 4 electrons are required for the conversion of one CO<sub>2</sub> molecule, which in the end almost halves the efficiency. The theoretical efficiency limit, as shown in Figure 1ac, largely varies based on the number of electrons consumed per CO<sub>2</sub> molecule, which is 2-one for oxalate, two  
15 for formic acid, 4-four for acetic acid and formaldehyde, and 6-six for methanol, ethanol, and 1-propanol. Therefore, using the carbon conversion rate as the benchmark for solar-driven negative emissions will result in a different choice of product compared to solar fuels, where energetic considerations dominate.

## Appendix B: Cost estimate

To roughly estimate the costs of negative emissions by photoelectrochemical CO<sub>2</sub> reduction, we assume the module costs  
20 to be twice the module costs (Chang et al., 2018) of current crystalline silicon photovoltaics. With a depreciation period of 20 years, and running costs of 10% of the investment sum, this would translate to 55.60 Eur per ton of CO<sub>2</sub>. Additional costs can arise from the diffusion limitation due to the high conversion rate, which might necessitate to technically create convection by means of mechanical fans. The energy costs of capturing atmospheric CO<sub>2</sub> are estimated to be about 30-88 kJ mol<sup>-1</sup>  
(Goeppert et al., 2012)(Goeppert et al., 2012). With an average of 50 kJ mol<sup>-1</sup> and a current photovoltaic electricity price of  
25 30 Eur/MWh, this adds another 9.50 Eur/ton, finally totalling 65 Eur/ton. Transport costs to the storage location will vary with the chosen product and the vicinity between production and storage facility. If we assume, as a very rough estimate, similar transport costs of formic acid as for crude oil over a distance of 2000 km (Verma et al., 2017), this would result in additional 24 Eur per ton of CO<sub>2</sub>. The overall volume to be transported would be in the same order of magnitude as the present day oil production. The costs for storage will vary with the sink product, the product volume, and the required post-processing.  
30 Some of the products could, in principle, be used as 'plastic-based' construction materials, creating an economic value and hence reduce the overall costs. Considering the required scale, however, the market volume for such construction materials will probably not be significant.

*Competing interests.* There are no conflicts to declare.

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5 [oxalate as a sink product.](#)

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