

# Why $\text{NH}_3$ is *not* a candidate reagent for ambient $\text{CO}_2$ fixation: a response to ‘Alternative Solution to Global Warming Arising from $\text{CO}_2$ Emissions – Partial Neutralization of Tropospheric $\text{H}_2\text{CO}_3$ with $\text{NH}_3$ ’ [Environmental Progress, 26, 355-359 (2007)]

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*It has been proposed that application of urea, or ammonium sulphate (plus lime) to non-agricultural land to evolve ammonia may provide a “solution” to increasing  $\text{CO}_2$  concentrations by neutralising atmospheric carbonic acid to ammonium bicarbonate at ambient concentrations and subsequent storage in the surface ocean [R. Apak, Environmental Progress, 26, 355-359 (2007)]. We identify a series of major flaws in this hypothesis, which indicate that the approach is unfeasible and would not succeed if attempted at any scale: (i) The phenomenal energy cost associated with breaking the  $\text{N}\equiv\text{N}$  bond and evolving  $\text{H}_2$  for  $\text{NH}_3$  production (and associated fossil fuel  $\text{CO}_2$  emissions under the current energy generation market); (ii) the radiative forcing associated with substantially increasing the concentration of ammonia in the atmosphere and (iii) a number of unwanted indirect effects, including eutrophication, enhanced  $\text{N}_2\text{O}$  emissions and the inhibition of the oxidation of strong greenhouse gases such as methane in the atmosphere. We strongly urge future efforts to be directed away from this approach and suggest that engagement with the climate, earth-system and biogeochemistry communities is essential when putting forward ideas for potential geoengineering approaches to mitigating global climate change.*

## 1 Introduction

In the study of Apak [1], the author proposes the use of gaseous ammonia ( $\text{NH}_3$ ) evolved from land application of ammonium sulfate ( $[\text{NH}_4]_2\text{SO}_4$ ) and lime ( $\text{CaO}$ ), or urea ( $\text{CO}[\text{NH}_2]_2$ ) to neutralise atmospheric carbon dioxide ( $\text{CO}_2$ ) (and thus fix it as bicarbonate,  $\text{HCO}_3^-$ ). This is advocated by the author as a potential “geoengineering” “solution” to global climate change. Apak [1] suggests that large scale application of ammonium salts or urea, and consequent “massive” release of ammonia will substantially neutralise carbonic acidity in the atmosphere and that a substantial amount of the

resulting ammonium bicarbonate will be deposited to the ocean, where bicarbonate ions are “stable” and thus CO<sub>2</sub> sequestration will be achieved. We foresee a number of serious problems with this approach and work through them systematically below. Prof. Apak sensibly asks pertinent questions at the end of his paper – such as how much land would be required to emit sufficient ammonia and what the environmental impact would be. We have tried to tackle these questions in the process of our analysis of the proposed geoengineering technique.

The term geoengineering means the “intentional large-scale manipulation of the environment” [2], and includes ideas such as reducing incoming solar radiation [3] and removing ambient atmospheric CO<sub>2</sub> [4, and references therein]. Whilst it is important that potential contributions to climate change amelioration are identified and brought forward from all fields for discussion, it is equally important that responses to such proposals receive proportionate airing, particularly as such ‘ideas’ papers may be adopted by commercial carbon sequestration initiatives, often without suitably deep consideration of wider impacts and long-term consequences. Here we demonstrate a number of major flaws with the suggested approach of Apak [1], based on our expertise in trace gas biogeochemistry, CO<sub>2</sub> mitigation and geoengineering evaluations, greenhouse gas physics, ocean carbonate chemistry and climate feedbacks.

## **2 Analysis**

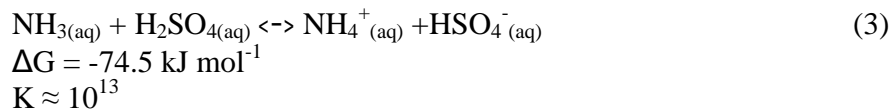
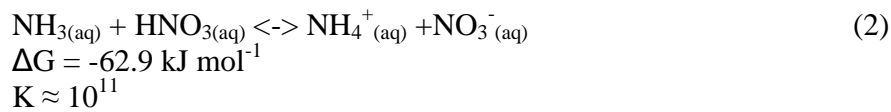
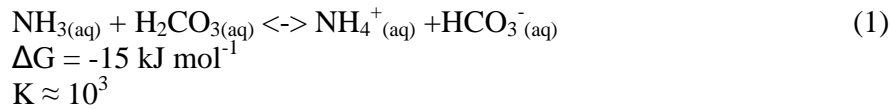
We assume here that Apak [1] envisages his proposed ‘solution’ to be applicable to all distributed sources of CO<sub>2</sub> emissions i.e., those that are not from large point sources for which carbon capture and storage (CCS) technologies are being developed [5]. We use a conservative estimate of the distributed CO<sub>2</sub> emissions for 2006 of 4.8 Pg-C yr<sup>-1</sup> (4.8 x 10<sup>15</sup> grams of carbon per year) [6, 7]. The following calculations are based on removing this quantity of CO<sub>2</sub> annually by the method of Apak [1]. We neglect the likely future rise in CO<sub>2</sub> emissions but also any other contributing CCS or geoengineering methods which might be applied to removing this fraction of CO<sub>2</sub> from the atmosphere. As will be seen, even to capture 10% of this amount by the proposed method is unfeasible.

### **2.1 Neutralisation**

The thermodynamics of the solubility of ammonia in meteoric water is complex, especially in solutions where the only source of acidity is H<sub>2</sub>CO<sub>3</sub> (carbonic acid), with solubilities often substantially lower than predicted by simple theory [e.g. 8, 9]. However, there are more fundamental problems with the method of Apak [1] so we do not consider this further and refer the reader to the referenced articles for more information on these issues. For the purposes of this analysis we assume that one mole of ammonia transferred to the aerosol phase will neutralise one mole of aerosol acidity.

Sulfate (SO<sub>4</sub><sup>2-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) in the aqueous phase in the atmosphere are the conjugate bases of the strong acids H<sub>2</sub>SO<sub>4</sub> (sulphuric) and HNO<sub>3</sub> (nitric), respectively. These are produced naturally, but in the contemporary atmosphere are predominantly anthropogenic in origin [e.g. 10]. Apak [1] suggests that neutralisation of H<sub>2</sub>CO<sub>3</sub> by NH<sub>3</sub> (Equation 1) will proceed spontaneously due to the (negative) Gibbs free energy change ( $\Delta G$ ) of the reaction of -15 kJ mol<sup>-1</sup> and an equilibrium constant ( $K$ ) for the reaction (at

standard T and P) of 776 (no units). We present  $\Delta G$  and K values for the reaction of ammonia with sulfuric and nitric acid in Equations 2 and 3 below. Values are calculated from standard thermodynamic data on Gibbs free energies of formation and demonstrate that the neutralisation of these strong acids in the atmosphere is thermodynamically much more favourable than neutralisation of  $\text{H}_2\text{CO}_3$ . Thus we argue that before any  $\text{CO}_2$  neutralisation can occur, effectively all of the strong acidity must be neutralised.



Global emissions to the atmosphere of  $\text{SO}_2$  and  $\text{NO}_x$  (the precursor species to atmospheric  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) and of ammonia are relatively well constrained [e.g. 11]. The net strong acidity of emissions to the atmosphere can be calculated according to Equation 4.

$$\langle \text{H}^+ \rangle = \langle \text{NO}_x \rangle + 2\langle \text{SO}_2 \rangle - \langle \text{NH}_3 \rangle \quad (4)$$

Where pointed brackets denote net global emission to the atmosphere. The input of  $\text{SO}_2$  is counted twice in the charge balance as both sulfuric acid and bisulfate ( $\text{HSO}_4^-$ ) are strong acids and will fully dissociate in water. Using Equation 4 and the latest emissions data [11] we calculate the present-day amount of un-neutralised strong acidity emitted to be  $2.42 \text{ Tmol yr}^{-1}$  ( $2.42 \times 10^{12}$  moles per year). Projections of future emissions are uncertain: Dentener et al. [11] present N and S emission scenarios from which we calculate a worst case of  $5.66 \text{ Tmol yr}^{-1}$  of strong acidity and best case  $-2.33 \text{ Tmol yr}^{-1}$  (i.e. net alkaline emission from ammonia). Assuming that the most likely outcome is sustained emission of un-neutralised acidity at the current rate,  $2.42 \text{ Tmol}$  of  $\text{NH}_3$  will be required annually to neutralise this. Multiplying by the molar mass of N (nitrogen,  $14.01 \text{ g mol}^{-1}$ ) we reach a value of  $34 \text{ Tg-N yr}^{-1}$ . This corresponds to an increase of ammonia emissions of approximately 65% over current values of  $53 \text{ Tg-N yr}^{-1}$  [11] before any effective neutralisation of carbonic acid will occur.

However, this amount is tiny compared to that required to neutralise the  $4.8 \text{ Pg}$  of  $\text{CO}_2$ . All of the following calculations are per year.  $0.4 \text{ Pmol}$  of carbonic acid ( $4.8 \text{ Pg-C}/12.0 \text{ g mol}^{-1}$ ) must be neutralised. Therefore  $0.4 \text{ Pmol}$  of ammonium bicarbonate must land on the ocean. Up-to-date deposition models suggest that only 36-51% of emitted ammonia is deposited (as ammonium) to the ocean [11]. We adopt a value of 50% and thus assume that  $0.8 \text{ Pmol}$  of  $\text{NH}_3$  must react to form ammonium bicarbonate globally. As 25% of

$\text{NH}_3$  in the atmosphere is oxidised by OH radical [1],  $0.8/0.75 \approx 1.1$  Pmol of ammonia must be emitted. This is equal to 15 Pg-N. We note here that as the atmosphere is increasingly neutralised, the proportion of ammonia staying in the gas phase is likely to increase and thus the relative importance of OH oxidation is likely also to increase. We do not consider this increased requirement for ammonia for effective neutralisation of the  $\text{CO}_2$ , but do calculate that  $1.1 \times 0.25 = 0.27$  Pmol- $\text{NH}_3$ , or 3.7 Pg-N will be oxidised to strong (nitric) acidity and thus require a further 0.27 Pmol of  $\text{NH}_3$  to neutralise it. If this is tackled with an additional  $\text{NH}_3$  emission, at least 25% of it will be oxidised, leading to further production of strong acidity...

Ignoring the acidifying effects of OH oxidation (for simplicity) we have calculated a very conservative total ammonia emission of 15 Pg-N; an increase over current anthropogenic ammonia emissions of approximately 350-fold.

## 2.2 Ammonia concentration and warming effect

Assuming the lifetime of ammonia in the atmosphere is unchanged by this massive additional loading, we can roughly calculate the new concentration of ammonia resulting from these emissions. We assume a mean global boundary layer  $\text{NH}_3$  concentration of 3 ppbv, after the estimate of 10ppbv of NRC [12] (the only published value of this parameter), which we assume to be a substantial overestimate, based on observations of very low concentrations in the clean marine boundary layer by our group [13] and others [14]; and the questionable quality and apparent systematic overestimation of early ammonia measurements [15]). We find that scaling by the increased emissions, the  $\text{NH}_3$  concentration as a result of the activities proposed by Apak [1] will be of the order of 1ppmv (3 ppbv  $\times$  350). This almost certainly an underestimate, because the lifetime of ammonia in the atmosphere is likely to increase substantially as emissions and concentration increase.

$\text{NH}_3$  is a potent greenhouse gas, absorbing strongly within the 'vapour-window' between 8 and 13  $\mu\text{m}$  [16] in which much of the terrestrial infra-red emission occurs. Probably because massive ammonia emissions have not previously been envisaged, there have been few estimates of the climatic consequences of increased gas phase ammonia concentrations. Wang et al. [17] show that a doubling of ammonia concentration from 6 to 12 ppbv (well mixed to up to 8km altitude) would give a temperature increase of  $\Delta T = 0.1$  K. In calculations for the Early Earth (so neglecting the 10  $\mu\text{m}$  ozone adsorption band), Kuhn and Atreya [18] show that adding 10 ppmv ammonia, starting near the present surface temperature, would give  $\Delta T = 15$  K. To estimate a conservative lower bound on temperature increase from enhanced ammonia concentrations, we extrapolate the result of Wang et al. [17], assuming  $\Delta T \propto \log[\text{NH}_3]$ . For concentrations of 0.1 ppmv and 1 ppmv, this gives  $\Delta T = 0.4\text{K}$  and  $\Delta T = 0.75\text{K}$  respectively. However, considering the results of Kuhn and Atreya [18], values of  $\Delta T = 1.5\text{K}$  and  $\Delta T = 5\text{K}$  might be realistic. Whilst ammonia from ground emissions may well be restricted to the lower atmosphere, the radiative effect per mol of ammonia will be highest here due to pressure broadening of absorption bands. The warming effect from the emitted ammonia is thus liable to far outweigh the reduction in warming from  $\text{CO}_2$  removal!

The consumption of tropospheric OH by large ammonia concentrations will also lead to the inhibition of methane oxidation and consequent increase in warming. This effect is likely to be profound for an NH<sub>3</sub> concentration of 0.1 or 1 ppmv as such concentrations are many orders of magnitude greater than the sum of the concentrations of all of the other atmospheric 'pollutants' that OH will normally oxidise.

## 2.3 Land application

Apak [1] proposes that either urea or a mixture of ammonium sulfate and lime is used to provide the ammonia. We focus here on urea, which is favoured by Apak [1] due to its greater volatilisation potential. Apak suggests that approximately 8% of the urea added to land surfaces will be emitted to the atmosphere. Therefore,  $1.1/0.08 = 13.3$  Pmol of N (6.65 Pmol urea) must be applied to ensure the necessary emission. We neglect here the energetic cost of producing urea from NH<sub>3</sub> and CO<sub>2</sub>, but point out that  $6.65 \times 12.0 = 79.8$  Pg-C as CO<sub>2</sub> will be used in producing this urea, which is approximately 50% of the total anthropogenic CO<sub>2</sub> currently stored in the atmosphere and more than an order of magnitude greater than the amount of CO<sub>2</sub> we're trying to fix in the first place...

### 2.3.1 Terrestrial ecological effects

Of the 13.3 Pmol of NH<sub>3</sub> applied to the land surface, only 0.4 Pmol will be deposited to the ocean. Therefore the total terrestrial nitrogen loading (assuming equal distribution over all  $1.5 \times 10^{14}$  m<sup>2</sup> of the Earth's land surface and neglecting the not insubstantial proportion which is urban area or agricultural land) is  $12.9 \text{ Pmol} / 1.5 \times 10^{14} \text{ m}^2 \approx 90 \text{ mol m}^{-2} \text{ (yr}^{-1}\text{)}$ . Deposition of nitrogen to terrestrial ecosystems causes a 'cascade' of detrimental environmental impacts including eutrophication and acidification [19] as well as changing ecosystem diversity. The critical load, i.e. the threshold level of N deposition at which negative effects on an ecosystem begin to occur [e.g. 20] varies between ecosystems, but a reasonable 'global average' is  $1 \text{ g-N m}^{-2} \text{ (yr}^{-1}\text{)}$  [11] or  $0.07 \text{ mol m}^{-2}$ . Thus the necessary application of nitrogen is more than 5 orders of magnitude greater than the N critical load for natural and semi-natural ecosystems. For comparison, a typical addition of nitrogenous fertiliser to intensively farmed fields in the UK is  $125 \text{ kg-N ha}^{-1} \text{ (yr}^{-1}\text{)}$  [21] or  $0.9 \text{ mol m}^{-2}$ . At the levels implied by Apak [1] nitrogen will be massively in excess, such that it will be toxic to most higher plants and thus we envisage as a worst-case a 'green scum' doomsday scenario [e.g. 22] for life on the planet!

## 2.4 NH<sub>3</sub> production

To produce ammonia by the Born-Haber cycle, the most efficient plants currently use about  $28 \text{ GJ ton}^{-1}$  ( $28 \times 10^9$  Joules per metric ton of ammonia)[23], or  $28 \times 17.03 = 0.5 \text{ MJ mol}^{-1}$ . As a by-product of molecular hydrogen production they also create approximately 15 g of CO<sub>2</sub> per gram of NH<sub>3</sub> [23], or 6 moles CO<sub>2</sub> per mole of NH<sub>3</sub>. Therefore, using current technologies, producing the required amount of NH<sub>3</sub> would require  $0.5 \times 10^6 \text{ J mol}^{-1} \times 13.3 \times 10^{15} \text{ mol} = 6.7 \times 10^{21} \text{ J}$  or 6700 EJ (exo-joules) of energy and emission of  $6 \times 13.3 = 80$  Pmol or 960 Pg-C (roughly equivalent to one quarter the total known fossil fuel reserve). However, Gálvez et al. [23] propose a new method of producing ammonia which incurs no CO<sub>2</sub> production other than that associated with production of the energy required to make the ammonia (approximately  $27 \text{ GJ ton}^{-1}$ ). If

we assume that their method will be used throughout, the annual energy cost is 6500 EJ, with no associated CO<sub>2</sub> emission (as long as alternative or nuclear energy sources are utilised). This is >10 times the total primary energy consumption of the human race (including electricity, transport, cooking, wood burning etc), which is currently 470 EJ yr<sup>-1</sup> [24]. Therefore, except given the development of cheap and abundant renewable or nuclear energy technology, the necessary ammonia production is unfeasible.

However, the majority of the CO<sub>2</sub> sink in the above processes is in the production of urea; of a magnitude such that atmospheric CO<sub>2</sub> would be depleted to zero in less than 10 years (although a great deal of CO<sub>2</sub> would be emitted from the ocean to compensate). What would be the effect of a much smaller application of urea to the land surface such that the 'target' CO<sub>2</sub> emissions are stored as bicarbonate? This at first appears sensible, in terms of chemistry, if not the energetics of urea production: One mole of urea decomposes to form two moles of NH<sub>3</sub> and one mole of CO<sub>2</sub>. Thus two moles of alkalinity are added to the land surface and have the potential to fix two moles of CO<sub>2</sub> as bicarbonate. However, the eventual fate of the majority of reduced nitrogen deposited on the land surface is nitrification Galloway [10], a biologically-mediated process which oxidises ammonia to nitrate, removing two moles of alkalinity for every mole nitrified. Thus the net effect of adding 1 mole of urea is to increase the acidity of the soil by four moles and drive more CO<sub>2</sub> into the atmosphere than was originally fixed. Furthermore, both nitrification and the subsequent process of denitrification (the reduction of nitrate to molecular nitrogen, which occurs ubiquitously in soils [e.g. 25]) produce the strong greenhouse gas, nitrous oxide (N<sub>2</sub>O); a further negative effect.

Let us neglect the warming and OH-consuming effects of enhanced atmospheric NH<sub>3</sub> and assume as a more reasonable alternative that instead of land application, NH<sub>3</sub> is emitted directly to the atmosphere to react. Taking our conservative estimate of 1.1 Pmol NH<sub>3</sub> emissions required per year, we calculate that, using current ammonia production technology, 550 EJ of energy will be required and 277 Pg-C would be emitted. Even to neutralise 10% of the CO<sub>2</sub> from distributed sources would require >10% of the human race's current energy consumption (55 EJ) and lead to the emission of 28 Pg-C as CO<sub>2</sub>; approximately 60 times that which would be sequestered in the ocean (0.5 Pg-C).

## 2.5 Deposition to the ocean

The crux of the proposed approach of Apak [1] is to convert gaseous atmospheric CO<sub>2</sub> into bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) dissolved in the ocean which, it is asserted, will remain sequestered there due to the stability of bicarbonate at seawater pH. To investigate this we used a numerical box model of the air-sea system based on Sarmiento and Toggweiler [26], utilising an explicit solution of ocean carbonate chemistry [27], and found that the assertion of Apak [1] is, to first order, correct. Within the model integrations, converting gaseous CO<sub>2</sub> into dissolved carbonate ions achieved almost identical carbon sequestration to the complete removal of an equal amount of CO<sub>2</sub> from the air-sea system, at least to millennial timescales. This is because converting gaseous CO<sub>2</sub> into dissolved HCO<sub>3</sub><sup>-</sup> adds both 1 mole of DIC (dissolved inorganic carbon) to the ocean and 1 mole of (titration) alkalinity. The addition of alkalinity allows the carbonate ion to remain in its charged

form indefinitely, and not react with a proton to form carbonic acid or aqueous CO<sub>2</sub>, from where it would re-enter the atmosphere.

Let us imagine a method by which we could add ammonium bicarbonate directly to the surface ocean to store the carbon as bicarbonate. This would require substantially less ammonia (although still at a large energy and CO<sub>2</sub> cost) than the approach of emission to the atmosphere, particularly if CO<sub>2</sub> was trapped at high concentration e.g. in the flue gas of a power station.

Unfortunately, a fundamental problem still exists, due to the fate of the deposited ammonium. Some of it will be utilised by primary producers, particularly in the N-limited portion of the ocean. As photosynthetic organisms will maintain electroneutrality when transferring chemical species across their cell membranes, the uptake of ammonium will release a proton, adding acidity and counteracting the effect of the one unit of added alkalinity associated with the ammonium bicarbonate deposition. Assuming the classic stoichiometry of 7:1 C:N in phytoplankton and complete phytoplanktonic utilisation of the deposited N, 0.4 Pmol of ammonium could drive approximately 34 Pg-C of primary production (increasing marine biogeochemical C uptake by 67%).

However, only a small area of the global ocean is substantially N-limited[28], so in most regions other nutrients (particularly P) would rapidly run out and the excess N would most likely be nitrified (releasing N<sub>2</sub>O in the process). As we saw above, the process of oxidising ammonia/um to nitrate removes 2 moles of alkalinity for every mole reacted. Therefore, the net effect of adding ammonium bicarbonate to the ocean is to add one mole of DIC, but to remove between 1 and 2 moles of alkalinity, thus driving the deposited carbon back into the atmosphere, along with some DIC which was previously stored stably in the surface ocean. For further information on ammonium deposition, nitrification and alkalinity effects in the ocean we refer the reader to Doney et al. [29].

### **3. Conclusion**

We have conducted a thorough analysis of the proposed geoengineering technique of ammonia emission to the atmosphere for the neutralisation of atmospheric CO<sub>2</sub>. We have found that the method is economically and energetically unfeasible and that should successful production of sufficient ammonia and its application to the land surface be achieved its negative results would include: i) drastic increase in ammonia concentrations that could lead to instantaneous global warming of between 1 and 5 °C; ii) nitrogen overload of the land surface, potentially leading to collapse in global food production and other important ecosystem services; iii) mass nitrification on land and in water, leading to substantial N<sub>2</sub>O emissions, and acidification, resulting in more CO<sub>2</sub> being emitted than was fixed in the first place and iv) acidification of and CO<sub>2</sub> emission from the surface ocean. Even in the absence of the commentary presented here it is unlikely that such an approach would reach the implementation stage at a scale that would result in such disastrous global effects. Economic analysis by any commercial organisation wishing to emit petamoles of ammonia into the atmosphere would demonstrate that it would be prohibitively expensive.

However, there is a growing and diverse market for carbon offsetting ideas, with great variations in the scientific rigour and validity of the analysis of the proposals. We are therefore concerned by the possibility that those outside the scientific community may attempt to adopt the proposed method of Apak[1] without critical review or analysis and use it to justify the release of small amounts of ammonia as a carbon offsetting technique. We have demonstrated that it will not have any effect on CO<sub>2</sub> concentrations due to the presence of much stronger acids in the atmosphere and that production of ammonia incurs huge energy costs and thus under the current energy market the method will result in substantial net CO<sub>2</sub> emissions. Furthermore, the deposition of excess emitted nitrogen currently has a significant deleterious effect on sensitive ecosystems worldwide, and increasing ammonia emissions would only confound the current global efforts to reduce these problems.

It is fundamental when considering geoengineering proposals associated with removal of CO<sub>2</sub> from the atmosphere to understand that the global biogeochemical carbon cycle is inextricably linked to the cycles of N, P, S, Si, Fe and other elements, and all of them to the global ecosystem. Therefore to attempt to solve increasing CO<sub>2</sub> concentrations by massive perturbations of other global elemental cycles is likely to result in strongly non-linear feedbacks on climate and ecology. Consensus must be built across many disciplines before such approaches are claimed as contributing an amelioration to global climate change.

As Earth-system scientists, we recognise that to deal with the impacts of global climate change there may be a role for large-scale engineering solutions in combination with the decarbonization of the global economy and as such we welcome the speculative paper of Prof. Apak for bringing to light an idea that may have contributed to climate change amelioration. However, we have provided a detailed analysis which responds to a number of the key questions he raises in his paper and demonstrates that the idea is not feasible. We hope that future geoengineering proposals will benefit from analysis by experts in the relevant components of the Earth-system before they are undertaken as carbon offsetting activities. We suggest that such proposals may be better aired in a dedicated journal for discussion of ideas for climate- and geo-engineering where the necessary in-depth analysis can be openly aired, the proposal discussed and consensus built.

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