

Why NH_3 Is Not a Candidate Reagent for Ambient CO_2 Fixation: A Response to “Alternative Solution to Global Warming Arising from CO_2 Emissions—Partial Neutralization of Tropospheric H_2CO_3 with NH_3 ”

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It has been proposed that application of urea, or ammonium sulfate (plus lime) to nonagricultural land to evolve ammonia may provide a “solution” to increasing CO_2 concentrations by neutralizing atmospheric carbonic acid to ammonium bicarbonate at ambient concentrations and subsequent storage in the surface ocean (Apak [2007]: Environmental Progress 26, 355–359). 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 H_2 for NH_3 production (and associated fossil fuel 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 N_2O 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 mitigate global climate change. © 2008 American Institute of Chemical Engineers Environ Prog, 27: 412–417, 2008

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INTRODUCTION

In the study of Apak [1], the author proposes the use of gaseous ammonia (NH_3) evolved from land application of ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$) and lime (CaO), or urea ($\text{CO}[\text{NH}_2]_2$) to neutralize atmospheric carbon dioxide (CO_2) (and thus fix it as bicarbonate, 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 neutralize 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_2 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_2 [4 and references therein]. Although 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_2 mitigation and geoengineering evaluations, greenhouse gas physics, ocean carbonate chemistry, and climate feedbacks.

ANALYSIS

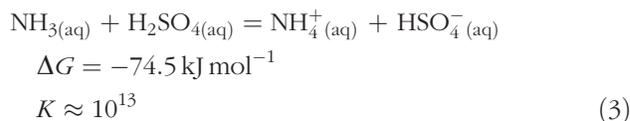
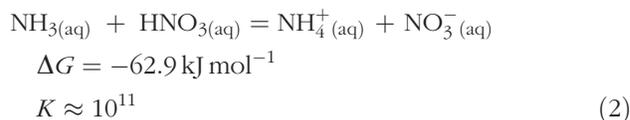
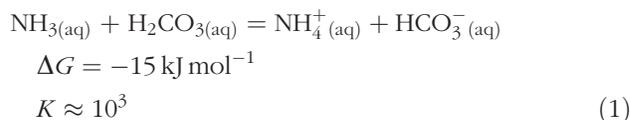
We assume here that Apak [1] envisages his proposed “solution” to be applicable to all distributed sources of CO_2 emissions, i.e. those that are not from large point sources for which carbon capture and storage (CCS) technologies are being developed [5]. We use a conservative estimate of the distributed CO_2 emissions for 2006 of 4.8 Pg-C yr^{-1} (4.8×10^{15} g of carbon per year) [6,7]. The following calculations are based on removing this quantity of CO_2 annually by the method of Apak [1]. We neglect the likely future rise in CO_2 emissions but also any other contributing CCS or geoengineering methods which might be applied to removing this fraction of CO_2 from the atmosphere. As will be seen, even to capture 10% of this amount by the proposed method is unfeasible.

Neutralization

The thermodynamics of the solubility of ammonia in meteoric water is complex, especially in solutions

where the only source of acidity is H_2CO_3 (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 neutralize one mole of aerosol acidity.

Sulfate (SO_4^{2-}) and nitrate (NO_3^-) in the aqueous phase in the atmosphere are the conjugate bases of the strong acids H_2SO_4 (sulfuric) and HNO_3 (nitric), respectively. These occur naturally, but in the contemporary atmosphere are predominantly anthropogenic in origin [e.g. 10]. Apak [1] suggests that neutralization of H_2CO_3 by NH_3 (Eq. 1) will proceed spontaneously due to the (negative) Gibbs free energy change (ΔG) of the reaction of -15 kJ mol^{-1} and an equilibrium constant (K) for the reaction (at standard T and P) of 776 (no units). We present ΔG and K values for the reaction of ammonia with sulfuric and nitric acid in Eqs. 2 and 3 below. Values are calculated from standard thermodynamic data on Gibbs free energies of formation and demonstrate that the neutralization of these strong acids in the atmosphere is thermodynamically much more favorable than neutralization of H_2CO_3 . Thus we argue that before any CO_2 neutralization can occur, effectively all of the strong acidity must be neutralized.



Global emissions to the atmosphere of SO_2 and NO_x (the precursor species to atmospheric SO_4^{2-} and 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 Eq. 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 SO_2 is counted twice in the charge balance because both sulfuric acid and bisulfate (HSO_4^-) are strong acids and will fully disso-

ciate in water. Using Eq. 4 and the latest emissions data [11] we calculate the present-day amount of un-neutralized strong acidity emitted to be $2.42 \text{ Tmol yr}^{-1}$ (2.42×10^{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-neutralized acidity at the current rate, 2.42 Tmol of NH_3 will be required annually to neutralize this. Multiplying by the molar mass of N (nitrogen, 14.01 g mol^{-1}) we reach a value of 34 Tg-N yr^{-1} . This corresponds to an increase of ammonia emissions of approximately 65% over current values of 53 Tg-N yr^{-1} [11] before any effective neutralization of carbonic acid will occur.

However, this amount is tiny compared to that required to neutralize the 4.8 Pg of CO_2 . All of the following calculations are per year. 0.4 Pmol of carbonic acid ($4.8 \text{ Pg-C}/12.0 \text{ g mol}^{-1}$) must be neutralized. Therefore 0.4 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 Pmol of NH_3 must react to form ammonium bicarbonate globally. As 25% of NH_3 in the atmosphere is oxidized by OH radical [1], $0.8/0.75 \approx 1.1 \text{ Pmol}$ of ammonia must be emitted. This is equal to 15 Pg-N . We note here that as the atmosphere is increasingly neutralized, the proportion of ammonia staying in the gas phase is likely to increase and thus the relative importance of OH oxidation is also likely to increase. We do not consider this increased requirement for ammonia for effective neutralization of the CO_2 , but do calculate that $1.1 \times 0.25 = 0.27 \text{ Pmol-NH}_3$, or 3.7 Pg-N will be oxidized to strong (nitric) acidity and thus require a further 0.27 Pmol of NH_3 to neutralize it. If this is tackled with an additional NH_3 emission, at least 25% of it will be oxidized, 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.

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 NH_3 concentration of 3 ppbv, after the estimate of 10 ppbv 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 gas phase

ammonia measurements [15]. We find that scaling by the increased emissions, the NH_3 concentration as a result of the activities proposed by Apak [1] will be of the order of 1 ppmv ($3 \text{ ppbv} \times 350$). This is almost certainly an underestimate, because the lifetime of ammonia in the atmosphere is likely to increase substantially as emissions and concentration increase.

NH_3 is a potent greenhouse gas, absorbing strongly within the “vapor-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 8 km altitude) would give a temperature increase of $\Delta T = 0.1 \text{ K}$. 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 $\Delta T = 15 \text{ K}$. 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 and 1 ppmv, this gives $\Delta T = 0.4$ and 0.75 K , respectively. However, considering the results of Kuhn and Atreya [18], values of $\Delta T = 1.5$ and 5 K might be realistic. While 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 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_3 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 oxidize.

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 favored by Apak [1] due to its greater volatilization potential. Apak suggests that approximately 8% of the urea added to land surfaces will be emitted to the atmosphere. Therefore, $1.1/0.08 = 13.3 \text{ Pmol}$ 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_3 and CO_2 , but point out that $6.65 \times 12.0 = 79.8 \text{ Pg-C}$ as CO_2 will be used in producing this urea, which is approximately 50% of the total anthropogenic CO_2 currently stored in the atmosphere and more than an order of magnitude greater than the amount of CO_2 we’re trying to fix in the first place.

Terrestrial Ecological Effects

Of the 13.3 Pmol of NH_3 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 $1.5 \times 10^{14} \text{ m}^2$ of the Earth's land surface and neglecting the not insubstantial proportion which is urban area or agricultural land) is $12.9 \text{ Pmol}/1.5 \times 10^{14} \text{ m}^2 \approx 90 \text{ mol m}^{-2} (\text{yr}^{-1})$. 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 $1\text{g-N m}^{-2} (\text{yr}^{-1})$ [11] or 0.07 mol m^{-2} . Thus the necessary application of nitrogen is more than 3 orders of magnitude greater than the N critical load for natural and seminatural ecosystems. For comparison, a typical addition of nitrogenous fertilizer to intensively farmed fields in the UK is $125 \text{ kg-N ha}^{-1} (\text{yr}^{-1})$ [21] or 0.9 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!

NH_3 Production

To produce ammonia by the Born-Haber cycle, the most efficient industrial plants currently use about 28 GJ ton^{-1} (28×10^9 Joules per metric ton of ammonia) [23] or $28 \times 17.03 = 0.5 \text{ MJ mol}^{-1}$. As a byproduct of molecular hydrogen production they also create approximately 15 g of CO_2 per gram of NH_3 [23], or 6 moles CO_2 per mole of NH_3 . Therefore, using current technologies, producing the required amount of NH_3 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 $6 \times 13.3 = 80 \text{ Pmol}$ 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_2 production other than that associated with production of the energy required to make the ammonia (approximately 27 GJ ton^{-1}). If we assume that their method will be used throughout, the annual energy cost is 6500 EJ, with no associated CO_2 emission (as long as alternative or nuclear energy sources are utilized). 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^{-1} [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_2 sink in the above processes is in the production of urea; of a magnitude such that atmospheric CO_2 would be depleted to zero in less than 10 years (although a great deal of CO_2 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_2 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_3 and one mole of CO_2 . Thus two moles of alkalinity are added to the land surface and have the potential to fix two moles of CO_2 as bicarbonate. However, the eventual fate of the majority of reduced nitrogen deposited on the land surface is nitrification [10], a biologically mediated process which oxidizes 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_2 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_2O); a further negative effect.

Let us neglect the warming and OH-consuming effects of enhanced atmospheric NH_3 and assume as a more reasonable alternative to land application: that NH_3 is emitted directly to the atmosphere to react. Taking our conservative estimate of 1.1 Pmol NH_3 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 neutralize 10% of the CO_2 from distributed sources would require 55 EJ (>10% of the human race's current energy consumption) and lead to the emission of 28 Pg-C as CO_2 ; approximately 60 times that which would be sequestered in the ocean (0.5 Pg-C).

Deposition to the Ocean

The crux of the proposed approach of Apak [1] is to convert gaseous atmospheric CO_2 into bicarbonate ions (HCO_3^-) 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], utilizing 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_2 into dissolved carbonate ions achieved almost identical carbon sequestration to the complete removal of an equal amount of CO_2 from the air-sea system, at least to millennial timescales. This is because converting gaseous CO_2 into dissolved HCO_3^- adds both 1 mol of DIC (dissolved inorganic carbon) to the ocean and 1 mol 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_2 , 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 CO₂ cost) than the approach of emission to the atmosphere, particularly if CO₂ was trapped at high concentration, e.g. in the flu gas of a power station.

Unfortunately, a fundamental problem still exists due to the fate of the deposited ammonium. Some of it will be utilized 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 utilization 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 N₂O in the process). As we saw above, the process of oxidizing 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].

CONCLUSION

We have conducted a thorough analysis of the proposed geoengineering technique of ammonia emission to the atmosphere for the neutralization of atmospheric CO₂. We have found that the method is economically and energetically unfeasible. 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 N₂O emissions, and acidification, resulting in more CO₂ being emitted than was fixed in the first place; and (iv) acidification of and CO₂ 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 organization 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 rigor 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ concentrations by massive perturbations of other global elemental cycles is likely to result in strongly nonlinear 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 recognize 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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