

Agricultural liming is a carbon sink in the Mississippi River Basin

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

Review of Suhrhoff et al. "Agricultural liming is a large carbon sink in the Mississippi River Basin" for Nature, Sept. 2025

Summary:

Suhrhoff and colleagues present a relatively novel analysis combining agricultural liming, atmospheric and fertilizer addition and river data, with reactive transport modeling, to suggest that liming has been a net carbon sink in the Mississippi River Basin over the last century. As far as I can tell, in an attempt to keep the message clear and make the results of this work useful for the emerging CDR industry, the authors have oversimplified their incredibly detailed modeling and the results. Firstly, the work is spatially explicit but the resulting figures (2 and 3) are just line plots through time. The supplement includes blurry map of the spatially explicit modeling that includes important heterogeneity (and substantial effort on the part of the authors as far as I can tell). Second, in efforts to over simplify and create what the authors call the 'counterfactual' argument, they argue that liming is just sink and acid contributions are a source of carbon to the atmosphere. This over simplifies the very scientific work they have done here, it's the next of all the reactions, with timescales included, that determines if a given field of agricultural land is a source or sink of carbon. It feels important and necessary to change this framing of the results. Finally, there are a lot of assumptions, I have questioned some of them below, but I would suggest that a much more comprehensive flow chart diagram is needed and outlining of assumptions in a supplemental table format is needed. Despite these comments (and significant work that would be needed to address them) the scientific basis for this work and the result (even if framed differently) is incredibly important and novel.

Major Comments:

138-140: I disagree shouldn't it just be the combination of both that should be evaluated? This whole counterfactual is basically being set up (as far as I can tell) so that places that do currently lime can then argue that they should be paid for doing so based on their CDR. Same goes for other places in the paper such as 275-279.

1034-1036: I think this is just where I have a different perspective than the authors, if is not just the addition of anthropogenic acidity as a source of CO₂ or the liming as a sink but the next set of reactions in combination that should determine if agriculture lands with a certain fertilizer rate, a certain atmospheric deposition and a certain liming frequency are a source or sink of C. And only when that full set of reactions can be accounted for should it then be put into a CDR accounting framework.

214-217: It is odd to me that the authors say this here but a quick glance at the USGS stream gauge network and papers by some of the coauthors make it pretty clear this analysis could have been done at a much more granular scale to make this point and likely needs to be given the huge size that the MRB is integrating (and tapping into the Rocky Mountains in it's headwaters). Is it possible to do this as a proof of concept in a few places?

315-323: Doesn't taking averages like this bias you to higher concentrations? The flow rate (discharge) distribution is not normally distributed it will be log-normal for example, and if you just take flow weighted average concentrations you are missing out on the tail of the distribution where the flux of water is very high but the concentrations are low? (i.e. "C-Q

relationships..")

335: Fraction strong acid weathering: What about the background silicate weathering and the additional silicate weathering in the catchment caused by the strong acids? It seems to me like this needs to be accounted for because it would produce/add additional Ca and Mg to the river water. Ok this is dealt with to some extent in the supplement but it needs to be much more explicit here in the main text.

Minor Line-by-Line Comments:

20: remove "widely"

26: specify the time lag w.r.t. the observation (in the river?) more precisely

26-30: This last sentence of the abstract is extremely convoluted and caveated and I actually don't understand what the main result is of the paper the just reading the abstract. Please clarify meaning, perhaps in 2-3 more concise sentences.

41: Can you tell us what proportion in a parenthetical perhaps?

49: Really dolomite is used? I think some references are needed in this sentence.

56: change to "results in the production..."

59: Ref(s) needed.

70-74: I realize this counterfactual argumentative framework is being used in the CDR world, but it is not yet standard, some additional set up is needed here.

92: Nationally or in the catchment? And line 93-94: what proportion was in the MRB?

144-147: What's surprising to me is that no 'natural' baseline fluxes were even considered/mentioned.

146-147: Also it is problematic that at this point of the paper the chemistry resulting the liming actually removing CO₂ has not yet been described in the same way the emissions are described early on (comes in the next section but readers have to take that logical leap..)

156-159: Some error bars in these estimates are needed to then be able to say that they correspondence bottom-up and top-down in lines 161-162.

178-179: But what is the residence time of that groundwater?

190: So why not also look at the Ca and Mg fluxes to verify this?

202-203: such a statement really needs a citation.

213: add "net" before "large-scale"

296: simplify to "Below we give detailed information..."

329: refs? Details of the MC?

420-428: As stated before we need to see this in map format.

442: What is the "quicklime and hydrated lime" assumed to be mineralogically?

535-537: But what percentage are?

566-580: It was not until this point in the paper that I realized that SPECTER was spatially explicit in this way, it really should be shown then where and at what areas the source vs sink of CO₂ is simulated as they must be calculated.

819: please professionalize, many titles are not properly capitalized.

Specific comments on section S3 (SPECTER model)

1044: is 0.5m good/realistic? Too shallow?

1061-1062: What is being assumed about the fluid and solute (since generated) residence/transit times here?

1074: "is" before "unlikely"

107-1074: I agree with this but in more arid parts of the catchment isn't soil carbonate precipitation observed? Particularly west of the 100/110 deg longitude?

1077-1082 and 1097 + Figure S8: I'm very surprised these spatially exploit calculation are just buried here in the supplement, in fact this is a super important set of maps that requires more interrogation on the spatially explicit nature of the work. Can the authors incorporate this and further analysis into the main text?

Figure 1. I would suggest that what is also needed is the region that actually has lime and fertilizer addition upstream both need to be visualized spatially.

Figure S2 is very blurry, as are some of the other supplemental figures.

Several supplemental figures - when plotting years in the supplemental data, are you plotting calendar years or water years?

Referee #2

(Remarks to the Author)

The authors present a re-assessment of agricultural lime's contribution to atmospheric CO₂ based on basin-level stoichiometry of river water exported from the Mississippi River catchment in the US Midwest, and argue for a flipped script – that lime is not a source of CO₂ as presumed by current GHG accounting practices but rather a sink, while at the same time identifying excess anthropic acidity (including particularly that produced by intensive agriculture) as a heretofore unrecognized source of CO₂. The first part is not quite as novel as presented – Hamilton et al. (2007; cited as the basis for their methodological approach in the online methods section) first suggested that agricultural liming is a net CO₂ sink, in their assessment responsible for US sequestration of a substantial 1.9 TgC / yr. This paper provides a much more rigorous upscaling of that earlier claim, though the current paper doesn't clearly assign a CO₂ number to sequestration. The second part, on the other hand, is quite novel and potentially even more important than the authors articulate.

The theoretical underpinning in which concentrations of dissolved Ca + Mg are compared against concentrations of HCO₃⁻ to estimate the relative importance of strong acid vs. carbonic acid weathering is sound, and consistent with that presented by Hamilton et al. (2007). The approach works for this particular river system because of the marked influence of carbonate mineral weathering on the ion concentrations. The interpolation for the early decades of the 1900s, which is unavoidable, takes account of strong acid inputs to the watershed from sulfur and nitrogen pollution, and the results make sense in light of what we know about temporal patterns in air pollution, nitrogen fertilizer use, and coal mining.

That said, there is one additional anthropic source of strong acid not included in the authors' acid deposition and N fertilizer summation, and this is soil organic N (SON) mineralization and its subsequent nitrification. Soil organic carbon loss since 1900 has been significant across the region, and the accompanying SON loss will have resulted in excess H⁺ generation equivalent (on a nitrogen basis) to about 50% of that generated by fertilizer inputs (while nitrification generates 2 moles of H⁺ per mole of NH₄, ammonification generates one offsetting mole of OH⁻). An estimate of this potential would be valuable to include as it could further amplify the anthropic CO₂ source, especially early in the century – land use for cropland agriculture peaked in the US in 1939 and SOC and SON loss continued for much longer.

Identifying excess acidity as an indirect source of CO₂ emissions is important for two reasons. First, it definitively removes lime as a significant contributor to agricultural global warming impacts (though its mining, transport, and application will remain a minor contributor). Second, it provides another avenue for land-based mitigation, showing, in effect, that liming is already operating as an enhanced rock weathering agent, and could be enhanced further. Neither of these points are made in the paper as effectively as they could be; suggestions for doing so are noted below in specific comments.

A common reaction among geoscientists to the notion of bicarbonate as a carbon sink is that it will re-precipitate when river water reaches the oceans, undoing the carbon sequestration. The question is one of time scales. This is alluded to in Line 922 where it states "timescales shorter than carbonate precipitation in the oceans (>10kyr70)" but this could use more attention in the paper. Surprisingly, the authors do not cite one of their own recent papers on this topic: doi.org/10.1038/s44221-025-00473-0

Specific comments:

1. Line 1: The title is captivating but it doesn't capture the real novelty of the paper, as noted above. The paper might be better titled something along the lines of "Excess soil acidity as a major unrecognized source of agricultural CO₂ emissions."

2. Abstract: Nowhere in the abstract is there an estimate of the total emissions impact of excess acidity in units of TgCO₂ or TgCO₂ per year. Most readers will not be able to parse the 75% statement, so there is no meaningful significance context.

3. Line 39 and throughout. There are often more references used than necessary to underscore a point. Here, for example, there seems little reason to cite three IAM papers when one will do.

4. Lines 41-42. This statement is outdated unless you are referencing national GHG inventories, which are not based on the most recent whole-system global warming impact analyses. The latter treat soil acidity as a minor source of emissions. Moreover, soil carbon loss remains important in many parts of the world. For a Midwest US example see Table 1 in Gelfand et al. 2013 (Nature 493:514). Also, please be precise (throughout) when talking about agricultural emissions – in this paper the context is cropland emissions, which excludes ruminants or grazing lands.

5. Line 45. "in soil" would be better than "in agricultural systems" here since nitrification occurs in all soils. Also, this sentence reads as though N fertilizer is the only anthropic source of acidity in agricultural soils. Keep in mind that about 50% of crop N needs are met by N mineralization of SOM, which produces H⁺ as noted above (while plant uptake of NO₃⁻ releases OH⁻ this is countered by excess cation uptake which further acidifies), and acidity is also generated by microbial and plant root respiration, and long-term by base cation uptake and removal in harvest (and of course from deposition). Maybe qualify acidity here and elsewhere as strong acidity to take care of the respiration and base cation bit).

6. Line 48. the usual formula for dolomite is CaMg(CO₃)₂

7. Line 51, Line 64. No need for "trace" here since all of the GHGs are trace gases (i.e., <1 ppt in the atmosphere).

8. Line 52: this last sentence is cryptic and could be readily deleted.

9. Line 56: "can result" = results

10. Line 63. This is where it would be logical and important to attribute the sink idea to Hamilton et al. (2007). At the very least insert a statement at the end of this sentence to the effect of "despite recent evidence that lime use is a sink rather than a source." with reference to 33. And then qualify the following sentence, perhaps by substituting "potentially erroneous" for "difficult".

11. Line 63 reference. Ogle et al. is not the appropriate reference for the US-GHG methodology; Ogle et al. provide recommended entity-level calculation methodologies. The correct citation is EPA. 2023. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2021. <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2021>.

12. Line 71. Sulfuric acid doesn't ordinarily result from fertilization.

13. Lines 70-72. This sentence needs more unpacking for a broader audience. Even readers who are knowledgeable about soil chemistry will wonder about other sources of acidity. Explain that you're specifically targeting strong acids like nitric and sulfuric not weak acids like carbonic—e.g., "... because it is only these strong acid sources that produce CO₂ emitted to the atmosphere (33)."

14. Line 74. alkalinity and with agricultural lime applications

15. Line 82. Something is wonky with the reference superscript here.

16. Line 86. over the past century

17. Line 86-89. Please better describe the overall approach either here or in the prior paragraph to give us an overview of where you're headed with the results. Maybe add at the end of this paragraph something like "This then allows us to estimate the net CO₂ impact of excess acidity as the difference between...."

18. Line 96. arising from SO₂...

19. Line 98. has been

20. Line 101. Here and elsewhere when you mention acidity or (here) acid-base balance please qualify acid as "excess acid".

21. Line 103. Teramoles

22. Line 104-105. And from SOM loss? See earlier comment.

23. Line 113. nitrogen fertilizer oxidation

24. Line 113. Also SON oxidation. Keep in mind that even without fertilizer and even where SOC stocks are stable, strong acids will be produced in agricultural soils "in excess" of pre-agricultural conditions. Midwest maize, for example, is about twice as productive as the forest it replaced (where forests were cleared), which means about twice as much residue is left for decomposition (~10 Mg/y) compared to the forest's litterfall (~4-5 Mg/y). This "excess residue" will mineralize, producing excess acid as noted earlier. Moreover, legumes whether forage crops like alfalfa, cover crops like clover, or oilseed crops like soybeans will fix nitrogen with unharvested portions remaining in the system to be mineralized. All of these additional sources of excess acid need to be acknowledged and quantified as possible – not all of the blame for excess acidity can be placed on fertilizer N and deposition.

25. Line 115. What do you mean by human intervention – cropland agriculture?

26. Line 126. Which figure does "our results" refer to?

27. Lines 191-193. The authors state that the reactive transport modeling indicates a "broadly constant carbon removal lag in the Mississippi catchment of 15-30 years from the time of lime application (after 1935; Figure 3b)." It is not clear in the main text whether this time lag refers to leaching export from the upper 0.5 m of soils, or if it also encompasses surface, tile drain, and groundwater hydrologic transport through catchment flow paths to the river. The SCEPTER modeling described in the Online Methods section seems to speak to the mass balance at the soil scale. If hydrologic transport is included in the modeling, it is unclear how that was modeled. If not included, one wonders about its importance relative to soil time lags.

Either way this issue of the hydrologic time lag should be clarified in the text. Perhaps include information on the hydrological residence time for the catchment. Hydrologic residence time has been estimated to the Mississippi, as for example in a study using tritium as a tracer (<https://www.usgs.gov/publications/tritium-hydrology-mississippi-river-basin>). However, the river chemistry changes suggest an even shorter time lag. "Preferential flow" is mentioned and could well be due largely to the tile drainage that is commonplace in the wetter parts of the catchment (and those parts have been implicated as the main sources of cropland export of nitrate to the river).

28. Line 207-208. "Much of the Mississippi catchment ...is below optimal soil pH" – this is a poorly supported statement that seems questionable. Lime is cheap, Midwest farmers understand its importance, and every agronomic soil fertility test includes both pH and a lime index indicating how much if any lime is called for. Moreover, the references given don't support the statement – one is a database on a preprint server that provides no analysis other than a legend-free map image; the other is a global assessment with everywhere under pH 6.5 considered lower than optimal, whereas the soil tests with which I'm familiar consider 6-6.5 normal for maize and soybean. Further, the STATSGO2 database used is based on upscaled SSURGO data which includes samples of indeterminate age including legacy. So knowledgeable readers (e.g., agronomists and soil scientists) won't put much stock in this notion. Unless you can find better sources (e.g., state extension bulletins or industry analyses), it would be better to be up front and call for a detailed assessment that would allow potentials to be fairly assessed.

29. Lines 214-220. The suggestion for catchment-scale and jurisdiction-level monitoring of alkalinity fluxes to judge the status and potential of liming is a good one. What is missing however is a discussion of the potential to judge the CO₂ benefits of liming on a parcel basis – how do we credit or understand the potential of liming to affect the global warming impact of lime on a given field? And should we be thinking about liming marginal lands – e.g., the substantial US acreage that has been abandoned from agriculture usually because of low productivity / low soil fertility and likely now maybe low pH?

30. Line 219. as = is

31. Line 230-244. Some authors missing.

32. Figure 2b, 2d, and elsewhere – SO₂ and NO_x are the gaseous precursors for sulfuric and nitric acids in atmospheric deposition, so we usually refer to sulfate (SO₄²⁻) and nitrate (NO₃⁻) when speaking of acidity in atmospheric deposition. Those anions are likely to be largely balanced by H⁺ in all but the driest parts of the catchment because there is little to no alkalinity in atmospheric deposition in wet climates. (Dry deposition of SO₂ would become SO₄²⁻ once in solution.) I am sure the authors are aware of this, but the text could be made more precise.

33. Line 251 Figure 2.

a. In (a) legend says “MI” do you mean “MS”?

b. In (b) where in the methods is the NUE calculation defined – state in legend. It looks like it comes from Cui et al. but how did they calculate – probably this is actually fertilizer use efficiency but without going to the reference can't know for sure, nor for what crop.

c. In (d), it's not clear why the line denoting alkalinity addition from lime doesn't exactly mirror the blue line in (a).

d. It would be helpful for the legend of (d) to state where to find the equation for cumulative excess acidity.

34. Line 264 Figure 3. It's not clear why it's valuable to compare the IPCC and US-GHG frameworks against the factual and counterfactual. Isn't it really the difference between the two factuals that should be compared against the IPCC and US-GHG frameworks? If so, might be worth hatching or shading the in-between. Not sure what we're supposed to take away from this figure, mentioned only(?) on line 148.

35. Line 276. addition = inputs

36. Line 330. Add “Considering the stoichiometry of carbonate mineral dissolution by reaction with carbonic acid at circumneutral pH,” before the sentence beginning with “Estimates of”

37. Line 331. then delete “the excess flux is caused by dissolution of lime,”

38. Line 337. Delete “classic”.

39. Line 339. Replace “historically” with “previously”.

40. Line 339. “was applied to soil solutions, tile drainage, and stream water”

41. Line 347. Typo in figure – “carbon acid” = carbonic acid

42. Figure 4. Best to say “meq L⁻¹” in axis labels.

43. Figure 4 and elsewhere incl. Line 307. Perhaps Ca and Mg do not have charges because at least the early measurements were total dissolved Ca and Mg, although the vast majority of dissolved Ca and Mg should be ionized (assuming the samples were filtered). You must have assumed that they were ions to calculate concentrations in meq L⁻¹. Explanation may be warranted – maybe include charges at first mention and say “hereafter, Ca and Mg” would help.

44. Line 356. Why put the square brackets after fstrong acid?

45. Line 416. driven by ongoing liming and reductions in strong acid input

46. Line 449. delete “as”

47. Line 450-452. this sentence needs improvement

48. Line 462. The references 51 and 52 aren't very good ones for referencing “fast nitrification” – better to have a soil microbiology reference like Robertson, G. P., and P. M. Groffman. 2024. Nitrogen transformations. Pages 407-438 in E. A. Paul and S. D. Frey, editors. Soil Microbiology, Ecology, and Biochemistry, 5th edition. Elsevier, Cambridge MA.

49. Line 462. add valence to NH₄⁺ or just use NH₃ in this paragraph (they exist in equilibrium in solution)

50. Line 465-471. Incorrect description of H⁺ generation by nitrification, which results in 2 moles of H⁺ per mole of NH₄ oxidized when the NH₄ is taken all the way to NO₃ (which is the typical case). Have a look at the aforementioned reference or another nitrification synthesis.
51. Line 468. italicize genera; but does it really make sense to describe nitrification as a two-step process here since nitrite oxidation is almost everywhere much faster than ammonium oxidation, such that very little nitrite is found in most soils and even less in agricultural soils.
52. Line 449. Is “as” supposed to be there?
53. Line 547. balanced
54. Line 822. should have same title as main text
55. Line 856. replace “Usually, this approach is applied to tile drainage and stream water” with “Previously, this approach has been applied for soil solutions, tile drainage, and stream water”
56. Line 877. 1940s
57. Line 882. Number of months
58. Line 893. Replace “rock” with “minerals”
59. Line 899. “CO₂ sinks strength” should be CO₂-C sink strength
60. Line 910. after “was lower than in 1900” it would be clearer to add “(<1900)” and similarly, add “(>1900)” after “increased over 1900 levels”
61. Line 917. between 1954 and the 1990s
62. Line 961. something is missing in this sentence
63. Line 972. “interpolated and modulate estimate of fstrong acid, which modulates fstrong acid based on changes in acidity pollution in that time period” would better be worded as: “interpolated and modulated estimate of fstrong acid as explained in the text.”
64. Line 1078. represent two different approaches
65. Line 1087. acidity
66. Line 1116. starts at
67. Line 1117. reacts
68. Line 1130. Flue gas, Clean Air Act
69. Line 1142. either directly or through?
70. Figure S5. on the x-axis, why put the square brackets after fstrong acid?
71. Figure S5. explain the error bars
72. Figure S5. on the x-axis, why put the square brackets after fstrong acid?
73. Figure S6 caption might better be “Two alternative approaches using the SCEPTER model to estimate the fraction of added acidity that reacts with bicarbonate to produce CO₂ emissions yield similar results.”
74. Figure S6. symbols not visible in legend. Also see comment about Line 910 above.
75. Figure S6b and S9b. why put the square brackets after label on y-axis?

Referee #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Referee #4

(Remarks to the Author)

Suhrhoff et al. report on a surprising finding that agricultural liming - addition of limestone - could be considered a "negative emissions technology" which removes CO₂ from the atmosphere, rather than emitting it. The main mechanism for this is the reaction of lime with carbonic acid in soils to form bicarbonate. They show this with a top-down simulations and bottom-up calculations of acidity balance. While it remains to be seen how this finding generalizes to other locations, this work presents a method for actually evaluating the potential CO₂ flux at the catchment scale rather than using crude conversion factors based on the applied mass of limestone. The policy implication of this work is furthermore broad and immense as it further promotes the use of agricultural liming, which is for the benefit of soil health. The paper is well written and technically sound, and is recommended for publication subject to addressing of minor comments below.

General comments:

There lacks a discussion of agricultural liming on enhancement of soil microbial activity and CO₂ expiration, but isn't it important to consider its magnitude to contrast the two scenarios (liming and without liming)?

p. 21 line 520: it is surprising that including wet deposition contributions do not change the magnitude of deposition since wet deposition is often similar in magnitude or greater than dry deposition. E.g., Vet et al. (doi:10.1016/j.atmosenv.2013.10.060) 2014. Do you know why the results are different in this model and is it possible that there is underestimation of the deposited acidity?

I did not find the discussion of the eventual fate of the removed CO₂ - i.e., the long-term storage mechanism. This eventual is precipitation in the ocean?

I understand the author's argument that there is a negative perception regarding limestone addition as a CO₂ emitter when it is the polluters that emit acidity in the form of SO₂ and NO_x who should be penalized. However, it seems that the evidence of CO₂ removal due to Eq. 2 is really the main point of the paper, and the argument of perception obfuscates it a bit in the way it is currently written.

Minor comments:

Strange formatting of chemical reactions - Eq. 2 for instance uses mixed fonts for the oxygen?

Figure S2 - how are the error bars derived - are these the propagated errors?

Figure axis labels using empty brackets [] to denote unitless quantities is... uncommon.

p. 23 - what was the SCEPTER time step?

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

Re-review of "Agricultural liming is a large carbon sink in the Mississippi River Basin", May 2026.

Thank you to the authors for a thorough response document to my previous comments and those of the other reviewers. The authors addressed most comments primarily just through changes to the writing or just responses in the response document, though some additional analysis was included. In general when additional substantive analysis was suggested such as C-q analysis and looking at impacts upstream of the sites beyond those analyzed in Louisiana the authors did not interrogate those suggestions. I am not sure if the uncertainty propagation is really laid out in a way that allows one to follow the set of calculations that was done here. After re-reading I am convinced that the sign of change of the results is likely correct but not necessarily the magnitude (e.g. in the timeseries of Figure 3b). I guess the validation is the reactive transport results which agree with the magnitude of change empirically determined? I see the reactive transport code is being provided, is the code associated with the calculations from the data and the associated uncertainty propagation being provided? As requested by Nature it would be helpful to be clear about this and also describe in the main text how errors are being propagated and represented in this work more clearly (a lot of this is hidden in the caption to the supplemental Figure S1 and online methods as far as I can tell). Finally, if I understand Figure 3d's map, a majority of the basin was a CO₂ source not sink in 1945? But then this doesn't really show up in Figure 3b because it is cumulative CDR, I think the annual CDR as well as the cumulative CDR should probably be shown, maybe as a pair to panel a which is the annual CO₂ emissions. Relatedly, Figures S11-17 are so rich in data and the county-level data I believe has been interpolated to the grid being used in the modeling (?), it is a shame that these are so small and granulated from the original finer resolution county-level data. Is this going to be provided in a way that subsequent lime amendments and their implications for CO₂ drawdown can be potentially understood at the county level? I think this is important for this paper and these dataset compilations to have an impact. For example as a GIS data product or a google earth engine product..? Sorry if this is outside the scope, but my feeling is this is where this work will be very useful beyond the academic realm.

Referee #2

(Remarks to the Author)

The authors have carefully and effectively addressed earlier comments, and all but one revision item seem fine. The one exception is the new inclusion of biological nitrogen fixation (BNF) as a source of excess acidity. This deserves further explanation. It's true that BNF amplifies the cation imbalance normally in plant tissue, with subsequent effects on soil acidity, but only insofar as more base cations are removed from the system in harvest as compared to non-BNF crops (to put another way, less nitrate uptake means less OH exudation per unit of biomass protein). Acidification could also result from more nitrate's being leached from BNF crops (though this is unlikely and in any case leaching losses are already accounted for in the hydrologic modeling?). From a whole system standpoint, BNF should not in theory acidify the soil if all base cations are returned to the soil and there is no nitrate leaching. See, for example, Tang and Rengel 2003.

Whatever the case, it bears stating the source of BNF acidity explicitly with primary literature references, so that it's clear how BNF is calculated to affect basin wide acidity generation. There is presently no mention of BNF in Figure S19, which is intended to illustrate "all of the N cycle processes considered in this study," so this is one of the places it needs to be included - in addition to the methods section where bnf acidity is listed but calculations not explained / justified.

Tang, C. and Z. Rengel. Role of plant cation/anion uptake ratio in soil acidification. pp. 57-81 In Handbook of Soil Acidity, Marcel Dekker.

Minor comments:

- Line 72 – "for instance" could be "particularly"
- L115 – could say "atmospheric deposition of acidity"
- L140 – add "0–0.5 m depth)" after "topsoil"
- L141 – add "(P)" after "precipitation-only"
- L141 – add "(i.e., P – P -ET)" after "range"
- L178 – replace "P and P-ET" with "P – P – ET"
- L721 – SCEPTER, not SPECTER
- L1105 – "contain" could be "include"
- L1108 – add "as well as" before "Raymond"
- L1123 – best to say "HCO₃ concentrations"
- Fig. S2 – panel a units should be meq/L
- Fig. S5 – correct axis labels from "meq" to "meq/L"
- L1126 – best to say "in meq/L"
- L1149 – CO₂-C sink strength
- L1204 – "climate change" could be "of climate variability"
- L1225 – can delete "parameters"
- L1234 – delete the colon?
- Fig. S6 caption ends in an unfinished sentence
- L1260 – replace "limestone" with "carbonate minerals" here and in following mentions
- L1319 – "of 0.5 m" could be "to 0.5 m"
- L1349 – precipitation
- L1353 - topsoils
- L1380 – topsoils

Referee #3

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Referee #4

(Remarks to the Author)

The authors have sufficiently addressed my previous comments regarding the role of biological activity (via BNF calculation), atmospheric inputs including wet deposition, and long-term storage of the carbon. It is not clear how the final estimates are changed by each modification, but in total the reported estimates of carbon sink have been revised but remain within the same magnitude as the original submission; and the main conclusions remain unchanged. The atmospheric deposition is treated rather phenomenologically, stating the model output variable rather than the way wet deposition is parameterized (which can vary by model). There are many uncertainties to the modeling of this process but admittedly is difficult to characterize; I do not think that think another estimate would change the conclusion. Following this assessment, I can recommend that this manuscript can be published in its current form.

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Referee #1 (Remarks to the Author):

Review of Suhrhoff et al. "Agricultural liming is a large carbon sink in the Mississippi River Basin" for Nature, Sept. 2025

Summary:

Suhrhoff and colleagues present a relatively novel analysis combining agricultural liming, atmospheric and fertilizer addition and river data, with reactive transport modeling, to suggest that liming has been a net carbon sink in the Mississippi River Basin over the last century. As far as I can tell, in an attempt to keep the message clear and make the results of this work useful for the emerging CDR industry, the authors have oversimplified their incredibly detailed modeling and the results. Firstly, the work is spatially explicit but the resulting figures (2 and 3) are just line plots through time. The supplement includes blurry map of the spatially explicit modeling that includes important heterogeneity (and substantial effort on the part of the authors as far as I can tell). Second, in efforts to over simplify and create what the authors call the 'counterfactual' argument, they argue that liming is just sink and acid contributions are a source of carbon to the atmosphere. This over simplifies the very scientific work they have done here, it's the next of all the reactions, with timescales included, that determines if a given field of agricultural land is a source or sink of carbon. It feels important and necessary to change this framing of the results. Finally, there are a lot of assumptions, I have questioned some of them below, but I would suggest that a much more comprehensive flow chart diagram is needed and outlining of assumptions in a supplemental table format is needed. Despite these comments (and significant work that would be needed to address them) the scientific basis for this work and the result (even if framed differently) is incredibly important and novel.

We thank the reviewer for the thoughtful and constructive comments. We agree that our initial presentation did not sufficiently foreground the spatial heterogeneity and mechanistic detail already present in the analysis. In response, we have now incorporated spatially explicit results into the main text and supplement, showing how the acidity balance and net alkalinity export vary across the basin through time. This makes the spatial structure of the modeled CDR signal directly visible.

Regarding the framing, our intention is not to present liming as inherently or universally a sink, but to evaluate its effect within a full acid–base balance relative to a counterfactual without liming. When expressed consistently in proton equivalents and tracked through soil–critical zone–river export pathways, our results indicate that liming has led to a net increase in alkalinity export and therefore a net CO₂ sink—albeit on decadal timescales. We recognize, however, that reaction pathways and residence times introduce important nuance, particularly in the short term when initial emissions may occur, and we now more explicitly discuss these timescales and the conditions under which the direction and magnitude of the CO₂ impact may vary locally.

To improve clarity and to be more transparent, we have now also added a structured summary of assumptions and parameter choices to the online methods. These materials lay out the acid and base generating processes, the associated stoichiometric relationships, and the logic of how they feed into the modeled net CDR estimate.

Please refer in particular to the new section in the online methods “Acidity and alkalinity budgets”, where we list the different approaches and key assumptions. We do not insert it here due to its length.

Major Comments:

138-140: I disagree shouldn't it just be the combination of both that should be evaluated? This whole counterfactual is basically being set up (as far as I can tell) so that places that do currently lime can then argue that they should be paid for doing so based on their CDR. Same goes for other places in the paper such as 275-279.

We appreciate the reviewer’s thoughtful comment and fully agree that the net CO₂ balance of agricultural soils depends on the full reaction network, including both anthropogenic acidity inputs and the dissolution and export of added alkalinity. Our framework (and reactive transport model; SCEPTER) is explicitly built around this combined system. In this stoichiometric setting—while acknowledging spatial and temporal heterogeneity—added acidity in the absence of added alkalinity drives CO₂ release, whereas added alkalinity in a system already receiving anthropogenic acidity generates net CO₂ drawdown over the hydrologic and soil residence times we model.

We also thank the reviewer for the opportunity to clarify the intended implication for carbon accounting. Our analysis does not imply that existing liming practices should be creditable simply because they induce CO₂ removal. Although market rules vary and are shifting, we are of the mind that carbon removal credited in voluntary markets must be additional to a business-as-usual baseline. Our results show that a substantial portion of CO₂ removal is already occurring under current liming, meaning that this existing removal must be included in the baseline and therefore cannot be credited—in many cases it needs to be subtracted even if silicate rock powders were to be used. The work is meant to safeguard against exactly the concern the reviewer raises: preventing crediting of non-additional liming. We now clarify this point in the revised main text and appreciate the opportunity to further elaborate on this issue. Revised text (always shown in green):

These findings underscore the need for carbon crediting frameworks to explicitly account for business-as-usual liming as an existing carbon sink, ensuring robust baselines and avoiding overestimation of additional CDR from enhanced weathering.

In short, our framework evaluates the incremental effect of alkalinity addition in a landscape already influenced by fertilizer, manure, atmospheric deposition, and soil organic N turnover. At Mississippi River Basin scale, and over decadal integration times, this leads to a net alkalinity export signal consistent with observed river chemistry. We now state this more explicitly, while noting that local outcomes can vary depending on soil buffering capacity, hydrology, and timescales of CO₂ equilibration.

1034-1036: I think this is just where I have a different perspective than the authors, if is not just the addition of anthropogenic acidity as a source of CO₂ or the liming as a sink but the next set of reactions in combination that should determine if agriculture lands with a certain fertilizer rate, a certain atmospheric deposition and a certain liming frequency are a source or sink of C. And only when that full set of reactions can be accounted for should it then be put into a CDR accounting framework.

We thank the reviewer for this perspective and fully agree that the net CO₂ outcome reflects the full reaction network, not liming and anthropogenic acidity considered in isolation. Our framework does not assume liming to be inherently carbon removing; instead, it evaluates the net acid–base balance after all relevant processes are included—fertilizer-, manure-, and deposition-derived acidity, SON mineralization, buffering, mineral dissolution, aqueous speciation, and hydrologic export.

Importantly, the reactive transport simulations used in this study also incorporate the full set of coupled reactions the reviewer refers to, including aqueous equilibrium speciation. Thus, the combined reaction network that determines whether liming results in net CO₂ release or uptake is already represented in the model, beyond the simplified acidity–alkalinity stoichiometry discussed in the conceptual framing.

The key empirical result is that, at Mississippi River Basin scale, observed alkalinity export increases over decadal timescales, and this pattern is consistent with both the river chemistry record and the spatially explicit SCEPTER simulations. Under these constrained conditions, liming acts as a net sink relative to the acid-only counterfactual. We now state this more explicitly and also highlight the local nuances to these basin-wide trends.

Updated relevant main text sections:

Despite a brief pulse of CO₂ emissions when liming first increased in the late 1930's (Fig. 3a,d), cumulatively, our modeling approach estimates that 0.23-0.39 GtCO₂ have been removed through agricultural liming in the period between 1900-2015 (P and P-ET scenario range; Fig. 3b), with all removal occurring in regions that receive (net) alkalinity inputs (Fig. 3c-f; Fig. S11).

In surface waters with pH buffered by bicarbonate and carbonate ions, the addition of strong acids lowers pH and shifts the carbonate system toward CO₂ by protonating bicarbonate, leading to CO₂ release either locally or following downstream transport. This acid-driven titration of bicarbonate constitutes a net source of CO₂ to the atmosphere at the catchment scale, as added acidity converts existing alkalinity to CO₂ irrespective of whether additional alkalinity is supplied. To accurately assess the impact of lime on CO₂ emissions one must consider the emissions that would have occurred without the addition of lime but with the addition of anthropogenic acidity (i.e., the “counterfactual” scenario). By comparing emissions occurring when lime is added to soils with this counterfactual scenario, we show that liming has been a net CO₂ sink in the MRB, albeit with a time lag

on the order of decades between agricultural lime application and net carbon export that results from soil cation exchange and solute transit times.

214-217: It is odd to me that the authors say this here but a quick glance at the USGS stream gauge network and papers by some of the coauthors make it pretty clear this analysis could have been done at a much more granular scale to make this point and likely needs to be given the huge size that the MRB is integrating (and tapping into the Rocky Mountains in it's headwaters). Is it possible to do this as a proof of concept in a few places?

We agree that sub-basin analysis is valuable, and we have added maps of both the acidity balance and CDR resulting from SCEPTER simulations. However, the Mississippi River Basin has a unique, continuous, century-scale record of alkalinity and discharge only for the lower Mississippi River, which is necessary to resolve the 1940 lime addition and decadal lag and CO₂ removal dynamics we evaluate here. While we agree that sub-basin applications of this framework are an interesting research direction, at smaller catchment scales, comparable temporal coverage, consistent river chemistry archives, and paleo-forcing reconstructions are unavailable or highly uncertain, making it difficult to meaningfully quantify net C outcomes over relevant timescales as done here for the MRB. Our approach is meant to specifically track a unique experiment—what happens at the roughly continental scale when we turn on liming.

That said, we have addressed the reviewer's point by now including spatially explicit maps of acidity balance and lime-driven CDR, which show how the net signal varies regionally within the MRB. These results make clear that the framework can be applied to sub-basins provided suitable data exist, and we highlight this as a priority direction for future monitoring where long-term hydrologic and geochemical records are sufficient. This has also added important nuance both in terms of acid-base balance and CDR, with both being markedly different within and outside regions of lime addition fluxes. We thank the reviewer for this suggestion.

Lastly, we have included a line noting that regional analysis may be possible if long term local records become available. Some of the water records we presented were rescued from old logbooks. We would love it if this work leads to rescue of other datasets.

Text sections that were added or adjusted in response:

Main text: Regardless, uncertainty in the modeled carbon removal lag times is substantial (~30 years across the hydrologic parameterizations considered here), indicating that additional modeling and empirical work at the regional scale **where sufficiently long, high-resolution time series are available is an important area for future research.**

Online methods: The focus on the lower Mississippi River reflects the availability of a uniquely continuous, century-scale record of discharge and alkalinity^{1,2}, which enables resolution of multi-decadal responses to liming and acidification. Comparable records are

not available for most sub-basins, where discontinuities in monitoring and limited historical coverage preclude robust reconstruction of long-term carbon fluxes and lag times. As a result, the basin-scale outlet provides the most reliable constraint on integrated carbon export dynamics over the timescales considered here. This long-term perspective is essential for resolving the decadal lag between lime application and alkalinity export, which cannot be robustly constrained using shorter or discontinuous sub-basin records.

315-323: *Doesn't taking averages like this bias you to higher concentrations? The flow rate (discharge) distribution is not normally distributed it will be log-normal for example, and if you just take flow weighted average concentrations you are missing out on the tail of the distribution where the flux of water is very high but the concentrations are low? (i.e. "C-Q relationships..")*

We agree that a full C–Q analysis is, in principle, the preferred approach for integrating concentration and discharge. However, for most of the early record used here, continuous daily discharge and chemistry measurements are not available, which means C–Q relationships cannot be fit or extrapolated to annual fluxes in a statistically robust way. We tested implementing a C–Q approach; however, doing so would require combining instantaneous, monthly, and sparse daily measurements, and in practice this led to biased and unstable estimates of annual solute fluxes when benchmarked against periods and locations with continuous daily discharge and concentration data. By contrast, the use of flow-weighted mean concentrations provides a robust and widely applied approach for estimating long-term fluxes from heterogeneous datasets (e.g.,^{2,3}), and has been shown to recover reliable flux estimates under similar data limitations. We therefore use annual flow-weighted mean concentrations, which partially addresses the bias the reviewer notes by weighting observations by discharge rather than simple averaging.

We now explicitly clarify this rationale in the revised manuscript (Supplementary Methods, section on riverine concentration calculations), where we outline the limitations of applying C–Q approaches to discontinuous historical records and justify the use of flow-weighted annual concentrations for consistent long-term analysis.

Importantly, this limitation applies only to the new cation, nitrate, and sulfate time series generated in this study and used to assess the fraction weathering occurring due to strong acid charge balancing. ***The alkalinity time series used for comparison with SCEPTR is based on continuous daily discharge and chemistry data as explained in the cited references.*** These daily records show a long-term increase in alkalinity that cannot be explained by discharge trends, consistent with our interpretation of increasing net alkalinity export driven by anthropogenic acidity neutralization. This distinction is now also made more explicit in the revised Methods.

Given these data constraints, we maintain that the flow-weighted averaging approach remains the most internally consistent method available for isolating long-term trends in anion-cation ratios. We have attempted to clarify in the revised manuscript that we are also utilizing continuous daily discharge and chemistry data.

These changes are reflected in the following text sections of the online methods:

Because daily and/or instantaneous discharge data are lacking for most of the record, robust estimation of concentration–discharge (C–Q) relationships across the full time series is not possible. While C–Q approaches would in principle provide additional resolution, their application would require combining heterogeneous and discontinuous datasets, which introduces substantial uncertainty. We therefore use flow-weighted annual concentrations as the most internally consistent method for capturing long-term trends.

335: Fraction strong acid weathering: What about the background silicate weathering and the additional silicate weathering in the catchment caused by the strong acids? It seems to me like this needs to be accounted for because it would produce/add additional Ca and Mg to the river water. Ok this is dealt with to some extent in the supplement but it needs to be much more explicit here in the main text.

We thank the reviewer for raising this point. We fully agree that changes in background (non-ag-lime) weathering can contribute to Ca+Mg export and now add discussion on this topic and some additional analyses.

In the revised manuscript, we address this in two complementary ways. First, we now include an explicit analysis of climate-driven changes in baseline weathering by scaling pre-liming alkalinity fluxes with precipitation and temperature (and P–ET) following established formulations (West, 2012⁴), allowing us to separate natural variability from excess alkalinity export attributable to liming (Supplementary S1).

Second, and more directly in response to the reviewer’s point, we now explicitly quantify the potential contribution of anthropogenic acidity to enhanced weathering of naturally occurring carbonates (new Supplementary Section and Figure S9). This analysis combines spatially resolved acidity inputs with gridded soil carbonate availability to estimate the fraction of excess acidity that could be neutralized by carbonate phases. While this approach is necessarily approximate, it provides a first-order constraint on the magnitude of this process.

These results show that acidity-driven increases in background carbonate weathering are likely to be small relative to the alkalinity and cation fluxes associated with agricultural liming (~2.6% of the combined total CDR-equivalent by 2015). This reflects both the limited spatial extent of carbonate-bearing soils in the MRB and the fact that a substantial fraction of acidity is buffered through other pathways (e.g., reactions with dissolved species)—see S4 for more details.

In principle, anthropogenic acidity can also enhance the weathering of silicate minerals, contributing additional Ca and Mg to riverine fluxes. However, silicate dissolution rates are substantially slower than carbonate dissolution and proton buffering by dissolved alkalinity pools. As a result, on decadal timescales relevant for this analysis, a large fraction of acidity is expected to be neutralized by these faster pathways, such that acidity-driven silicate weathering likely represents a secondary contribution to the observed cation and alkalinity fluxes relative to agricultural liming

Together, these new analyses make the treatment of background weathering processes more explicit in both the main text and Supplement, and better constrain their contribution relative to liming.

The updated text sections are contained in supplements S1 and S4, which we omit here due to their length.

Minor Line-by-Line Comments:

20: remove "widely"

Done.

26: *specify the time lag w.r.t. the observation (in the river?) more precisely*

We thank the reviewer for this helpful comment. In the main text of the revised manuscript we now specify the river signal time lag more clearly relative to the time of lime application.

Results from river timeseries data indicate a broadly constant carbon removal lag in the Mississippi catchment on the order of ~20-40 years from the time of lime application to net carbon export, and this is generally consistent with the carbon removal time lag independently estimated from our reactive transport model ensemble (Fig. 3b)

26-30: *This last sentence of the abstract is extremely convoluted and caveated and I actually don't understand what the main result is of the paper the just reading the abstract. Please clarify meaning, perhaps in 2-3 more concise sentences.*

We agree that the final sentence of the abstract was overly complex. In the revised manuscript we have split this statement into two shorter sentences to clarify the main conclusion of the study: that anthropogenic acidity inputs act as the primary source of the associated CO₂ emissions, whereas agricultural liming itself represents a net carbon sink with clear co-benefits:

Our analysis indicates that current frameworks implicitly apply an incorrect counterfactual, attributing CO₂ emissions to lime addition rather than to underlying anthropogenic acidity inputs. When evaluated against the more encompassing counterfactual, agricultural liming represents a net carbon sink. This supports that optimized soil pH management can reduce agricultural greenhouse gas emissions while simultaneously improving crop yields and soil health.

41: *Can you tell us what proportion in a parenthetical perhaps?*

We have revised this section, and the referenced text has been removed.

49: *Really dolomite is used? I think some references are needed in this sentence.*

Yes, lime in the US is 20% dolomite. E.g., West & McBride (2005)⁵: “Based on our best estimate, the application of 20–30 Tg of aglime in the U.S., consisting of 80% limestone and 20% dolomite, would have resulted in a net 4.4–6.6 Tg CO₂ emissions in 2001.”

Dolomite is often used because it is present in significant abundance in the early Paleozoic carbonate sources (predominantly Ordovician in age) that source aglime to the Corn Belt.

We have added the reference here.

56: *change to "results in the production..."*

Done.

59: *Ref(s) needed.*

We have added the appropriate references here.

70-74: *I realize this counterfactual argumentative framework is being used in the CDR world, but it is not yet standard, some additional set up is needed here.*

Thanks for this push. This is a core concept of this paper and more generally for accurately quantifying the impact of any process on soils. We have expanded our introduction of this counterfactual framework and appreciate the opportunity to do so. The text is now updated to:

In surface waters with pH buffered by bicarbonate and carbonate ions, the addition of strong acids lowers pH and shifts the carbonate system toward CO₂ by protonating bicarbonate, leading to CO₂ release either locally or following downstream transport. This acid-driven titration of bicarbonate constitutes a net source of CO₂ to the atmosphere at the catchment scale, as added acidity converts existing alkalinity to CO₂ irrespective of whether additional alkalinity is supplied. To accurately assess the impact of lime on CO₂ emissions one must consider the emissions that would have occurred without the addition of lime but with the addition of anthropogenic acidity (i.e., the “counterfactual” scenario). By comparing emissions occurring when lime is added to soils with this counterfactual scenario, we show that liming has been a net CO₂ sink in the MRB, albeit with a time lag on the order of decades between agricultural lime application and net carbon export that results from soil cation exchange and solute transit times.

92: Nationally or in the catchment? And line 93-94: what proportion was in the MRB?

This text has been removed from the revised text attendant to the updated spatially explicit detail.

144-147: What's surprising to me is that no 'natural' baseline fluxes were even considered/mentioned.

Fair point. We now include information on the baseline fluxes in the supplement. They are within uncertainty of previous empirical estimates, which we now note in the SI.

146-147: Also it is problematic that at this point of the paper the chemistry resulting the liming actually removing CO₂ has not yet been described in the same way the emissions are described early on (comes in the next section but readers have to take that logical leap..)

This is a fair point. We have revised the main text with this in mind. We now outline the basics of liming much earlier in the paper, and clearly reference the SI where this is explained in details.

156-159: Some error bars in these estimates are needed to then be able to say that they correspondence bottom-up and top-down in lines 161-162.

We have added uncertainty estimates to all these numbers.

178-179: But what is the residence time of that groundwater?

The ground water residence time (~10 years⁶) is now explicitly mentioned, and the impact on the observed lag times explicitly discussed in the paragraph below.

It is well-known that base cations released into soils (e.g., Ca²⁺ from dissolving limestone or silicates) can become bound to cation exchange sites within the soil, resulting in a time lag between input of cations to the system and cation export^{41–44} that can vary considerably depending on soil properties and land use practices^{41–44}. **In the riverine timeseries, this mechanism should be augmented to some extent by hydrologic transport lags (for instance, hydrologic residence times are estimated to be ~10 years in the Mississippi system⁴⁰).** In contrast, our reactive transport model analysis implicitly assumes immediate transfer of solutes to river/stream waters after passage through upper soil horizons. Indeed, the first-order correspondence between the empirical and modeled estimates of cumulative carbon throughput suggest that preferential flow of solutes from surface soils (e.g., through macropores or along restrictive layers) and/or pervasive tile drainage⁴⁵ in agricultural areas may be critical for reducing carbon and alkalinity lags due to cation exchange processes in the MRB. Regardless, uncertainty in the modeled carbon

removal lag times is substantial (~30 years across the hydrologic parameterizations considered here), indicating that additional modeling and empirical work at the regional scale where sufficiently long, high-resolution time series are available is an important area for future research.

190: So why not also look at the Ca and Mg fluxes to verify this?

This is a great point that we have investigated extensively. The big difference between alkalinity data and Ca and Mg data is that the earliest available records for Ca and Mg begin in the mid 1950s (see also Figure S1) – hence it is impossible to get an accurate pre-liming baseline estimate. We have tried multiple ways but ultimately the finding is highly sensitive to the assumptions on constructing a pre-liming baseline. Alkalinity data is also more continuous, as mentioned above. Hence our focus on alkalinity data which have the more complete record.

202-203: such a statement really needs a citation.

We removed the corresponding sentence from the manuscript.

213: add "net" before "large-scale"

We removed the corresponding sentence from the manuscript.

296: simplify to "Below we give detailed information..."

Done.

329: refs? Details of the MC?

We have greatly increased the detail on the used statistical methods:

To estimate the increase of riverine bicarbonate fluxes relative to the pre-liming baseline, we first calculate the average pre-1935 bicarbonate concentration and flux as a reference state and define the excess over this baseline for the post-1934 period. Uncertainties on the baseline value, excess riverine bicarbonate fluxes, and their cumulative sums are propagated using a Monte Carlo framework. Baseline bicarbonate concentrations are characterized using bootstrap resampling of the pre-1935 data (20-point resamples over 1,000 iterations), yielding bootstrap estimates of the baseline mean and its uncertainty. Excess alkalinity for each post-1934 year is then computed as the difference between observed annual fluxes and the bootstrap-derived baseline distribution. To quantify uncertainty in both annual excess and its cumulative sum, we draw 1,000 Monte Carlo realizations in which observed fluxes

and baseline values are sampled from normal distributions defined by their propagated standard deviations; each realization produces a full time series of annual and cumulative excess. The reported means and standard deviations at each time step correspond to the ensemble statistics of these 1,000 realizations. A minimum fractional uncertainty is enforced to avoid artificially small variances in years with sparse or low-magnitude data.

420-428: *As stated before we need to see this in map format.*

This is included now both within the main text and supplementary figures.

442: *What is the "quicklime and hydrated lime" assumed to be mineralogically?*

CaO/Ca(OH)₂ – but we would like to stress that this is << 1% of total alkalinity input. Hence we decided to model it here as lime on an alkalinity-equivalence basis.

535-537: *But what percentage are?*

We appreciate the reviewer's point and agree that acid mine drainage (AMD) can be a major acidity source in specific mining-impacted catchments. However, at the scale of the Mississippi River Basin, AMD represents a very small fraction of both basin area and integrated acidity flux. The coal-mining regions that generate AMD are spatially limited—typically individual watersheds on the order of 100–1000 km² (e.g., Raymond & Oh, 2009⁷)—compared to the >3 million km² MRB, and their contributions are rapidly diluted and neutralized as they enter higher-alkalinity tributaries. In contrast, fertilizer-, manure-, SON-, BNF-, and deposition-derived acidity affect the entire agricultural Midwest and dominate basin-wide proton budgets by orders of magnitude. Long-term USGS chemistry records used in our analysis capture basin-integrated signals from these widespread sources; AMD impacts are too localized to measurably influence century-scale trends in lower-Mississippi alkalinity. For these reasons, while important locally, AMD is not expected to materially affect the MRB-wide acid–base balance assessed here. However, we now explicitly mention the effects of AMD in the revised text.

566-580: *It was not until this point in the paper that I realized that SPECTER was spatially explicit in this way, it really should be shown then where and at what areas the source vs sink of CO₂ is simulated as they must be calculated.*

We thank the reviewer for this suggestion! We have now included spatially explicit model outputs in both Fig. 2 and Fig. 3.

819: *please professionalize, many titles are not properly capitalized.*

We apologize for this oversight. We made sure that all first words of titles are capitalized in this resubmitted version, thank you for pointing this out!

Specific comments on section S3 (SCEPTER model)
1044: is 0.5m good/realistic? Too shallow?

Great point. We take this zone to be representative of an idealized upper soil column, and more to the point an approximate zone for which we consider a 1-D reactive transport model to be a realistic representation of fluid flow. In practical terms, for most of the Midwest this will encompass the A horizon (plough layer) and most or all of the B horizon — e.g., the soil horizons in which primary feedstock dissolution/reaction and secondary processes are most intense (indeed, soil thickness in cultivated lands has been decreasing over the last century primarily through erosion). When moving into the lower vadose zone (and with horizontal flow) there is a greater chance that fluids will be channeled through preferential flow paths, which our current model architecture does not represent. We now more clearly acknowledge this in the manuscript. However, given that in areas with preferential flow cation sorption will play a much more muted role in controlling solute flux rates (e.g., more effective flushing of more dilute fluids) we anticipate the aggregate impact of this to be relatively small.

1061-1062: What is being assumed about the fluid and solute (since generated) residence/transit times here?

If we understand the reviewer correctly, there is a misunderstanding here resulting from our somewhat confusing language. All that is meant by this clause is that for each acidity and alkalinity flux we reconstruct for the MRB, we convert this to an area-normalized flux for each grid cell as a boundary condition for running the reactive transport model. We have attempted to clarify this in the revised text and figures, which now focus more discretely on the spatially explicit results.

We transfer the acidity and alkalinity fluxes into the Mississippi River catchment (Fig. 2) into corresponding mass fluxes for each grid cell (see Fig. S11 to Fig. S16). The fraction of nitrogen pollution that remains as acidity pollution (i.e., leaches from soils, see online methods and Fig. S19) is fed into the system as NH_4NO_3 – essentially the compound does not affect the system trend as for both NH_4NO_3 and HNO_3 , 1 mol of acidity is released per mol of N. Lime is introduced in the model as a 80:20 (by alkalinity) mix of CaCO_3 and dolomite $\text{CaMg}(\text{CO}_3)_2$. SO_2 pollution is inserted into the model domain as H_2SO_4 . Example outputs of spatially explicit model outputs are shown in Fig. S7 and Fig. S8.

1074: "is" before "unlikely"

We have rewritten this sentence in the final version.

We suppress carbonate precipitations in the SCEPTER runs because (1) there is considerable uncertainty for the threshold oversaturation required for such precipitation to occur⁸⁹ (2) SIC formation as a response to agriculture predominantly occurs in arid and semi-arid regions⁹⁰, i.e., not the corn belt where most of the lime inputs occur (Fig. S11),

and (3) that there is no evidence that carbonates are accumulating in top-soils in the corn belt where most liming occurs^{91,92}. In contrast, multiple studies in the mid-west and corn belt regions indicate that both dissolved inorganic carbon and base cations are efficiently exported from soils (e.g., via tile drainage) combined with losses of SIC, rather than observing a buildup of SIC.

107-1074: I agree with this but in more arid parts of the catchment isn't soil carbonate precipitation observed? Particularly west of the 100/110 deg longitude?

This is an interesting point. Soil carbonate formation is a general challenge in reactive transport modeling of soil acid-base processes. As we note in the manuscript, it is difficult to constrain the degree of oversaturation required to precipitate carbonate. Further, in many cases even if carbonate precipitates in part of the year (e.g., in more arid settings) it will redissolve later in the year. Although we consider it unlikely that permanent carbonate hardpan formation would be impacting our results on large scales (see also answer to comment above), we now more explicitly acknowledge this uncertainty in the text. The dynamics of secondary carbonate formation are an important topic for future work.

1077-1082 and 1097 + Figure S8: I'm very surprised these spatially explicit calculation are just buried here in the supplement, in fact this is a super important set of maps that requires more interrogation on the spatially explicit nature of the work. Can the authors incorporate this and further analysis into the main text?

We thank the reviewer for this great suggestion; highlighting the spatially explicit nature of the simulations and including them in the main text is one of the major updates of this version compared to the initial submission. We have also included Figures showing the spatial distributions of all input fluxes.

Figure 1. I would suggest that what is also needed is the region that actually has lime and fertilizer addition upstream both need to be visualized spatially.

We thank the reviewer for this suggestion. Rather than modifying Figure 1, we have addressed this point by explicitly visualizing the spatial distribution of both liming and fertilizer-derived acidity inputs in Figures 2 and 3 (and associated Supplementary Figures S11–S17). These figures now show where alkalinity and acidity inputs co-occur across the basin, making the spatial structure of the system and the regions contributing to net CO₂ fluxes directly visible.

Figure S2 is very blurry, as are some of the other supplemental figures.

We are really sorry for the inconvenience. We checked, the files that we submitted have high quality figures; this must be something that is happening during the editorial process? We will make sure to submit all figures as high quality vector graphics for the final version.

Several supplemental figures - when plotting years in the supplemental data, are you plotting calendar years or water years?

We are plotting calendar years. This is now explicitly noted in the caption to Fig S1.

Referee #2 (Remarks to the Author):

The authors present a re-assessment of agricultural lime's contribution to atmospheric CO₂ based on basin-level stoichiometry of river water exported from the Mississippi River catchment in the US Midwest, and argue for a flipped script – that lime is not a source of CO₂ as presumed by current GHG accounting practices but rather a sink, while at the same time identifying excess anthropogenic acidity (including particularly that produced by intensive agriculture) as a heretofore unrecognized source of CO₂. The first part is not quite as novel as presented – Hamilton et al. (2007; cited as the basis for their methodological approach in the online methods section) first suggested that agricultural liming is a net CO₂ sink, in their assessment responsible for US sequestration of a substantial 1.9 TgC / yr. This paper provides a much more rigorous upscaling of that earlier claim, though the current paper doesn't clearly assign a CO₂ number to sequestration. The second part, on the other hand, is quite novel and potentially even more important than the authors articulate.

We thank the reviewer for this thoughtful and generous summary. We now state more clearly in the Introduction that this builds on work done by Hamilton⁸ while emphasizing that our contribution is to (i) extend the analysis to a fully spatially and temporally explicit, basin-integrated framework over >100 years, (ii) incorporate anthropogenic acidity sources and soil N mineralization into the net acid–base balance, and (iii) quantify the resulting CO₂ removal signal through both climate-adjusted river chemistry and spatially explicit reactive transport modeling.

We appreciate the reviewer's recognition that identifying excess anthropogenic acidity as a CO₂ source term is a central advance, a framing we clearly agree with. We now highlight this point more clearly in the text, as it provides a mechanistic basis for evaluating liming and related interventions within a net acid–base accounting perspective, consistent with both Hamilton et al. and broader biogeochemical theory.

The theoretical underpinning in which concentrations of dissolved Ca + Mg are compared against concentrations of HCO₃⁻ to estimate the relative importance of strong acid vs. carbonic acid weathering is sound, and consistent with that presented by Hamilton et al. (2007). The approach works for this particular river system because of the marked influence of carbonate

mineral weathering on the ion concentrations. The interpolation for the early decades of the 1900s, which is unavoidable, takes account of strong acid inputs to the watershed from sulfur and nitrogen pollution, and the results make sense in light of what we know about temporal patterns in air pollution, nitrogen fertilizer use, and coal mining.

We thank the reviewer for this affirmation. We agree that the $\text{Ca}+\text{Mg}$ vs. HCO_3^- approach follows directly from the stoichiometry introduced by Hamilton et al. (2007)⁸, and that the dominance of carbonate weathering in the MRB makes this framework particularly well-suited here. We also appreciate the reviewer's recognition that interpolation in the early record is unavoidable and that the reconstructed trends align with known temporal patterns in sulfur and nitrogen pollution and agricultural intensification.

We also now make this explicit in the main text:

For instance, despite some previous evidence to the contrary (e.g., Hamilton et al., 2007 18), the current framework used by the IPCC to evaluate country- and sector-level greenhouse gas emissions assumes that all carbon contained in agricultural lime is emitted to the atmosphere⁵,

That said, there is one additional anthropic source of strong acid not included in the authors' acid deposition and N fertilizer summation, and this is soil organic N (SON) mineralization and its subsequent nitrification. Soil organic carbon loss since 1900 has been significant across the region, and the accompanying SON loss will have resulted in excess H^+ generation equivalent (on a nitrogen basis) to about 50% of that generated by fertilizer inputs (while nitrification generates 2 moles of H^+ per mole of NH_4 , ammonification generates one offsetting mole of OH^-). An estimate of this potential would be valuable to include as it could further amplify the anthropic CO_2 source, especially early in the century – land use for cropland agriculture peaked in the US in 1939 and SOC and SON loss continued for much longer.

We thank the reviewer for highlighting the importance of soil organic N (SON) mineralization as an additional source of strong acidity. We agree that SON losses associated with early 20th-century cropland expansion and SOC decline would have contributed meaningfully to acidity generation, particularly before synthetic fertilizer inputs became dominant. Addressing this directly is one of the major changes to the manuscript.

In response, we have now included a spatially explicit SON-derived acidity term in the analysis. We estimate SON change using historical SOC trajectories combined with a C:N conversion and year-specific nitrogen use efficiencies, yielding a century-scale, spatially resolved SON mineralization flux. This term is now incorporated into the net acid–base balance and SCEPTER runs and discussed in the revised manuscript.

In addition to SON mineralization, we have expanded spatially explicit inputs to account for all potential anthropogenic N additions, including also manure as well as biological nitrogen fixation due to N-fixing crops in agricultural settings.

Please see in particular Online method sections “Acidity generation from fertilizer and manure oxidation” and “Acidity generation from soil organic nitrogen mineralization and biological nitrogen fixation”, which we omit here due to its length.

Identifying excess acidity as an indirect source of CO₂ emissions is important for two reasons. First, it definitively removes lime as a significant contributor to agricultural global warming impacts (though its mining, transport, and application will remain a minor contributor). Second, it provides another avenue for land-based mitigation, showing, in effect, that liming is already operating as an enhanced rock weathering agent, and could be enhanced further. Neither of these points are made in the paper as effectively as they could be; suggestions for doing so are noted below in specific comments.

We thank the reviewer for highlighting this point. We agree that framing excess anthropogenic acidity as a CO₂ source, and liming as a contributor to net alkalinity export, has important implications for how agricultural carbon impacts are understood. In the revised manuscript, we now state these implications more clearly in the Discussion: (i) when evaluated through the net acid–base balance, liming is not a major CO₂ emission source in agricultural systems, and (ii) widespread agricultural liming already functions as a form of enhanced weathering, with potential for targeted expansion where agronomic and environmental conditions support durable alkalinity export. These clarifications make the broader significance of excess acidity and liming for land-based CO₂ removal more explicit, as the reviewer suggests.

A common reaction among geoscientists to the notion of bicarbonate as a carbon sink is that it will re-precipitate when river water reaches the oceans, undoing the carbon sequestration. The question is one of time scales. This is alluded to in Line 922 where it states “timescales shorter than carbonate precipitation in the oceans (>10kyr⁷⁰)” but this could use more attention in the paper. Surprisingly, the authors do not cite one of their own recent papers on this topic: doi.org/10.1038/s44221-025-00473-0

We thank the reviewer for raising this important point. We agree that the long-term fate of exported alkalinity is central to interpreting liming-driven CO₂ removal. The key issue is timescale: while some bicarbonate will eventually precipitate as marine carbonate, the ocean residence time of alkalinity and the timescales for carbonate compensation are on the order of 10⁵ years, far longer than both soil residence times and policy-relevant carbon accounting horizons.

To make this clearer, we have expanded the discussion to emphasize that the CO₂ removal quantified here reflects enhanced riverine alkalinity export to the ocean, during which the carbon remains effectively stored within the ocean–alkalinity system. We now explicitly reference and cite recent work⁹, which provides additional mechanistic context for the persistence of alkalinity in the ocean and the distinction between short-term storage and eventual carbonate burial.

Main text: Our corresponding empirical estimate derived from excess riverine bicarbonate fluxes^{22,23} compared to a pre-1935 baseline (see also Fig. S1, Online Methods, and Supplement S1) equates to 0.387 (± 0.086) GtCO₂ removed through liming and transported out of the MRB (Fig. 3b) , **where it is stored as dissolved inorganic carbon in the ocean–alkalinity system on ~105 year timescales**³⁹.

SI: Although some fraction of this alkalinity will ultimately be removed through marine carbonate precipitation, the residence time of ocean alkalinity and the adjustment of the carbonate system occur over timescales of $\geq 10^4$ – 10^5 years⁷⁹, far exceeding both soil residence times and conventional carbon accounting horizons—which is the main reason carbonates can be effective for CDR on shorter timescales⁴⁹.

Specific comments:

1. Line 1: The title is captivating but it doesn't capture the real novelty of the paper, as noted above. The paper might be better titled something along the lines of "Excess soil acidity as a major unrecognized source of agricultural CO₂ emissions."

We thank the reviewer for this thoughtful comment and fully agree that alkalinity-driven CO₂ removal from liming and CO₂ release associated with excess anthropogenic acidity represent two sides of the same acid–base balance; a point we make throughout the manuscript. Because Nature titles and abstracts require a single concise focus, we chose to foreground the carbon-removal perspective associated with liming, which we felt aligns most directly with current discussions around enhanced weathering and CDR. However, the manuscript now makes clearer that the complementary interpretation—excess anthropogenic acidity as a CO₂ source—arises from the same underlying framework. We are happy to revise this subject to editorial discretion, but have opted to leave the title as-is.

2. Abstract: Nowhere in the abstract is there an estimate of the total emissions impact of excess acidity in units of TgCO₂ or TgCO₂ per year. Most readers will not be able to parse the 75% statement, so there is no meaningful significance context.

We appreciate the reviewer's point, but we feel that the flow of the text is better when presenting a relative efficiency. We have added the amount of maximum CDR potential based on lime added and refer to the realized amounts as a percentage of that.

Our analysis of empirical records suggests that at least 82% of the ideal carbon dioxide removal potential of agricultural lime added since **1900 (~0.47 GtCO₂)** has been realized on the catchment scale, with a decade-scale time lag due to soil cation exchange and solute transport.

3. Line 39 and throughout. There are often more references used than necessary to underscore a point. Here, for example, there seems little reason to cite three IAM papers when one will do.

We thank the reviewer for this suggestion. We appreciate the point that the number of references could be reduced in places. In this case, as well as in other sections, the cited studies emphasize slightly different aspects of the statement, and we aimed to attribute these contributions accurately. As the reference limit permits this level of citation, we have retained the references but carefully reviewed the manuscript to avoid unnecessary redundancy elsewhere.

4. Lines 41-42. This statement is outdated unless you are referencing national GHG inventories, which are not based on the most recent whole-system global warming impact analyses. The latter treat soil acidity as a minor source of emissions. Moreover, soil carbon loss remains important in many parts of the world. For a Midwest US example see Table 1 in Gelfand et al. 2013 (Nature 493:514). Also, please be precise (throughout) when talking about agricultural emissions – in this paper the context is cropland emissions, which excludes ruminants or grazing lands.

We agree that the original framing was overly broad. In the revised manuscript, we have clarified that our analysis specifically concerns cropland greenhouse gas emissions associated with nutrient cycling and soil acid–base processes, rather than the full agricultural sector. As part of rewriting this section, we have removed the original sentence We also acknowledge that soil carbon dynamics remain an important component of agricultural greenhouse gas budgets, but are not the focus of this analysis.

5. Line 45. “in soil” would be better than “in agricultural systems” here since nitrification occurs in all soils. Also, this sentence reads as though N fertilizer is the only anthropic source of acidity in agricultural soils. Keep in mind that about 50% of crop N needs are met by N mineralization of SOM, which produces H^+ as noted above (while plant uptake of NO_3^- releases OH^- this is countered by excess cation uptake which further acidifies), and acidity is also generated by microbial and plant root respiration, and long-term by base cation uptake and removal in harvest (and of course from deposition). Maybe qualify acidity here and elsewhere as strong acidity to take care of the respiration and base cation bit).

We thank the reviewer for this helpful comment. The original sentence has been removed in the revised manuscript. More broadly, we have substantially expanded and clarified our treatment of acidity sources in response to this point. The revised analysis now explicitly accounts for multiple contributors to soil acidity, including fertilizer-derived nitrification, atmospheric deposition, soil organic nitrogen (SON) mineralization, and other biogeochemical processes relevant at the catchment scale. We also clarify that our focus is on anthropogenic strong acidity inputs that drive CO_2 -generating reactions in the

carbonate system, while acknowledging that additional processes (e.g., respiration, base cation uptake and removal) influence soil pH but are treated separately in the acid–base framework.

6. Line 48. the usual formula for dolomite is $\text{CaMg}(\text{CO}_3)_2$

We thank the reviewer for pointing this out. The reviewer is correct that the usual formula for dolomite is $\text{CaMg}(\text{CO}_3)_2$. In the previous version we expressed the formula differently to emphasize the emission of one mole of CO_2 per base unit of mineral during dissolution. However, we agree that the conventional mineral formula is clearer and have corrected this in the manuscript.

As a result, it is often standard agronomic practice to manage soil pH through the addition of fine-grained limestone (CaCO_3) or dolomite (**$\text{CaMg}(\text{CO}_3)_2$**) to soils¹.

7. Line 51, Line 64. No need for “trace” here since all of the GHGs are trace gases (i.e., <1 ppt in the atmosphere).

We thank the reviewer for this helpful suggestion and agree that the term was unnecessary in this context. We have removed “trace” at both locations in the revised manuscript.

8. Line 52: this last sentence is cryptic and could be readily deleted.

Done.

9. Line 56: “can result” = results

Done.

10. Line 63. This is where it would be logical and important to attribute the sink idea to Hamilton et al. (2007). At the very least insert a statement at the end of this sentence to the effect of “despite recent evidence that lime use is a sink rather than a source.” with reference to 33. And then qualify the following sentence, perhaps by substituting “potentially erroneous” for “difficult”.

We thank the reviewer for this helpful suggestion. We agree that it is important to acknowledge earlier work suggesting that agricultural liming may act as a CO_2 sink. We have therefore added a reference to Hamilton et al. (2007) at this point in the manuscript and clarified the wording accordingly.

For instance, **despite some previous evidence to the contrary (e.g., Hamilton et al., 2007 18)**, the current framework used by the IPCC to evaluate country- and sector-level greenhouse gas emissions assumes that all carbon contained in agricultural lime is emitted to the atmosphere⁵, while national GHG accounting in the United States includes the assumption that roughly half of the carbon contained in agricultural lime is emitted to the atmosphere³.

11. Line 63 reference. Ogle et al. is not the appropriate reference for the US-GHG methodology; Ogle et al. provide recommended entity-level calculation methodologies. The correct citation is EPA. 2023. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2021. <https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2021>.

Thank you very much for pointing this out, we have updated the reference.

12. Line 71. Sulfuric acid doesn't ordinarily result from fertilization.

We thank the reviewer for pointing this out. We did not intend to imply that sulfuric acid results from fertilization. We have revised the sentence to clarify that anthropogenic acidity arises from fossil fuel emissions as well as nitrogen fertilization and associated soil nitrogen cycling.

Specifically, we argue that it is the input of anthropogenic strong acids to agricultural systems, for instance sulfuric and nitric acids arising from fossil fuel use and nitrogen fertilization and cycling in soils, that drives CO₂ emissions rather than inputs of agricultural lime (see also Supplement S2).

13. Lines 70-72. This sentence needs more unpacking for a broader audience. Even readers who are knowledgeable about soil chemistry will wonder about other sources of acidity. Explain that you're specifically targeting strong acids like nitric and sulfuric not weak acids like carbonic—e.g., "... because it is only these strong acid sources that produce CO₂ emitted to the atmosphere (33)."

We thank the reviewer for this helpful comment. We agree that distinguishing between strong and weak acids is important in this context. In the revised manuscript, we clarify that we are referring to anthropogenic acidity inputs associated with fertilization and fossil fuel combustion, and this distinction is unpacked in detail in the subsequent text and Supplementary Section S2. We have expanded this section and therefore believe that the current framing provides sufficient clarification for a broad readership without adding additional detail at this point in the sentence.

Specifically, we argue that it is the input of anthropogenic strong acids to agricultural systems, for instance sulfuric and nitric acids arising from fossil fuel use and nitrogen fertilization and cycling in soils, that drives CO₂ emissions rather than inputs of agricultural lime (see also Supplement S2). In surface waters with pH buffered by bicarbonate and carbonate ions, the addition of strong acids lowers pH and shifts the carbonate system toward CO₂ by protonating bicarbonate, leading to CO₂ release either locally or following downstream transport. This acid-driven titration of bicarbonate constitutes a net source of CO₂ to the atmosphere at the catchment scale, as added acidity converts existing alkalinity to CO₂ irrespective of whether additional alkalinity is supplied. To accurately assess the impact of lime on CO₂ emissions one must consider the emissions that would have occurred without the addition of lime but with the addition of anthropogenic acidity (i.e., the “counterfactual” scenario). By comparing emissions occurring when lime is added to soils with this counterfactual scenario, we show that liming has been a net CO₂ sink in the MRB, albeit with a time lag on the order of decades between agricultural lime application and net carbon export that results from soil cation exchange and solute transit times.

14. Line 74. alkalinity and with agricultural lime applications

We thank the reviewer for this comment. We believe the suggestion stems from our confusing language on how the counterfactual is defined in the manuscript. The counterfactual refers to the scenario in which anthropogenic acidity inputs occur but no agricultural lime is added, such that acidity reacts only with natural background sources of alkalinity and inorganic carbon. In the revised manuscript we have expanded the definition and explanation of this counterfactual earlier in the text, and we hope that this clarification resolves the potential ambiguity.

See reply above for relevant text section.

15. Line 82. Something is wonky with the reference superscript here.

Thanks for pointing this out, it is fixed now.

16. Line 86. over the past century

Changed as suggested.

17. Line 86-89. Please better describe the overall approach either here or in the prior paragraph to give us an overview of where you’re headed with the results. Maybe add at the end of this paragraph something like “This then allows us to estimate the net CO₂ impact of excess acidity

as the difference between....”

We thank the reviewer for this helpful suggestion. We agree that the overall analytical approach should be signposted more clearly at this point in the manuscript. We have therefore added a sentence explaining that the compiled records allow us to estimate the net CO₂ impact of excess anthropogenic acidity and agricultural liming over time:

Together, these records allow us to estimate the net CO₂ impact of excess anthropogenic acidity as the difference between acidity inputs and alkalinity additions across the MRB through time.

18. Line 96. arising from SO₂...

We thank the reviewer for this suggestion. We have revised the sentence to clarify that the acidity deposition arises from the atmospheric oxidation of SO₂ and NO_x emitted during fossil fuel combustion.

Atmospheric acidity deposition arising from the oxidation of SO₂ and NO_x emitted primarily during anthropogenic fossil fuel combustion gradually increased throughout the early part of the century but has been decreasing sharply in recent decades due to the expansion of regulations on emissions and air quality³².

19. Line 98. has been

Fixed.

20. Line 101. Here and elsewhere when you mention acidity or (here) acid-base balance please qualify acid as “excess acid”.

We thank the reviewer for this suggestion. In this sentence we refer to the construction of the acid–base balance itself, which integrates anthropogenic acidity inputs and alkalinity additions. Excess acidity is then quantified as the outcome of this balance rather than being part of the balance definition. We therefore retain the wording here but clarify elsewhere in the manuscript that the analysis focuses on excess anthropogenic acidity where appropriate.

21. Line 103. Teramoles

Fixed

22. Line 104-105. And from SOM loss? See earlier comment.

We thank the reviewer for raising this important point. In the revised manuscript we now explicitly include acidity generated from soil organic matter loss and associated nitrogen mineralization in the acid–base budget. The text and analysis have been updated accordingly.

See in particular the new online method section “Acidity generation from soil organic nitrogen mineralization and biological nitrogen fixation”

23. Line 113. nitrogen fertilizer oxidation

We have adjusted this to reflect that oxidation is the acidity source but have worded it such that it also includes other N inputs.

24. Line 113. Also SON oxidation. Keep in mind that even without fertilizer and even where SOC stocks are stable, strong acids will be produced in agricultural soils “in excess” of pre-agricultural conditions. Midwest maize, for example, is about twice as productive as the forest it replaced (where forests were cleared), which means about twice as much residue is left for decomposition (~10 Mg/y) compared to the forest’s litterfall (~4-5 Mg/y). This “excess residue” will mineralize, producing excess acid as noted earlier. Moreover, legumes whether forage crops like alfalfa, cover crops like clover, or oilseed crops like soybeans will fix nitrogen with unharvested portions remaining in the system to be mineralized. All of these additional sources of excess acid need to be acknowledged and quantified as possible – not all of the blame for excess acidity can be placed on fertilizer N and deposition.

We thank the reviewer for this insightful comment and for highlighting additional sources of excess acidity associated with soil organic nitrogen mineralization and biological nitrogen fixation. In the revised manuscript we now explicitly account for these processes in the acid–base budget. Specifically, we include acidity generated from oxidation of soil organic nitrogen associated with historical soil organic matter loss, as well as contributions from biological nitrogen fixation on agricultural lands (e.g., legumes) and subsequent nitrogen cycling. The text and analysis have been updated accordingly to reflect these additional sources of anthropogenic acidity.

See in particular the new online method section “Acidity generation from soil organic nitrogen mineralization and biological nitrogen fixation”

25. Line 115. What do you mean by human intervention – cropland agriculture?

We thank the reviewer for pointing out that this wording was unclear. Here, “human intervention” refers more broadly to anthropogenic perturbations of the acid–base balance, including both agricultural processes (such as fertilizer use and liming) and atmospheric pollution. We have clarified this wording in the revised manuscript.

This imbalance in the acidity budget implies that non-agricultural soil and river pH levels are lower than they would otherwise be **without anthropogenic perturbations of the acid–base balance**.

26. Line 126. Which figure does “our results” refer to?

We thank the reviewer for pointing this out. Here, “our results” refers specifically to the CO₂ emissions from the acid-only counterfactual scenario shown in Figure 3a. We have clarified the sentence to explicitly reference the relevant line in this figure.

Our results suggest that the potential CO₂ emissions from excess anthropogenic acidity are significantly larger than estimated CO₂ emissions from agricultural lime using the conventional IPCC and US GHG accounting frameworks (**Fig. 3a; SCEPTER acidity simulations**).

27. Lines 191-193. The authors state that the reactive transport modeling indicates a “broadly constant carbon removal lag in the Mississippi catchment of 15-30 years from the time of lime application (after 1935; Figure 3b).” It is not clear in the main text whether this time lag refers to leaching export from the upper 0.5 m of soils, or if it also encompasses surface, tile drain, and groundwater hydrologic transport through catchment flow paths to the river. The SCEPTER modeling described in the Online Methods section seems to speak to the mass balance at the soil scale. If hydrologic transport is included in the modeling, it is unclear how that was modeled. If not included, one wonders about its importance relative to soil time lags.

Either way this issue of the hydrologic time lag should be clarified in the text. Perhaps include information on the hydrological residence time for the catchment. Hydrologic residence time has been estimated to the Mississippi, as for example in a study using tritium as a tracer (<https://www.usgs.gov/publications/tritium-hydrology-mississippi-river-basin>). However, the river chemistry changes suggest an even shorter time lag. “Preferential flow” is mentioned and could well be due largely to the tile drainage that is commonplace in the wetter parts of the catchment (and those parts have been implicated as the main sources of cropland export of nitrate to the river).

We thank the reviewer for this thoughtful comment and for highlighting the need to distinguish between soil-scale and hydrologic transport timescales. The lag times derived from the reactive transport modeling primarily reflect soil-scale processes, particularly

cation exchange and the subsequent leaching of base cations from surface soils. In the revised manuscript we now clarify this point and explicitly compare the modeled soil lag times to the basin-scale river signal.

We further note that the cumulative alkalinity export observed in the Mississippi River falls within the range predicted by the reactive transport simulations, indicating strong agreement between modeled soil-scale processes and catchment-scale observations.

Additional hydrologic transport, especially through deeper pathways, will increase the lag observed in river fluxes. Mean hydrologic residence times in the Mississippi system are on the order of ~10 years based on tritium tracer analyses⁶. We now directly state in the main text that the river signal includes lag from cation sorption and hydrologic retention.

These discussions are embedded in the following paragraph in the main text:

Results from river timeseries data indicate a broadly constant carbon removal lag in the Mississippi catchment on the order of ~20-40 years from the time of lime application to net carbon export, and this is generally consistent with the carbon removal time lag independently estimated from our reactive transport model ensemble (Fig. 3b). It is well-known that base cations released into soils (e.g., Ca^{2+} from dissolving limestone or silicates) can become bound to cation exchange sites within the soil, resulting in a time lag between input of cations to the system and cation export^{41–44} that can vary considerably depending on soil properties and land use practices^{42–45}. In the riverine timeseries, this mechanism should be augmented to some extent by hydrologic transport lags (for instance, hydrologic residence times are estimated to be ~10 years in the Mississippi system⁴¹). In contrast, our reactive transport model analysis implicitly assumes immediate transfer of solutes to river/stream waters after passage through upper soil horizons. Indeed, the first-order correspondence between the empirical and modeled estimates of cumulative carbon throughput suggest that preferential flow of solutes from surface soils (e.g., through macropores or along restrictive layers) and/or pervasive tile drainage⁴⁶ in agricultural areas may be critical for reducing carbon and alkalinity lags due to cation exchange processes in the MRB. Regardless, uncertainty in the modeled carbon removal lag times is substantial (~30 years across the hydrologic parameterizations considered here), indicating that additional modeling and empirical work at the regional scale where sufficiently long, high-resolution time series are available is an important area for future research.

28. Line 207-208. “Much of the Mississippi catchment ...is below optimal soil pH” – this is a poorly supported statement that seems questionable. Lime is cheap, Midwest farmers understand its importance, and every agronomic soil fertility test includes both pH and a lime index indicating how much if any lime is called for. Moreover, the references given don’t support the statement – one is a database on a preprint server that provides no analysis other than a legend-free map image; the other is a global assessment with everywhere under pH 6.5 considered lower than optimal, whereas the soil tests with which I’m familiar consider 6-6.5 normal for maize and

soybean. Further, the STATSGO2 database used is based on upscaled SSURGO data which includes samples of indeterminate age including legacy. So knowledgeable readers (e.g., agronomists and soil scientists) won't put much stock in this notion. Unless you can find better sources (e.g., state extension bulletins or industry analyses), it would be better to be up front and call for a detailed assessment that would allow potentials to be fairly assessed.

We thank the reviewer for this helpful comment. We agree that the statement regarding soil pH across the Mississippi catchment was not sufficiently supported by the cited references and could be misleading given regional variability in soil management practices. We have therefore removed this statement from the revised manuscript and generally sharpened empirical grounding of the closing section.

29. Lines 214-220. The suggestion for catchment-scale and jurisdiction-level monitoring of alkalinity fluxes to judge the status and potential of liming is a good one. What is missing however is a discussion of the potential to judge the CO₂ benefits of liming on a parcel basis – how do we credit or understand the potential of liming to affect the global warming impact of lime on a given field? And should we be thinking about liming marginal lands – e.g., the substantial US acreage that has been abandoned from agriculture usually because of low productivity / low soil fertility and likely now maybe low pH?

We thank the reviewer for this thoughtful comment. A number of emerging enhanced weathering crediting frameworks already include approaches to attribute CO₂ removal and account for acid–base reactions at the parcel or project scale, see e.g., ^{10,11}. A detailed discussion of these accounting approaches is beyond the scope of this manuscript and not unique to agricultural liming. Our focus here is instead on demonstrating that catchment-scale monitoring of alkalinity export provides a robust constraint on the net carbon effects of liming and related enhanced weathering interventions.

But we do now specifically call out that this should force us to reevaluate extents of possible lime application, including in marginal lands where low soil fertility is linked in part to acidic conditions.

The last sentence of the main text is now:

Taken together, our results indicate that agricultural liming can be a net carbon sink on large scales with agronomic benefits that warrants renewed attention in crop- and marginal lands worldwide⁵⁰.

30. Line 219. as = is

Fixed in the updated wording.

31. Line 230-244. Some authors missing.

Fixed.

32. Figure 2b, 2d, and elsewhere – SO₂ and NO_x are the gaseous precursors for sulfuric and nitric acids in atmospheric deposition, so we usually refer to sulfate (SO₄²⁻) and nitrate (NO₃⁻) when speaking of acidity in atmospheric deposition. Those anions are likely to be largely balanced by H⁺ in all but the driest parts of the catchment because there is little to no alkalinity in atmospheric deposition in wet climates. (Dry deposition of SO₂ would become SO₄²⁻ once in solution.) I am sure the authors are aware of this, but the text could be made more precise.

We thank the reviewer for this helpful suggestion. We have revised the caption to clarify that the atmospheric acidity input reflects deposition of sulfur and nitrogen derived from oxidation of anthropogenic SO₂ and NO_x emissions. We have also clarified this in the corresponding methods section.

Considered anthropogenic acidity inputs are fertilizer and manure oxidation, atmospheric deposition of sulfuric and nitric acid derived from oxidation of anthropogenic SO₂ and NO_x emissions, soil organic nitrogen (SON) mineralization, and biological nitrogen fixation (BNF).

33. Line 251 Figure 2.

a. In (a) legend says “MI” do you mean “MS”?

We thank the reviewer for pointing this out. The figure has been updated in the revised manuscript and this issue is no longer present.

b. In (b) where in the methods is the NUE calculation defined – state in legend. It looks like it comes from Cui et al. but how did they calculate – probably this is actually fertilizer use efficiency but without going to the reference can’t know for sure, nor for what crop.

We thank the reviewer for this helpful comment. While NUE is no longer shown explicitly in the figure, we now clarify its definition in the revised manuscript. Nitrogen use efficiency (NUE) is defined as the ratio of nitrogen removed in harvested crop products to total nitrogen inputs to cropland (i.e., $NUE = N_{\text{output}} / N_{\text{input}}$), following standard definitions in the literature¹². The time series used here is based on published national-scale estimates for the United States, which integrate fertilizer inputs, biological nitrogen fixation, atmospheric deposition, and crop removal across major cropping systems. These data therefore reflect system-level NUE rather than crop-specific fertilizer-use efficiency.

Online methods: Nitrogen use efficiency for the time series is based on published data from 1961-2012⁵³, where NUE is defined as the ratio of nitrogen removed in

harvested crop products to total nitrogen inputs to cropland (including fertilizer, biological fixation, and atmospheric deposition) 53.

c. In (d), it's not clear why the line denoting alkalinity addition from lime doesn't exactly mirror the blue line in (a).

We thank the reviewer for this comment. The updated version of the figure no longer presents this comparison. In the underlying calculations, alkalinity addition from lime is directly derived from the lime application mass flux.

d. It would be helpful for the legend of (d) to state where to find the equation for cumulative excess acidity.

This line is no longer shown in this Figure, but the underlying calculation is clarified in the online methods section.

34. Line 264 Figure 3. It's not clear why it's valuable to compare the IPCC and US-GHG frameworks against the factual and counterfactual. Isn't it really the difference between the two factuals that should be compared against the IPCC and US-GHG frameworks? If so, might be worth hatching or shading the in-between. Not sure what we're supposed to take away from this figure, mentioned only(?) on line 148.

We thank the reviewer for this helpful comment. The intent of Figure 3a is to first show the total CO₂ emissions associated with anthropogenic acidity inputs (the acidity-only counterfactual), and then the total emissions of the combined system including agricultural liming. This presentation highlights both the magnitude of emissions that would occur in the absence of liming and the impact of lime additions. We agree that the true climate impact of liming is represented by the difference between these two scenarios, which is implicitly shown in panel (a) and presented explicitly as the cumulative difference in panel (b).

35. Line 276. addition = inputs

Included.

36. Line 330. Add "Considering the stoichiometry of carbonate mineral dissolution by reaction with carbonic acid at circumneutral pH, " before the sentence beginning with "Estimates of"

Done

37. Line 331. then delete "the excess flux is caused by dissolution of lime,"

This is changed in the updated version of the text.

38. Line 337. Delete “classic”.

Done

39. Line 339. Replace “historically” with “previously”.

Done

40. Line 339. “was applied to soil solutions, tile drainage, and stream water”

Done, thanks for the clarification

41. Line 347. Typo in figure – “carbon acid” = carbonic acid

Fixed

42. Figure 4. Best to say “meq L⁻¹” in axis labels.

Done

43. Figure 4 and elsewhere incl. Line 307. Perhaps Ca and Mg do not have charges because at least the early measurements were total dissolved Ca and Mg, although the vast majority of dissolved Ca and Mg should be ionized (assuming the samples were filtered). You must have assumed that they were ions to calculate concentrations in meq L⁻¹. Explanation may be warranted – maybe include charges at first mention and say “hereafter, Ca and Mg” would help.

We thank the reviewer for this helpful suggestion. We now clarify in the methods that, although the USGS parameters report total dissolved Ca and Mg, these quantities are assumed to be dominated by their ionic forms (Ca²⁺ and Mg²⁺) for the purposes of the charge-balance calculations used in this study.

Online methods: Although reported as total dissolved Ca and Mg, throughout this manuscript we assume that these quantities are dominated by their dissolved ionic forms (Ca²⁺ and Mg²⁺).

44. Line 356. Why put the square brackets after fstrong acid?

We thank the reviewer for pointing this out. The square brackets were originally included to indicate that fraction strong acid is a unitless quantity. To avoid confusion, we have removed this notation in the revised manuscript.

45. Line 416. driven by ongoing liming and reductions in strong acid input

Included

46. Line 449. delete “as”

Done

47. Line 450-452. this sentence needs improvement

Done

And third, to relate acidity generation to the associated CO₂ emissions in order to evaluate whether emissions arising from reactions between bicarbonate and strong acids should be attributed to lime application or acidity inputs.

48. Line 462. The references 51 and 52 aren't very good ones for referencing “fast nitrification” – better to have a soil microbiology reference like Robertson, G. P., and P. M. Groffman. 2024. Nitrogen transformations. Pages 407-438 in E. A. Paul and S. D. Frey, editors. Soil Microbiology, Ecology, and Biochemistry, 5th edition. Elsevier, Cambridge MA.

We updated the reference, thank you for the suggestion.

49. Line 462. add valence to NH₄⁺ or just use NH₃ in this paragraph (they exist in equilibrium in solution)

Done

50. Line 465-471. Incorrect description of H⁺ generation by nitrification, which results in 2 moles of H⁺ per mole of NH₄ oxidized when the NH₄ is taken all the way to NO₃ (which is the typical case). Have a look at the aforementioned reference or another nitrification synthesis.

We thank the reviewer for this important comment. We fully agree that nitrification of NH₄⁺ to NO₃⁻ produces 2 mol H⁺ per mol NH₄⁺ oxidized. Our intention here, however, was to express acidity generation per mole of fertilizer N added across the full set of in-soil reactions represented in Figure S19, rather than for the nitrification step alone. For major fertilizer forms such as urea and anhydrous ammonia, NH₃ is first converted to NH₄⁺ within soils, a step that consumes 1 mol H⁺ per mol N before nitrification subsequently releases 2 mol H⁺ per mol N. In the case of ammonium nitrate, only the NH₄⁺ fraction produces acidity during nitrification, meaning that the effective acidity generation is likewise ~1 mol H⁺ per mol N added. Under this system boundary, which includes NH₄⁺ generation and subsequent nitrification within soils, the net acidity production therefore remains approximately 1 mol H⁺ per mol N added. We have revised the text to clarify this distinction.

Assuming that, due to fast nitrification reactions¹³, ammonia (NH₃) is nitrified to NO₃⁻ before it is taken up by plants, N added via fertilizer produces 1 mol H⁺ per mol of N. Fertilizers usually contain a significant amount of NH₄ producing substances¹⁴, such as Urea or anhydrous ammonia (NH₃). The reaction of these to NH₄⁺ consumes 1 mol H⁺ per mol of N. NH₄⁺ is rapidly nitrified to nitrate (NO₃⁻) in soils through microbial

oxidation, producing 2 mol H^+ per mol NH_4^+ oxidized, such that overall 1 mol H^+ is produced per mol N added (NO_3^-) **when assessed over the relevant system boundary including both NH_4^+ nitrification as well as its initial production**. This is also true for fertilizer added as ammonium nitrate (NH_4NO_3), where the nitrification of ammonia releases 2 H^+ (for two N).

51. Line 468. italicize genera; but does it really make sense to describe nitrification as a two-step process here since nitrite oxidation is almost everywhere much faster than ammonium oxidation, such that very little nitrite is found in most soils and even less in agricultural soils.

We have removed the genera from the text and are no longer describing it as a two-step process. Thank you for the suggestion.

See adjusted text in the comment above.

52. Line 449. Is “as” supposed to be there?

We have deleted “as”.

53. Line 547. Balanced

This text is no longer included in the updated methods section.

54. Line 822. should have same title as main text

Fixed

55. Line 856. replace “Usually, this approach is applied to tile drainage and stream water” with “Previously, this approach has been applied for soil solutions, tile drainage, and stream water”

Done

56. Line 877. 1940s

Fixed

57. Line 882. Number of months

Fixed

58. Line 893. Replace “rock” with “minerals”

Done

59. Line 899. “CO₂ sinks strength” should be CO₂-C sink strength

Fixed

60. Line 910. after “was lower than in 1900” it would be clearer to add “(<1900)” and similarly, add “(>1900)” after “increased over 1900 levels”

Done

61. Line 917. between 1954 and the 1990s

Fixed – thank you for catching these typos!

62. Line 961. something is missing in this sentence

Fixed – this sentence is not included in the updated version

63. Line 972. “interpolated and modulate estimate of fstrong acid, which modulates fstrong acid based on changes in acidity pollution in that time period” would better be worded as: “interpolated and modulated estimate of fstrong acid as explained in the text.”

Done

64. Line 1078. represent two different approaches

Fixed – this sentence is not included in the updated version. Instead we now show full representation of modeled emissions via the SCETER model domain.

65. Line 1087. Acidity

This text section is not included in the updated version of the SI.

66. Line 1116. starts at

This text section is not included in the updated version of the SI.

67. Line 1117. Reacts

This text section is not included in the updated version of the SI.

68. Line 1130. Flue gas, Clean Air Act

Fixed

69. Line 1142. either directly or through?

Fixed

70. Figure S5. on the x-axis, why put the square brackets after fstrong acid?

All figures denote units in square brackets. F_strong_acid had empty brackets as it is a unitless parameter. We removed empty brackets for unitless quantities throughout the manuscript.

71. Figure S5. explain the error bars

Added – they are based on Monte Carlo simulations considering all relevant input parameters used to calculate the shown quantities. This is now specified in figure captions and the underlying Monte Carlo simulations are now introduced in more details in the online methods.

Monte Carlo framework. Baseline bicarbonate concentrations are characterized using bootstrap resampling of the pre-1935 data (20-point resamples over 1,000 iterations), yielding bootstrap estimates of the baseline mean and its uncertainty. Excess alkalinity for each post-1934 year is then computed as the difference between observed annual fluxes and the bootstrap-derived baseline distribution. To quantify uncertainty in both annual excess and its cumulative sum, we draw 1,000 Monte Carlo realizations in which observed fluxes and baseline values are sampled from normal distributions defined by their propagated standard deviations; each realization produces a full time series of annual and cumulative excess. The reported means and standard deviations at each time step correspond to the ensemble statistics of these 1,000 realizations. A minimum fractional uncertainty is enforced to avoid artificially small variances in years with sparse or low-magnitude data.

72. Figure S5. on the x-axis, why put the square brackets after fstrong acid?

All figures denote units in square brackets. F_strong_acid has empty brackets as it is a unitless parameter. They have been removed.

73. Figure S6 caption might better be “Two alternative approaches using the SCEPTER model to estimate the fraction of added acidity that reacts with bicarbonate to produce CO₂ emissions yield similar results.”

This likely referred to Figure S8 as S6 does not show SCEPTER outputs, but S8 showed outputs matching this prompt – nevertheless we removed this figure in favor of spatial representation of CO₂ emissions from both acidity and acidity+lime simulations such that it is no longer relevant.

74. Figure S6. symbols not visible in legend. Also see comment about Line 910 above.

We thank the reviewer for this suggestion. We have clarified in the caption that the marker colors correspond to the color bar indicating the year of observation.

75. Figure S6b and S9b. why put the square brackets after label on y-axis?

Square brackets denote units. We have removed empty brackets for unitless quantities.

Referee #3 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Thank you very much for your effort!

Referee #4 (Remarks to the Author):

Suhrhoff et al. report on a surprising finding that agricultural liming - addition of limestone - could be considered a "negative emissions technology" which removes CO₂ from the atmosphere, rather than emitting it. The main mechanism for this is the reaction of lime with carbonic acid in soils to form bicarbonate. They show this with a top-down simulations and bottom-up calculations of acidity balance. While it remains to be seen how this finding generalizes to other locations, this work presents a method for actually evaluating the potential CO₂ flux at the catchment scale rather than using crude conversion factors based on the applied mass of limestone. The policy implication of this work is furthermore broad and immense as it further promotes the use of agricultural liming, which is for the benefit of soil health. The paper is well written and technically sound, and is recommended for publication subject to addressing of minor comments below.

General comments:

There lacks a discussion of agricultural liming on enhancement of soil microbial activity and CO₂ expiration, but isn't it important to consider its magnitude to contrast the two scenarios (liming and without liming)?

We thank the reviewer for raising this point. This is a complex (and often non-linear¹⁵) issue — although there is some evidence for increased soil microbial activity and respiration when soil pH increases, there is also strong evidence for increases in soil organic carbon stocks with liming¹⁶, along with extensive evidence for enhancement of soil organic matter storage linked to calcium (Ca) bridging^{17–19}. Indeed, over longer timescales, field studies frequently report stable or increased soil organic matter under sustained liming, as improved plant productivity and reduced acid stress can offset short-term respiratory pulses. This suggests that transient microbial CO₂ release does not lead to persistent soil carbon loss and is consistent with the multi-decadal alkalinity export signal that underpins the net CO₂ removal quantified here. In any case, our inclusion of SON mineralization in the net acidity budget captures some of the contribution of soil organic matter turnover to acidity generation and CO₂ exchange.

Importantly, this interpretation does not contradict the treatment of soil organic matter turnover as a source of acidity in our budget (see also response to Reviewer 2), as these terms reflect short-term fluxes in the acid–base balance, whereas longer-term changes in soil carbon stocks are governed by a broader set of ecological and environmental controls. The associated changes are reflected primarily in the addition of the online method section “Acidity generation from soil organic nitrogen mineralization and biological nitrogen fixation”.

p. 21 line 520: it is surprising that including wet deposition contributions do not change the magnitude of deposition since wet deposition is often similar in magnitude or greater than dry deposition. E.g., Vet et al. (doi:10.1016/j.atmosenv.2013.10.060) 2014. Do you know why the results are different in this model and is it possible that there is underestimation of the deposited acidity?

We appreciate this question. In our revised analysis we use total (wet + dry) deposition from a spatially explicit product; acidity is evaluated at the point of soil entry, so both pathways are included.

I did not find the discussion of the eventual fate of the removed CO₂ - i.e., the long-term storage mechanism. This eventual is precipitation in the ocean?

We thank the reviewer for raising this important point. The removed CO₂ is eventually stored as dissolved inorganic carbon in the ocean–alkalinity system. CO₂ taken up during carbonate dissolution enters the river as bicarbonate, is transported to the ocean, and resides in the oceanic DIC pool. The residence time of alkalinity in the ocean is on the order of 10⁵ years, meaning that on policy- and climate-relevant timescales, this dissolved carbon is effectively stored.

Over much longer geologic timescales, a portion of this alkalinity will eventually be converted to marine carbonate minerals and buried, but this occurs on >10 kyr timescales. For clarity, we now state explicitly that our CO₂ removal estimates refer to long decadal–centennial storage, consistent with the durability definition used in carbon accounting frameworks, and we cite recent work demonstrating the long residence time and stability of alkalinity in the ocean.

Relevant text in the main text: Our corresponding empirical estimate derived from excess riverine bicarbonate fluxes^{22,23} compared to a pre-1935 baseline (see also Fig. S1, Online Methods, and Supplement S1) equates to 0.387 (±0.086) GtCO₂ removed through liming and transported out of the MRB (Fig. 3b), where it is stored as dissolved inorganic carbon in the ocean–alkalinity system on ~10⁵ year timescales³⁹.

Relevant text in S1: On policy- and soil-system–relevant timescales, this sink reflects the export of alkalinity to the ocean, where dissolved inorganic carbon remains stored within the ocean–alkalinity system for timescales far longer than those governing soil and river transport. Although some fraction of this alkalinity will ultimately be removed through

marine carbonate precipitation, the residence time of ocean alkalinity and the adjustment of the carbonate system occur over timescales of $\geq 10^4$ – 10^5 years²⁰, far exceeding both soil residence times and conventional carbon accounting horizons—which is the main reason carbonates can be effective for CDR on shorter timescales⁹.

I understand the author's argument that there is a negative perception regarding limestone addition as a CO₂ emitter when it is the polluters that emit acidity in the form of SO₂ and NO_x who should be penalized. However, it seems that the evidence of CO₂ removal due to Eq. 2 is really the main point of the paper, and the argument of perception obfuscates it a bit in the way it is currently written.

We appreciate this helpful clarification. We agree that the central contribution of the study is the empirical evidence for net CO₂ removal arising from anthropogenic alkalinity addition, as formalized in Eq. 2. The discussion of historical perception and attribution was intended only to provide context for why liming has been treated as a CO₂ source in existing accounting frameworks and to demonstrate the importance of this work, not to serve as a primary narrative.

In response, we have streamlined the relevant passages to foreground the geochemical result—that the observed increase in basin-scale alkalinity export, supported by both our spatially explicit SCEPTER simulations and the climate-adjusted river chemistry record, indicates net CO₂ drawdown relative to the acidified counterfactual. The contextual remarks now play a more limited role, ensuring that the main finding remains the clear focus of the manuscript.

Minor comments:

Strange formatting of chemical reactions - Eq. 2 for instance uses mixed fonts for the oxygen?

We are sorry for the inconvenience – all of these are formatted as the same capital “O”. We will make sure all equations look consistent in the final typeset version of the article.

Figure S2 - how are the error bars derived - are these the propagated errors?

We thank the reviewer for this helpful question. Yes, the error bars represent fully propagated uncertainties based on the uncertainty ranges of all relevant input parameters and 1000 Monte Carlo simulations. We have clarified this in the revised figure caption, as well as introduced Monte Carlo Simulations in more detail in the online methods.

See answer to comment #71 of reviewer 2 for the relevant text section.

Figure axis labels using empty brackets [] to denote unitless quantities is... uncommon.

Fair point. These have been removed where applicable.

p. 23 - what was the SCEPTER time step?

Good question, we should have included this. The time step in SCEPTER by default is adaptive — time step duration evolves depending on the time to convergence of the previous integrations step (ranging from 10^{-20} to 10^2 years). The default criterion for convergence is a solution difference of $<10^{-9}$ (mol m^{-3} or $\text{m}^3 \text{m}^{-3}$) from the previous iteration in each time-integration step. This has now been added explicitly to the supplementary information:

The time step in SCEPTER is adaptive by default, meaning that the duration of each time step evolves depending on the time required for convergence of the previous integration step (ranging from 10^{-20} to 10^2 years). In practice, time steps typically range from ~ 10 – 20 to $\sim 10^2$ years. The default criterion for convergence is a solution difference of $<10^{-9}$ (mol m^{-3} or $\text{m}^3 \text{m}^{-3}$) from the previous iteration in each time-integration step.

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Referee #1 (Remarks to the Author):

Re-review of "Agricultural liming is a large carbon sink in the Mississippi River Basin", May 2026

Thank you to the authors for a thorough response document to my previous comments and those of the other reviewers.

We are grateful for the reviewer's continued engagement with the manuscript across review rounds. The comments have helped us clarify several important aspects of the analysis, especially the uncertainty structure, the distinction between annual and cumulative CO₂ fluxes, and the data products needed to make the work useful beyond the immediate manuscript. We appreciate the time and effort invested in this careful re-review.

Please find our answers below following each of the reviewer's points.

The authors addressed most comments primarily just through changes to the writing or just responses in the response document, though some additional analysis was included. In general when additional substantive analysis was suggested such as C-q analysis and looking at impacts upstream of the sites beyond those analyzed in Louisiana the authors did not interrogate those suggestions.

We did indeed investigate C–Q relationships, as discussed in our previous response. While such approaches are preferable where sufficiently resolved data exist, applying them to the historical record considered here would require combining heterogeneous instantaneous, monthly, sparse daily, and reconstructed data products, which we found to be not robust. We therefore retained flow-weighted annual concentrations as the most internally consistent approach and now explain this rationale more clearly in the Methods. We also note that this limitation applies to the newly generated cation and anion data shown in Fig. S1a–d but not to alkalinity fluxes, which are based on previously published daily records as clarified in the legend and Methods.

I am not sure if the uncertainty propagation is really laid out in a way that allows one to follow the set of calculations that was done here.

We thank the reviewer for highlighting this point. In response, we have substantially clarified and consolidated the uncertainty treatment in a dedicated Online Methods section, while avoiding unnecessary expansion by bringing together material that was previously distributed across several methodological sections and figure captions. The revised text now clearly distinguishes uncertainty in the empirical river-flux estimate, uncertainty in the reconstructed spatial input layers, and model-structural uncertainty associated with the hydrological parameterizations.

Importantly, we have also added a new quantitative propagation of the spatially explicit ± 1 SD acidity and lime-input uncertainties through matched SCEPTER simulations under both hydrological forcings. The resulting sensitivity analysis is described in Supplementary Section S3.3 and shown in Figures S12–S15, with the full range incorporated into Figure 3. The bootstrap and Monte Carlo procedure used for the riverine alkalinity estimate is now described more explicitly, and the corresponding analysis code is included with the Zenodo repository. Together, these revisions make the sequence of calculations and the representation of uncertainty substantially more transparent and reproducible.

The updated Online Method section “Treatment of uncertainty”, of which ~80% of the content already existed in the Online methods in various places but was now bundled into one:

Treatment of uncertainty

We distinguish conceptually between three sources of uncertainty:

1. Uncertainty in the empirical river-flux estimate, propagated via bootstrapping and Monte Carlo simulations, as well as novel river Ca, Mg, SO₄²⁻, and NO₃⁻+NO₂⁻ records.
2. Uncertainty in the reconstructed components of the acid base balance, propagated here by assuming nominal uncertainties depending on temporal proximity to years with reference data and through additional SCEPTER sensitivity simulations
3. Model-structural uncertainty, represented by the precipitation-only and P–ET hydrological endmembers in the SCEPTER simulations below.

Because annual uncertainties were not reported for the published bicarbonate-carbon fluxes, uncertainties in excess riverine bicarbonate export were estimated by assigning each annual flux a nominal one-standard-deviation uncertainty of 15% and propagating these uncertainties through the excess flux calculations. Baseline uncertainty was estimated by generating synthetic flux time series and bootstrap resampling the available pre-1935 baseline years with replacement. For each of 1,000 Monte Carlo/bootstrap iterations, annual excess fluxes were calculated as the difference between the synthetic post-1934 fluxes and the bootstrapped baseline mean, and cumulative excess fluxes were calculated by summing annual excess values through time. Reported uncertainty envelopes correspond to ± 1 standard deviation across these 1,000 Monte Carlo realizations. The processed data and analysis scripts are available on Zenodo [insert Zenodo link/DOI during proofs]. Uncertainty on the novel MRB Ca, Mg, SO₄²⁻, and NO₃⁻+NO₂⁻ data was estimated by propagating within-month concentration variability across the five considered stations, represented as 1SD, together with assumed 10% discharge uncertainties to the calculation of annual flow-weighted average concentrations and fluxes from monthly data. A minimum monthly concentration uncertainty of 5% was retained where sample variability implied lower values.

Because the acid–base budget integrates heterogeneous datasets with different reference years and temporal resolutions, we adopt a uniform uncertainty treatment across all reconstructed spatial input layers. Specifically, to reflect increasing uncertainty with distance from empirically or model-constrained reference years, we apply a uniform time-dependent uncertainty scheme across all spatial input layers: pixel-scale uncertainty is set to 10% for years with direct reference data and increased by 1.5% per year with distance from the nearest reference year. This treatment is applied consistently to lime, fertilizer and manure inputs, BNF, SON mineralization, and atmospheric deposition (see Figure S18). Basin-wide uncertainties are calculated by spatially averaging the corresponding uncertainty layers using the same gridding procedures applied to compute mean fluxes. Propagated uncertainties of all acidity and alkalinity inputs for MRB average input fluxes are shown in Figure 2.

To bracket model structural uncertainty in the reactive transport simulations, we consider two endmember scenarios for water inputs to topsoils: precipitation-only (P) and precipitation minus evapotranspiration (P–ET; with ET encompassing evaporation from bare soil, evaporation from canopy, sublimation of snow, and transpiration). These two scenarios represent plausible endmember bounds on the hydrologic flux available to drive weathering reactions and solute export from soils. Using precipitation alone likely overestimates water available for subsurface reactions because a fraction of precipitation is lost through interception, surface runoff, or rapid evaporation before infiltrating and interacting with soil minerals. Conversely, precipitation minus evapotranspiration (P–ET) approximates the net vertical water flux available for drainage or recharge and is widely used as a first-order estimate of effective recharge in hydrologic water-balance frameworks and reactive-transport models^{79,80}. However, this formulation likely underestimates the water participating in weathering reactions because some water removed via evapotranspiration has already interacted with soil minerals before being lost from the system. Taken together, these two representations provide reasonable hydrologic endmembers that constrain the effective water flux controlling mineral dissolution and solute export from soils. Uncertainties in reconstructed acidity and alkalinity inputs were propagated through SCEPTER by varying the corresponding inputs by ± 1 SD in several combinations under both hydrological parameterizations. Figure 3 shows the maximum and minimum across all simulations considered; the individual uncertainty scenarios and their interpretation are described in Supplementary S3.3 and Figures S12–S15.

Please see supplement S3.3 & the code/data repository for additional clarifications on uncertainty analyses.

After re-reading I am convinced that the sign of change of the results is likely correct but not necessarily the magnitude (e.g. in the timeseries of Figure 3b).

We agree that the sign of the liming effect is better constrained than its exact magnitude, and we have revised the manuscript to make this distinction explicit. Reconstructing interacting biogeochemical, hydrological, and agricultural processes over more than a century necessarily involves uncertainty, although we have parameterized the available historical data as robustly as possible. The new sensitivity analysis in Supplementary S3.3 further demonstrates that uncertainty in acidity inputs strongly affects absolute simulated emissions but has comparatively little influence on the inferred effect of lime relative to the matched acidity-only counterfactual. Across all evaluated hydrological and input-uncertainty scenarios, liming nevertheless remains a cumulative CO₂ sink.

The online methods now include the following, and similar statements are included elsewhere, too:

The parameterization of both reconstructed input fluxes and the reactive transport model itself affects the exact magnitude of simulated CO₂ fluxes. We have parameterized these processes as robustly as possible given the available historical records, but uncertainties and parameter choices—similar to the hydrological endmembers considered here and the baseline-weathering corrections discussed in Supplementary S1.3—necessarily influence

the precise magnitude of the inferred effect. Importantly, these choices primarily affect the magnitude rather than the sign of the result: across the P–P-ET model range and parameterizations evaluated here, liming consistently reduces CO₂ emissions relative to the acidity-only counterfactual and emerges as a net carbon sink at catchment scale. Furthermore, as shown in Supplementary S3.3, the inferred effect of lime is comparatively robust to uncertainty in acidity inputs, which primarily affects absolute emission levels in the matched acidity-only and acidity-plus-lime simulations rather than the difference between them. We therefore consider the sign of the liming effect to be better constrained than its exact magnitude.

I guess the validation is the reactive transport results which agree with the magnitude of change empirically determined?

We have clarified that the agreement between the empirical river-flux estimate and the reactive transport model should be interpreted as convergence between two independent approaches rather than validation of an exact magnitude. The river-based estimate is derived from excess alkalinity export relative to the pre-liming baseline, whereas the SCEPTEr estimate is based on spatially explicit reactive transport simulations forced with reconstructed acidity and alkalinity inputs. The empirical estimate is consistent with the range obtained across the expanded hydrological and input-uncertainty simulations, strengthening the basin-scale sink interpretation. However, this correspondence does not establish a uniquely correct magnitude or, by itself, prove that all observed excess alkalinity is attributable to liming.

This is acknowledged and extensively discussed also for example in S1.3 and S4, which we do not insert here due to their length.

I see the reactive transport code is being provided, is the code associated with the calculations from the data and the associated uncertainty propagation being provided? As requested by Nature it would be helpful to be clear about this and also describe in the main text how errors are being propagated and represented in this work more clearly (a lot of this is hidden in the caption to the supplemental Figure S1 and online methods as far as I can tell).

We have clarified both code availability and uncertainty propagation in the revised manuscript. As described above, the Methods and figure legends now state more clearly how uncertainties are propagated and represented. The SCEPTEr code is publicly available, and the Zenodo repository includes the processed gridded input layers required to reproduce the simulations, key model outputs, and analysis scripts used to calculate MRB-wide fluxes and perform the bootstrap/Monte Carlo uncertainty analysis of riverine fluxes. The input layers and outputs from the additional SCEPTEr uncertainty simulations are also included. These resources are now described explicitly in the revised Code Availability statement.

The corresponding section is:

Code availability

The SCEPTEr reactive transport model code used in this study is publicly available at <https://github.com/cdr-laboratory/SCEPTEr>. The processed gridded input layers required to reproduce the SCEPTEr simulations, key model outputs, and analysis scripts used to

perform the bootstrap/Monte Carlo analysis of riverine fluxes are available from Zenodo at [DOI to be added during proofs].

Finally, if I understand Figure 3d's map, a majority of the basin was a CO₂ source not sink in 1945? But then this doesn't really show up in Figure 3b because it is cumulative CDR, I think the annual CDR as well as the cumulative CDR should probably be show shown, maybe as a pair to panel a which is the annual CO₂ emissions.

We agree and have clarified the annual dynamics of the modeled CO₂ fluxes, including the initial emissions pulse, in the Abstract, main text, and Figure 3 legend. We have also added Figure S19, which presents the annual ideal lime-CDR potential, SCEPTER-derived CDR, empirical riverine CDR, and a direct comparison of all three estimates. The 1945 map captures the early response following the onset of large-scale liming, when liming increased CO₂ emissions relative to the acidity-only counterfactual across parts of the basin. The revised text now makes clear that this initial annual emissions pulse precedes the cumulative net sink shown in Figure 3b.

Abstract:

“These results are consistent with reactive transport modeling of soil cation throughput, which indicates that net CO₂ removal emerges after an initial emissions pulse associated with neutralization of soil acidity pools.”

Main-text introduction:

“By comparing emissions occurring when lime is added to soils with this counterfactual scenario, we show that after an initial emissions pulse, liming has been a net time-integrated CO₂ sink in the MRB...”

Efficiency and timescales section:

“Despite a brief pulse of CO₂ emissions when liming first increased in the late 1930's (Figure 3a,d), cumulatively, our modeling approach estimates that 0.22–0.37 GtCO₂ have been removed...”

Figure 3 legend:

“Annual CDR potentials and fluxes are shown in Figure S19. The simulations show an initial pulse of CO₂ emissions following lime addition (d) before sustained carbon removal emerges...”

Relatedly, Figures S11-17 are so rich in data and the county-level data I believe has been interpolated to the grid being used in the modeling (?), it is a shame that these are so small and granulated from the original finer resolution county-level data. Is this going to be provided in a way that subsequent lime amendments and their implications for CO₂ drawdown can be potentially understood at the county level? I think this is important for this paper and these dataset compilations to have an impact. For example as a GIS data product or a google earth engine product..? Sorry if this is outside the scope, but my feeling is this is where this work will be very useful beyond the academic realm.

We agree that a county-level or GIS-ready data product, particularly for lime, would be valuable beyond the present manuscript. The source-specific acidity and lime input layers used here are derived from published datasets, including public county-level lime census data (<https://www.icpsr.umich.edu/web/ICPSR/studies/35206>) and other published products, and are therefore not redistributed separately. These sources are cited in the Methods and Supplementary Information, and the mapped products are shown to document the spatial structure of the inputs.

For this paper, we are depositing the processed annual gridded products at the 1° resolution used in the modeling, including summed acidity inputs, agricultural-lime alkalinity inputs, the resulting acid–base balance, SCEPTER input layers, and key SCEPTER output layers. These gridded model input and output products are the data most directly needed to interpret, verify, and reuse the main results presented here.

Referee #2 (Remarks to the Author):

The authors have carefully and effectively addressed earlier comments, and all but one revision item seem fine. The one exception is the new inclusion of biological nitrogen fixation (BNF) as a source of excess acidity. This deserves further explanation. It's true that BNF amplifies the cation imbalance normally in plant tissue, with subsequent effects on soil acidity, but only insofar as more base cations are removed from the system in harvest as compared to non-BNF crops (to put another way, less nitrate uptake means less OH exudation per unit of biomass protein). Acidification could also result from more nitrate's being leached from BNF crops (though this is unlikely and in any case leaching losses are already accounted for in the hydrologic modeling?). From a whole system standpoint, BNF should not in theory acidify the soil if all base cations are returned to the soil and there is no nitrate leaching. See, for example, Tang and Rengel 2003.

Whatever the case, it bears stating the source of BNF acidity explicitly with primary literature references, so that it's clear how BNF is calculated to affect basin wide acidity generation. There is presently no mention of BNF in Figure S19, which is intended to illustrate “all of the N cycle processes considered in this study,” so this is one of the places it needs to be included - in addition to the methods section where bnf acidity is listed but calculations not explained / justified.

Tang, C. and Z. Rengel. Role of plant cation/anion uptake ratio in soil acidification. pp. 57-81 In Handbook of Soil Acidity, Marcel Dekker.

We thank the reviewer for this helpful clarification and agree that plant growth and biomass removal can acidify soils through cation/anion imbalance, particularly where excess base-cation charge is removed in harvested biomass and not returned in residues, as discussed by Tang and Rengel (2003). However, this is distinct from the process quantified by our BNF term, and we apologize that this was not sufficiently clear.

We treat cultivation-associated BNF as an additional reactive-N input to agricultural soils. The revised Methods now explain explicitly how this N is converted to persistent

acidity: the fraction remaining after crop removal is estimated using $1 - \text{NUE}$, and only the fraction of the remaining N surplus that is ultimately leached as nitrate is assigned acidity. We assume that 80% of this surplus is leached, yielding a combined factor of approximately 0.25 for most of the record. Thus, while we assess this acidity source through an N lens rather than based on cation-anion imbalances, we do not assume that all BNF-derived N causes acidification.

We have also clarified that this reactive-N leaching pathway is distinct from the plant cation/anion-balance mechanism raised by the reviewer. The latter is acknowledged but not quantified because doing so at the MRB scale would require crop-specific historical information on tissue charge balance, biomass removal, residue return, and management practices that is unavailable consistently over the study period. Finally, Figure S29 now presents the full N-cycle and charge-balance framework, and Figure S30 shows the simplified parameterization applied to fertilizer, manure, SON mineralization, agricultural BNF, and atmospheric N inputs. We thank the reviewer for identifying where these explanations and figures required clarification.

There are multiple text sections where this has been clarified. The most important ones are:

Both agricultural BNF and mineralization of SON introduce additional reactive nitrogen into agricultural soils and can generate acidity through the same downstream nitrogen-cycle pathways considered for fertilizer and manure input^{36,61,62}. We define agricultural BNF as cultivation-driven fixation associated with leguminous crops and free-living fixation in agricultural soils above background natural BNF. This flux converts atmospheric N_2 into reduced organic/reactive N within the crop–soil system; following plant and microbial turnover, rhizodeposition, residue return, and mineralization, this N enters the soil inorganic N pool in a form that is functionally analogous to an added NH_4^+ /organic-N input. The acidifying component quantified here is the fraction of this reduced N that is ultimately nitrified to NO_3^- and leached from the system, such that nitrate export remains charge-balanced by proton production and/or retention in soils (see Figure S29 and Figure S30). We therefore treat agricultural BNF and SON mineralization as additional reactive-N inputs that can generate acidity through mineralization, nitrification, and nitrate leaching, rather than as direct acidity fluxes at the point of fixation or organic-N turnover. This treatment is deliberately distinct from the separate plant cation/anion-balance mechanism, whereby crops can acidify soils through net uptake and harvest export of base-cation charge in excess of anion charge³⁶. That mechanism is discussed below but is not quantified separately here.

For the MRB, SON- and BNF-derived N inputs are converted to acidity using the same stoichiometric framework as fertilizer and manure but with an additional term accounting for plant N removal and gaseous N losses. Because total N inputs are only weakly correlated with riverine N fluxes in the MRB⁴⁵, the amount of BNF- and SON-derived N assigned to persistent leaching-related acidity is estimated from the molar N input after accounting for nitrogen use efficiency and denitrification/degassing (eq. 10): (...)
Nitrogen use efficiency for the time series is based on published data from 1961-2012⁶⁴, where NUE is defined as the ratio of nitrogen removed in harvested crop products to total

nitrogen inputs to cropland (including fertilizer, biological fixation, and atmospheric deposition)⁶⁴. Values prior to 1965 are assumed to be constant at the 1961–1965 average. Based on a global analysis, we assume that on average, 80% of the nitrate not taken up by plants is ultimately leached and remains charge balanced by H^+ (i.e., fN surplus, leached)⁶⁵. The resulting value ((1-NUE)fN surplus, leached; ~0.25 for most of the record) is consistent for the fraction of total N watershed inputs that is transported in rivers⁴⁵. We therefore use it as a first-order estimate of the fraction of SON- and BNF-derived reactive N that remains charge balanced as acidity in topsoils.

The combined SON + BNF acidity fields provide a spatially explicit, first-order, century-scale representation of internal soil N cycling and its contribution to anthropogenic acidity inputs. We note that plant cation/anion balance represents an additional potential source of soil acidity⁶⁶, particularly where crops take up excess base cations relative to anions and biomass removal prevents the associated charge from being returned to soils. This mechanism is distinct from the reactive-N leaching term estimated here for BNF and SON that are mechanistically linked to the addition of N to surface soils. We do not quantify this cation-balance term separately because doing so robustly at the MRB scale would require crop-specific information on biomass removal, tissue charge balance, residue return, and management practices over the full historical period. Given the relatively small net excess cation charge in plant biomass compared with the N fluxes considered here, we assume this term is likely secondary. Based on the available data, we consider the approach used here to be a robust first-order representation of SON- and BNF-related acidity over century-scale MRB reconstructions.

Minor comments:

Line 72 – “for instance” could be “particularly”

Done.

L115 – could say “atmospheric deposition of acidity”

Done.

L140 – add “0–0.5 m depth)” after “topsoil”

Great idea, done!

L141 – add “(P)” after “precipitation-only”

Done.

L141 – add “(i.e., $P - P - ET$)” after “range”

This is a great clarification, done!

L178 – replace “P and P-ET” with “ $P - P - ET$ ”

Done.

L721 – SCEPTER, not SPECTER
Great catch! Thank you.

L1105 – “contain” could be “include”
Done.

L1108 – add “as well as” before “Raymond”
We have not made this change because this reference (e) signifies a different data source than the preceding (d), and adding “as well as” here makes it sound like ref (e; Raymond & Hamilton, 2018) was also used to constrain the data in (d).

L1123 – best to say “HCO₃ concentrations”
Done.

Fig. S2 – panel a units should be meq/L
Correct, we fixed this.

Fig. S5 – correct axis labels from “meq” to “meq/L”
Correct, we fixed this.

L1126 – best to say “in meq/L”
Done.

L1149 – CO₂-C sink strength
Done.

L1204 – “climate change” could be “of climate variability”
Okay.

L1225 – can delete “parameters”
Done.

L1234 – delete the colon?
Done.

Fig. S6 caption ends in an unfinished sentence
Fixed, thank you!

L1260 – replace “limestone” with “carbonate minerals” here and in following mentions
Done where appropriate (i.e., not when indicating that lime = 80% limestone, 20% dolomite)

L1319 – “of 0.5 m” could be “to 0.5 m”
Done.

L1349 – precipitation
Done.

L1353 – topsoils
Done.

L1380 – topsoils
Done.

We would like to once more thank the reviewer for their careful reading of the manuscript and for the constructive comments throughout the review process.

Referee #3 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.
We thank the reviewer for their effort.

Referee #4 (Remarks to the Author):

The authors have sufficiently addressed my previous comments regarding the role of biological activity (via BNF calculation), atmospheric inputs including wet deposition, and long-term storage of the carbon. It is not clear how the final estimates are changed by each modification, but in total the reported estimates of carbon sink have been revised but remain within the same magnitude as the original submission; and the main conclusions remain unchanged. The atmospheric deposition is treated rather phenomenologically, stating the model output variable rather than the way wet deposition is parameterized (which can vary by model). There are many uncertainties to the modeling of this process but admittedly is difficult to characterize; I do not think that another estimate would change the conclusion. Following this assessment, I can recommend that this manuscript can be published in its current form.

We thank the reviewer for their careful assessment of the revised manuscript and for recommending publication. We are grateful that the reviewer found that our revisions sufficiently addressed their previous comments regarding biological activity, atmospheric inputs, and long-term carbon storage.

We also appreciate the reviewer's point that the effects of the individual modifications are not fully separated in the revised estimates. The revisions introduced several additional terms and clarifications, including BNF, soil organic nitrogen mineralization, and updated treatments of wet and dry atmospheric deposition. While these changes affect the detailed partitioning of acidity sources and the exact magnitude of reconstructed fluxes, the revised estimates remain within the same order of magnitude as the original submission and do not change the main conclusion that agricultural liming has acted as a net carbon sink at Mississippi River Basin scale.

We agree that reconstructed atmospheric deposition remains uncertain and should be interpreted as a first-order basin-scale estimate. This uncertainty is included within the spatially explicit uncertainty layers for reconstructed N- and S-derived acidity inputs. In response to this concern and Reviewer 1's related comments, we propagated the resulting ± 1 SD acidity uncertainties through matched acidity-only and acidity-plus-lime SCEPTER simulations under both hydrological forcings. Perturbing the acidity inputs substantially affects absolute modeled CO₂ emissions, but most of this response occurs in both members of the matched counterfactual and therefore largely cancels when the effect of lime is calculated as their difference. When lime inputs are held constant, acidity uncertainty changes the estimated cumulative lime-associated sink by less than 1% under P forcing and approximately 4% under P–ET forcing. Moreover, liming remains cumulatively carbon-removing by 2015 across all hydrological and input-uncertainty scenarios evaluated, including the conservative out-of-phase cases. These analyses do not establish an exact magnitude, but demonstrate that the sign of the inferred liming effect is robust to the uncertainties considered.