
Supplementary information

Agricultural liming is a carbon sink in the Mississippi River Basin

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Supporting Information

Agricultural liming is a carbon sink in the Mississippi River Basin

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S1 River chemistry records and extended discussion

S1.1 Changes in river chemistry and strong acid weathering

In combination with published riverine alkalinity concentrations and water fluxes within the MRB^{1,2}, the data compiled here (**Figure S1**) can be used to investigate strong acid weathering. It is possible to assess the extent to which strong acids are involved in the dissolution of lime³ by comparing the concentrations of Ca^{2+} and Mg^{2+} to HCO_3^- (in meq/L; **Figure S2a**, see also Online Methods and **Extended Data Figure 1**). If $\text{Ca}^{2+} + \text{Mg}^{2+}$ concentrations were the same as HCO_3^- , all lime dissolution would occur due to reaction with carbonic acid³. Typically, HCO_3^- concentrations are lower, with the difference representing either loss of bicarbonate because of reaction with strong acids (cf., Supplement S2, eq. 15), or dissolution of lime with strong acids which produces $\text{Ca}^{2+} + \text{Mg}^{2+}$ but not HCO_3^- (cf., Supplement S2, equation 16). The difference between these concentrations may be used to estimate the fraction of lime dissolution that has occurred because of strong acid weathering ($f_{\text{strong acid}}$) as well as the CO_2 -sink strength³. Both measures are related, with the latter expressing the CDR impact of lime relative to the amount of carbon the lime itself contains (see Online Methods).

Previously, this approach has been pioneered by Hamilton et al. (2007) and applied for soil solutions, tile drainage, and stream water³. Here, we assume that this framework also applies to the Mississippi watershed for three reasons. First, ~58% of the catchment is covered with croplands⁴. Hence, overall riverine processes are heavily impacted by agriculture^{1,2,5-8}, facilitating the emergence of an agricultural liming signal. Second, although on catchment scale not only carbonate but also silicate and evaporite weathering clearly impact dissolved loads, including K and Na in the analysis (reflecting these lithologies) does not impact the observed trend in cation vs. HCO_3^- space (compare **Figure S2a** and **Figure S5a**). Third, weathering fluxes in the Mississippi catchment are generally dominated by carbonate weathering⁹, such that this framework would be expected to reflect carbonate weathering dynamics also on the catchment scale.

The reactions of strong acids with lime and bicarbonate (equations 14-16) can be visualized as vectors (vectors labeled 1-3 in **Figure S2a**), which allows us to qualitatively assess how the relative importance of the different reaction pathways has changed through time in the Mississippi watershed.

Compared to the year 1900, changes in the composition of Mississippi River water suggest that the reaction of carbonate minerals with strong acids (either through reaction eq. 16 or eq. 14+15) dominates the evolution of water chemistry up until ~1980. After 1980, the impact of strong acids has decreased while cation concentrations stay similar (reduction in equation 15), which also causes $f_{\text{strong acid}}$ to decrease below 1900 levels after ~2000. Measured values for the fraction of strong acid weathering ($f_{\text{strong acid}}$) are between 30-40% (CO_2 -sink strength of 20-40%) between 1954 and 1990 before they drop to ~20% (CO_2 -sink strength of 60-80%; **Figure S2**), indicating that carbonate weathering has been a CO_2 sink throughout the whole period. In terms of CO_2 -C sink strength, the values are consistent with measurements from agricultural streams for the pre-1990 period³ before increasing to more pristine values, demonstrating evolution into a more CO_2 -removing regime.

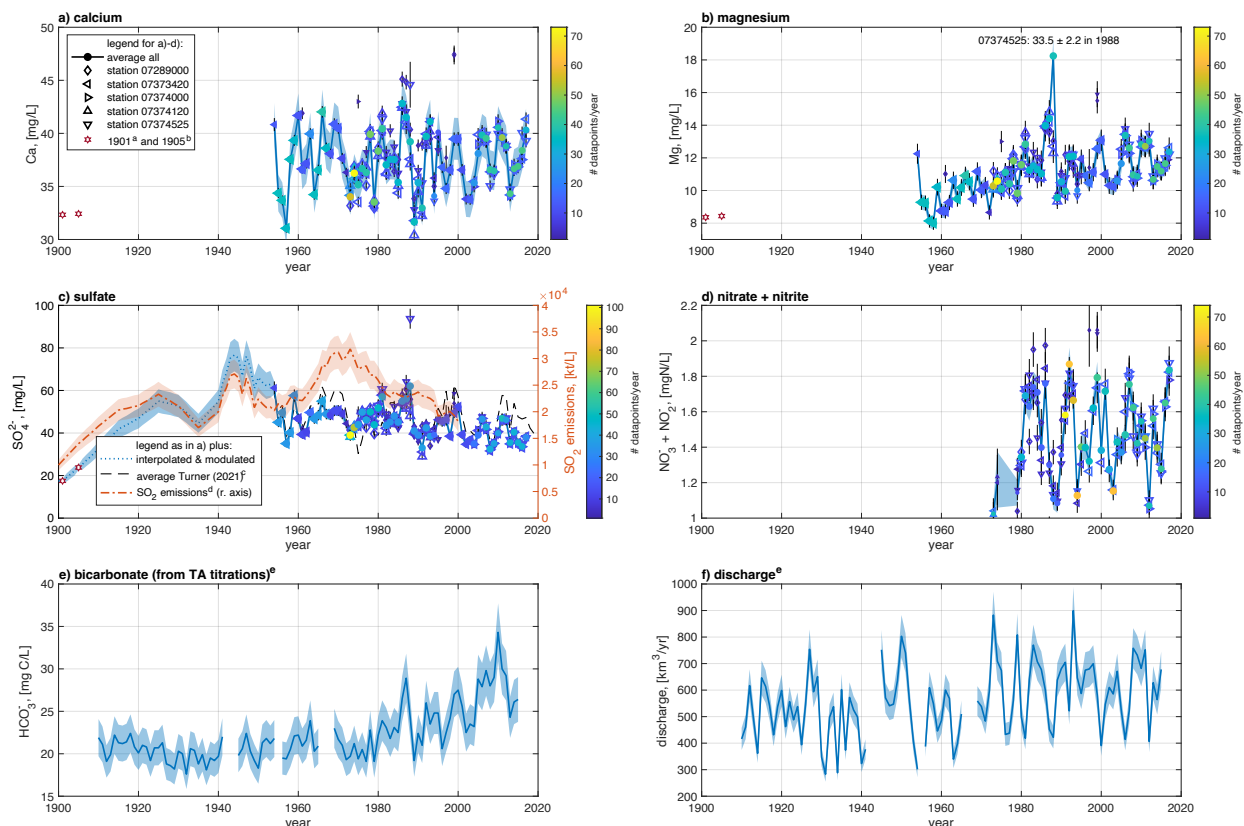


Figure S1: Average annual concentration of Ca (a), Mg (b), SO_4^{2-} (c), $\text{NO}_3^- + \text{NO}_2^-$ (d), HCO_3^- (e), and water discharge in the Lower Mississippi River. Calcium concentrations (a) show large interannual variability with no discernible trend (although discharge increases (f), suggesting an increase in annual fluxes). Magnesium concentrations (b) increase during the instrumental record while SO_4^{2-} concentrations (c) decrease. For the gaps in the record, SO_4^{2-} concentrations are interpolated and modulated by SO_2 emissions, suggesting increased concentrations in the 1940s, while, bounded by data from 1901¹⁰ and 1905¹¹, concentrations were low at the beginning of the 20th century. Nitrate and nitrite concentrations have a high variability with no discernible trend (d). Bicarbonate concentrations² increase after 1980 (e), similarly to discharge (f) though the discharge signal has a lower signal to noise ratio. Average flow-weighted concentrations in (a)–(d) are calculated from 5 USGS stations¹² in the Lower Mississippi (see **Figure 1** for locations), the data for each station and the average are shown, with marker size being proportional to the number of months with data within a year, and the color corresponding to the datapoints within a given year. Uncertainties in (a)–(d) were estimated by propagating the within-month variability in concentrations across the five stations, represented as 1 SD, together with an assumed 10% uncertainty in discharge. A minimum monthly concentration uncertainty of 5% was retained where the observed variability implied a lower value when propagating uncertainties to annual values. Bicarbonate concentrations (e) are derived from total alkalinity titrations, assuming that the majority of alkalinity is derived from HCO_3^- , and originate from the Sewerage and Water Board of New Orleans^{1,2}. Estimates of annual Mississippi discharge are derived from long records of 84 USGS sites and include discharge diverted into the Atchafalaya River¹. Uncertainties on HCO_3^- and discharge are assumed to be 10%. Note that all years shown on the x-axis in this figure and elsewhere correspond to calendar years. The annual average data across all stations presented in (a)–(d) are included in the Zenodo directory associated with this publication; data for panels (e) and (f) have been published previously (<https://doi.org/10.6084/m9.figshare.5753049>)².

^a Sewerage and Water Board (New Orleans, LA) (1903)¹⁰ ^b (Dole, 1909)¹¹ ^c Turner (2021)¹³ ^d based on data from Turner (2021), EPA and U.S. Census Bureau^{13–15} ^e Raymond & Hamilton, 2018²

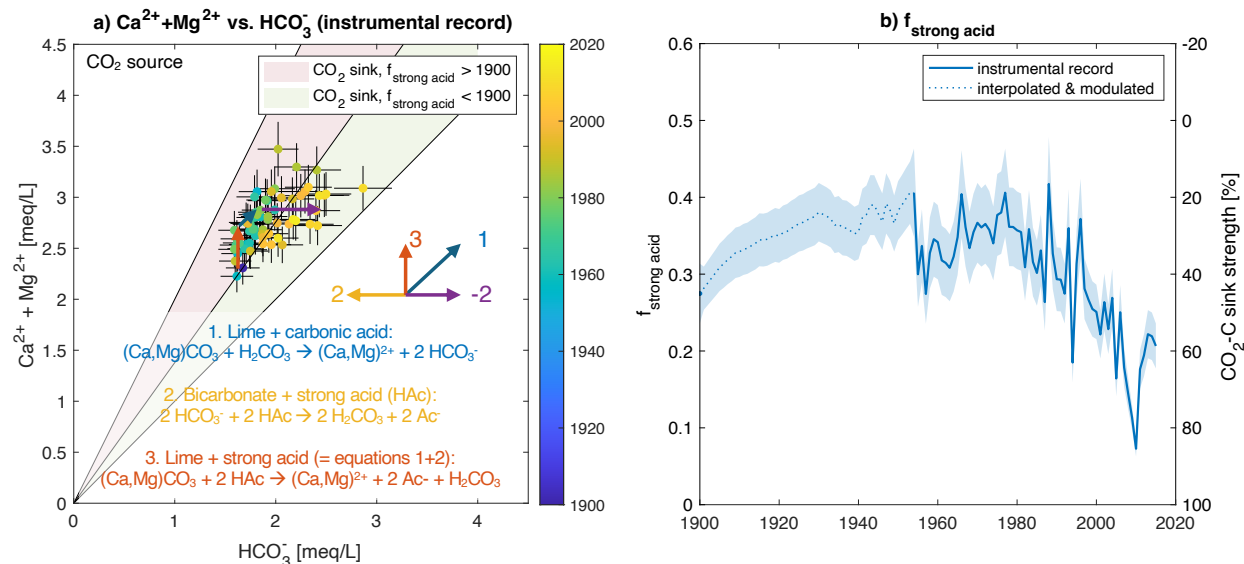


Figure S2: Panel a) shows how Ca+Mg and HCO₃⁻ concentrations changed over time (corresponding to the marker color). Marker colors correspond to the color bar shown in the figure, which indicates the year of observation. Error bars represent fully propagated uncertainties based on all relevant input parameters using 1000 Monte Carlo simulations. The data from all years fall into the CO₂ sink area as defined by [HCO₃⁻] > 0.5 * [Ca+Mg] (in meq/L)³. The vectors shown in the panel a refer to the effect that the reactions displayed in the bottom have in [Ca+Mg] vs. [HCO₃⁻] space, with -2 being the effective trend imposed by a reduction in the extent to which reaction 2 occurs. The trend observed over time is consistent with an increase in Ca+Mg concentrations being driven by reactions of lime with strong acid (process 3; panel a), and a reduction of strong acid weathering (reduction of reaction 2) at equal lime dissolution rates. As a result, before ~1980, the CO₂ sink strength was lower than in 1900 (<1900), but has increased over 1900 levels since then (>1900; lower f_{strong acid}, panel b). Including K and Na in the analysis (reflecting silicate and evaporite weathering) does not impact the observed trend in cation vs. HCO₃⁻ space (compare **Figure S5**). Panel b) shows the f_{strong acid} in the Lower Mississippi from 1900-2015. The fraction of strong acid for the post 1953 period is calculated based on the USGS cation data and published alkalinity/bicarbonate data^{1,2}. Between 1901-1953, it is interpolated between measured data points in 1900 and 1954 and modulated by changes in total acidity inputs (see methods). During the period constrained by instrumental records, the fraction strong acid is 30-40% between 1954 and the 1990s, when it starts dropping to below 20% in the years 2007-2012. CO₂-C sink strength³ (right y-axis panel b) essentially refers to the fraction of C in lime that is a CO₂ sink (positive values) or CO₂ source (negative values; see online methods).

Driven by both a lower fraction of strong-acid weathering and larger overall weathering fluxes, carbonate weathering today represents a stronger CO₂ sink in the MRB than it did in 1900. 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 years¹⁶, far exceeding both soil residence times and conventional carbon accounting horizons—which is the main reason carbonates can be effective for CDR on shorter timescales¹⁷. The decrease in f_{strong acid} partially driving this effect (and related increase in CO₂ C-sink strength) is primarily caused by decreases in acidity input, which is consistent with the decreased acidity input after 1970 (**Figure 2a, c**), the evolution in cation vs. carbonate alkalinity space (**Figure S2a**), and the fact that strong acid derived cation loads are correlated with riverine strong acid anions, with both decreasing over time (particularly SO₄²⁻; R²=0.52, **Figure S3**). At the same time, the increase in overall weathering

flux is likely driven by the increase in catchment wide liming starting in the late 1930s as the increase in cation fluxes is consistent with the amount of cations contained in the lime added to the Mississippi watershed. Post-1953 $\text{Ca}^{2+}+\text{Mg}^{2+}$ concentrations are ~21% higher than the 1900 value, which is similar to the fraction of $\text{Ca}^{2+}+\text{Mg}^{2+}$ added to the MRB via lime compared to total river $\text{Ca}^{2+}+\text{Mg}^{2+}$ fluxes (lime $\text{Ca}^{2+}+\text{Mg}^{2+}$ / river flux $\text{Ca}^{2+}+\text{Mg}^{2+}$).

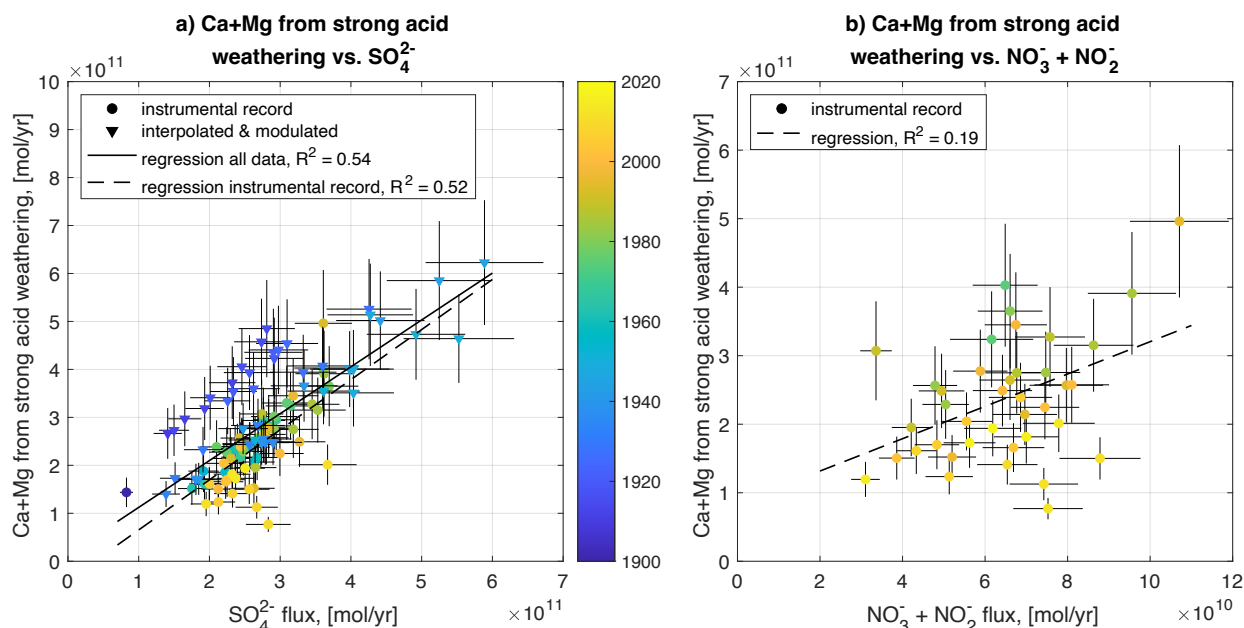


Figure S3: The flux of Ca+Mg driven by strong acid weathering (i.e., pseudo-cation flux * $f_{\text{strong acid}}$) has a high correlation with riverine SO_4^{2-} fluxes (panel b), suggesting the observed changes may be driven by changes in sulfuric acid inputs. The correlation with $\text{NO}_3^- + \text{NO}_2^-$ is lower ($R^2 = 0.19$, panel c), consistent with constant fertilizer oxidation at dropping $f_{\text{strong acid}}$.

The decrease in strong acid addition and increase in liming also have combined effects. The negative correlation between bicarbonate fluxes and $f_{\text{strong acid}}$ (**Figure S4**; $R^2 = 0.38$ for the instrumental record) suggests that the increase in bicarbonate export (**Figure S1e**) may be, among other factors^{1,2,5-8,13,18-20}, driven by reductions in CO_2 degassing due to lower acidity inputs. Furthermore, although ultimately forced by acidity inputs, the decrease of $f_{\text{strong acid}}$ is also impacted by lime addition simply because it increases both cation and bicarbonate fluxes, causing $f_{\text{strong acid}}$ to decrease. Collectively these strands of river-chemistry-based evidence are consistent with the notion that acidity addition drives CO_2 emissions, and that liming can be considered a CO_2 sink.

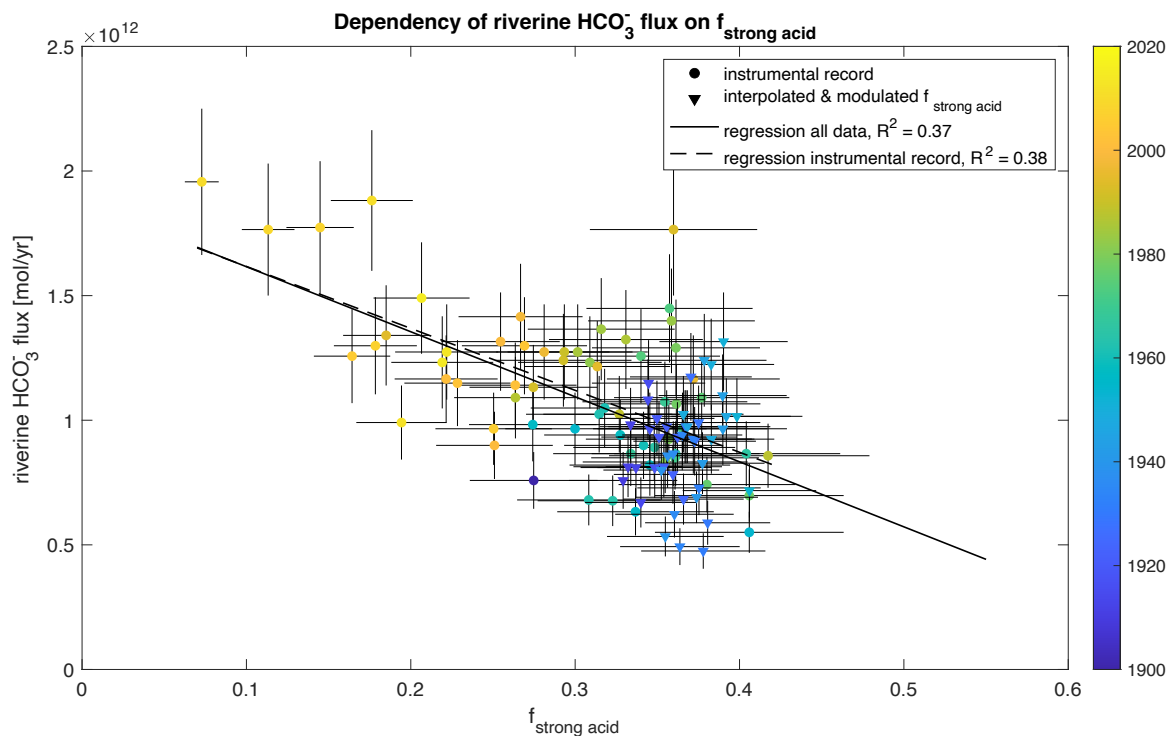


Figure S4: Riverine bicarbonate fluxes are negatively correlated with $f_{\text{strong acid}}$, which may indicate that at higher $f_{\text{strong acid}}$ some of the HCO_3^- is degassing as a result of reaction with H^+ derived from strong acids. Data based on the instrumental record is for the year 1900 as well as post-1953, while the period in between is based on the interpolated and modulated estimate of $f_{\text{strong acid}}$ as explained in the text. Error bars represent propagated uncertainties of all relevant input parameters, estimated using their individual uncertainty ranges and Monte Carlo simulations (1000 iterations).

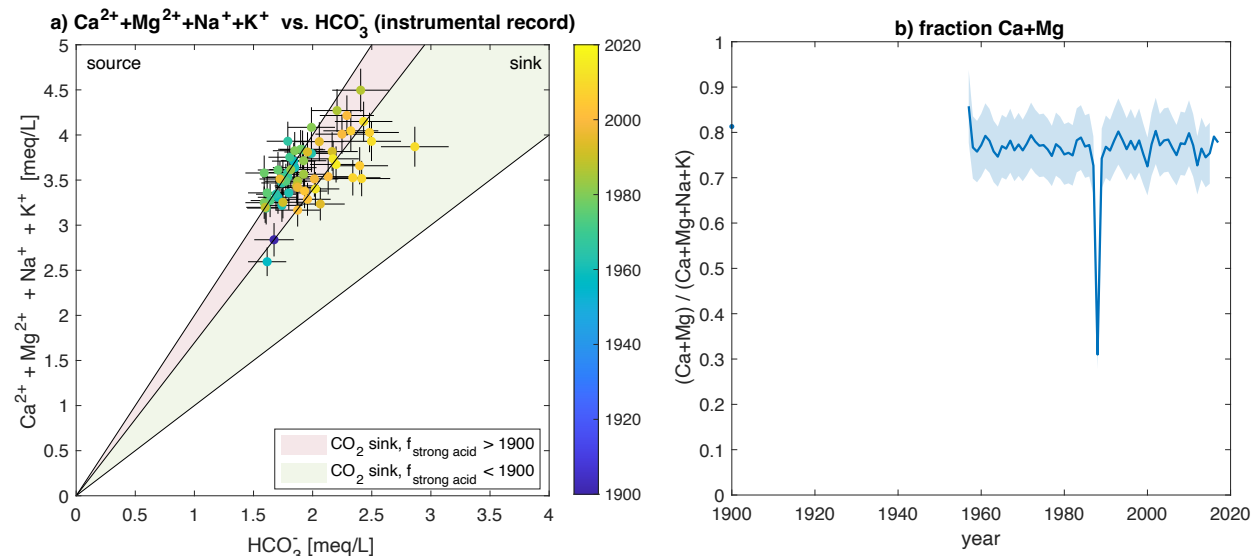


Figure S5: Panel (a) shows major cations vs. bicarbonate concentrations (in meq/L). Such plots but based only on Ca+Mg are commonly used to gauge the fraction of strong acid weathering or the carbon sink strength of lime dissolution³, which is shown in **Figure S2**. Marker colors correspond to the color bar shown in the figure, which indicates the year of observation. The version shown in panel (a) in addition also includes K+Na concentrations on the y-axis, demonstrating that the overall trends are equivalent in terms of an initial increase of cation concentrations followed by a recovery of HCO_3^- concentrations due to decreases in acidity pollution (**Figure S2a**). Because the sum of Ca+Mg+Na+K is by definition higher than the sum of Ca+Mg, values are shifted to higher y-axis values, i.e., higher $f_{\text{strong acid}}$ and lower carbon sink strength (it is a stronger relative C source compared to just using Ca+Mg). Panel (b) shows the fraction of Ca+Mg relative to Ca+Mg+Na+K (in meq/L), which has stayed constant from 1960 to 2016 at ~ 0.775 , likely because overall weathering fluxes are dominated by carbonate weathering overall⁹. The low value in 1988 is the result of anomalously high Na concentrations. These high concentrations were only observed at station 07374525, and not at stations 07373420 and 07289000 which also have data in this year (although less datapoints) and is therefore likely the result of local pollution.

S1.2 Calculation of excess alkalinity export and conversion to lime-CDR equivalents

To quantify excess riverine alkalinity export, we used published annual MRB bicarbonate-carbon flux estimates² and calculated the mean pre-liming flux for all available years ≤ 1934 as the baseline. Annual excess flux was then defined as the difference between each post-1934 annual flux and this baseline, and cumulative excess flux was calculated as the cumulative sum of annual excess values. Because the published record contains several missing years after the start of the analysis period, we generated a gap-filled version in which missing post-baseline years (1942–1944, 1955, and 1966–1968) were filled by interpolation between the mean of the three nearest observed years before and after each gap. Because years adjacent to data gaps generally have flux values comparable to baseline fluxes, this gap filling had negligible influence on the inferred annual and cumulative excess fluxes compared with omitting these years (**Figure S6**).

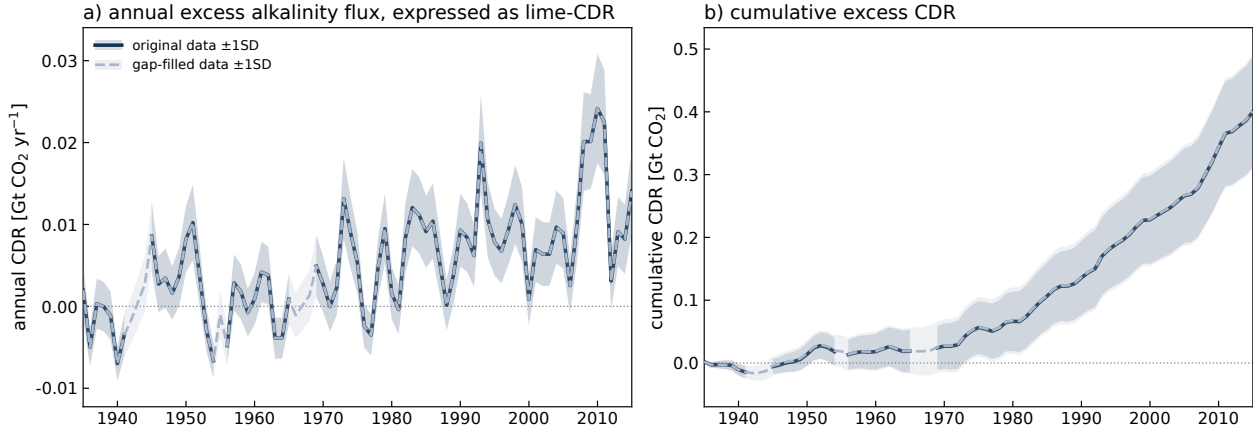


Figure S6: Sensitivity of riverine CDR estimates to gap filling in the published bicarbonate-flux record². Panel (a) compares annual excess alkalinity export expressed in lime-CDR equivalents calculated from the original annual bicarbonate-flux record and from a gap-filled version in which missing post-baseline years were interpolated. Panel (b) shows the corresponding cumulative excess CDR. Lines show estimates derived from the primary flux data, and shaded areas indicate ± 1 SD from the Monte Carlo/bootstrap uncertainty analysis. Gap filling has negligible influence on the inferred annual or cumulative riverine CDR.

Uncertainty in excess alkalinity export was estimated using a combined Monte Carlo and bootstrap approach. For each annual flux value, synthetic realizations were generated assuming a relative one-standard-deviation uncertainty of 15%. For each realization, baseline values were resampled with replacement from the synthetic pre-1935 baseline period, and annual and cumulative excess fluxes were recalculated. This procedure was repeated 1000 times, and the mean and standard deviation across realizations were used to characterize uncertainty. Excess bicarbonate-carbon fluxes were converted to lime-CDR equivalents by converting Tg C to GtCO₂ using molar masses and multiplying by 0.5, reflecting the stoichiometric assumption that half of the excess bicarbonate carbon is derived from atmospheric CO₂ and half from carbonate minerals. The python code used for this analysis is contained in the Zenodo directory associated with this publication.

S1.3 Estimating the impact of changes in natural background weathering

Because multi-decadal changes in riverine alkalinity can arise not only from liming but also from natural, climate-driven variability in background weathering, we explore a climate-adjusted baseline correction using a baseline-normalized, linearized scaling derived from the climate-sensitive reaction-rate terms in West (2012)²¹. Because MRB discharge is strongly modified by tile drainage, irrigation, reservoirs, changes in crop type grown, and urban development^{1,2,7,22}, and therefore does not necessarily scale proportionally with weathering reaction supply, we estimate impacts of climate variability on weathering rates primarily based on precipitation as well as precipitation minus evapotranspiration to bracket the potential sensitivity of background weathering to changes in water availability (though we also show the correction based on river runoff; Q). A pre-impact baseline period (years < 1935) is used to estimate baseline precipitation (P, precipitation minus evapotranspiration P-ET, and river discharge Q), and temperatures (T, in K). For each year $t \geq 1935$, we compute a West-style climate scaling factor ($S(t)$; see **Figure S7a**):

$$S(t) = \frac{X(t)}{X_{base}} e^{\frac{E_a}{R} \left(\frac{1}{T_{base}} - \frac{1}{T(t)} \right)} \quad (\text{Eq. 13})$$

with R being the universal gas constant and E_a effective activation energy (assumed as 45 kJ mol^{-1}) and X the considered water input term (P , $P-ET$, and Q , respectively). Missing annual Q values after 1935 were linearly interpolated between the nearest available annual discharge observations. Because Q is included only as a secondary sensitivity scenario, this gap filling does not affect the primary P - or $P-ET$ -based results.

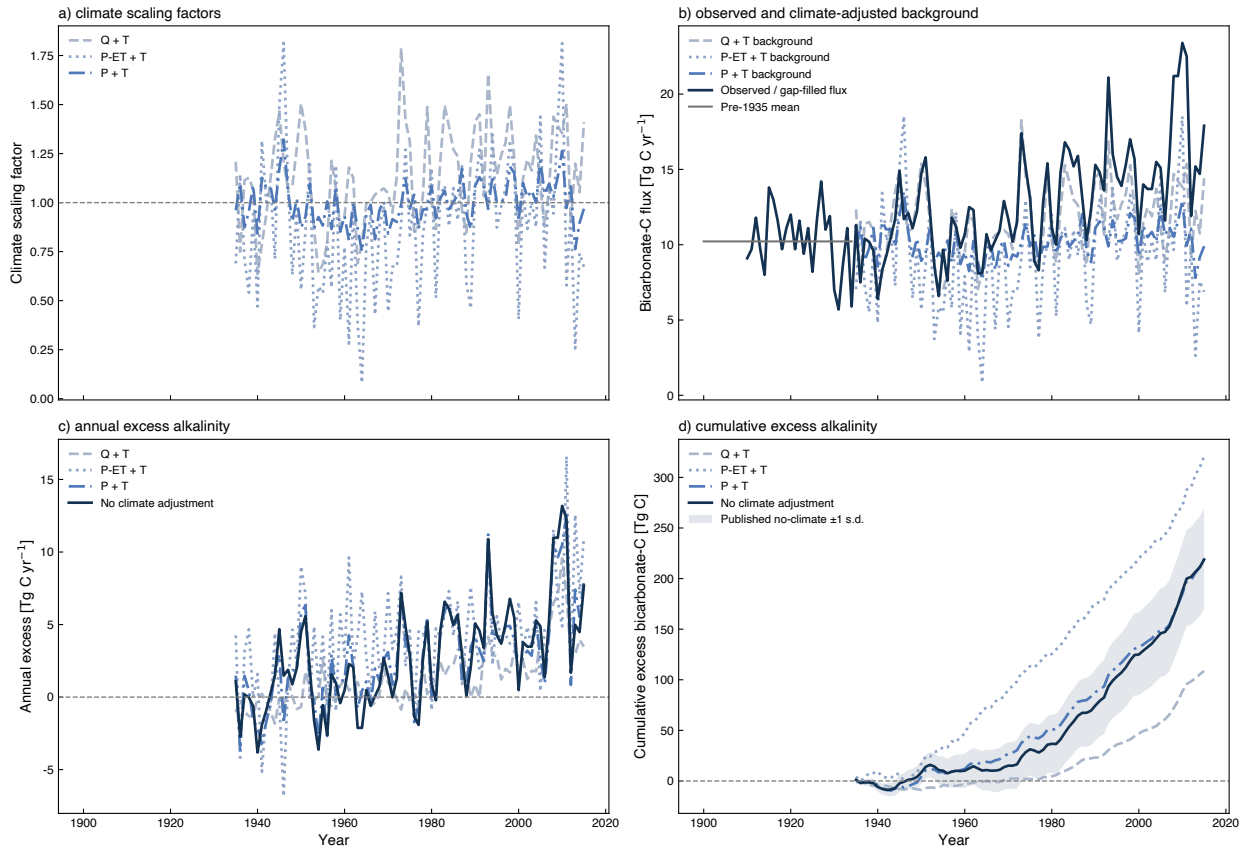


Figure S7: Sensitivity of estimated excess riverine alkalinity export to climate-driven variability in background weathering. a) Annual baseline-normalized scaling factors calculated using $P + T$, $P-ET + T$, and $Q + T$. b) Climate-adjusted background bicarbonate-associated carbon fluxes and the observed MRB bicarbonate-associated carbon flux. c) Annual observed flux in excess of each climate-adjusted background. d) Cumulative excess flux relative to each dynamic baseline and to the unadjusted pre-1935 baseline. The $P + T$ and $P-ET + T$ scenarios are treated as the primary climate-sensitivity cases. The $Q + T$ scenario is shown as a secondary comparison because long-term discharge is affected by drainage, irrigation, reservoirs, land-use change, urbanization, and river management and therefore may not scale directly with natural background weathering.

Equation 13 represents a first-order, baseline-normalized approximation to the climate-sensitive terms in West (2012). Specifically, the West runoff term $1-\exp(-k_w Q)$ is approximated as proportional to water input, which applies when $k_w Q$ is small; using West’s best-fit k_w , retaining the exact baseline-normalized hydrologic term changed the cumulative excess estimates by less than 1% for all three hydrologic proxies. The total background weathering flux is assumed to vary proportionally with the climate-dependent reaction-rate term. We do not implement the outer weathering-flux saturation term or explicitly model denudation, weathering-zone thickness,

mineral supply, or other non-climatic controls. The calculation is therefore interpreted only as a sensitivity test of potential changes in background weathering driven by hydroclimate. In applying this scaling, we assume that non-climatic controls on background weathering, including catchment lithology, weathering supply, regolith structure, and effective reaction-zone properties, do not vary systematically between the baseline period and year t . Under this simplifying assumption, temporal variability in background weathering is represented only through changes in water input, approximated here using primarily precipitation or $P-ET$, and temperature. The resulting correction should therefore be interpreted as a sensitivity test for climate-driven variability in baseline weathering, rather than as a full reconstruction of changes in weathering supply, hydrologic routing, erosion, or critical-zone structure. MRB wide annual average precipitation, evapotranspiration and temperature was calculated based on PRISM data with a 4 km resolution²³.

This factor is used to calculate annual baseline alkalinity fluxes that are adjusted for variation in climate (**Figure S7b**). Excess alkalinity as well as cumulative excess alkalinity fluxes are calculated relative to this dynamic baseline (**Figure S7c and d**). Estimates of excess riverine bicarbonate fluxes in terms of lime-driven CDR are calculated assuming that the excess alkalinity derives from carbonate dissolution, and that half of the released bicarbonate carbon originates from the atmosphere and half from the mineral phase.

The magnitude and direction of the climate sensitivity depend strongly on the hydrologic variable used to scale background weathering. Scaling with $P-ET$ yields a mean climate factor of 0.877 over 1935–2015 and increases estimated cumulative excess export from 0.401 to 0.588 GtCO₂ when expressed in lime-CDR terms, an increase of approximately 47%. In contrast, scaling with precipitation and temperature gives a mean factor of 1.000 and produces almost no change in cumulative excess export (0.402 GtCO₂; <1% difference from the unadjusted estimate). Scaling with river discharge and temperature gives a mean factor of 1.133, increasing the inferred background flux and reducing cumulative excess export to 0.199 GtCO₂, approximately 50% below the unadjusted estimate. The Q-based result must be interpreted cautiously because discharge is influenced by drainage, irrigation, reservoirs, land-use change, and river management in addition to climate.

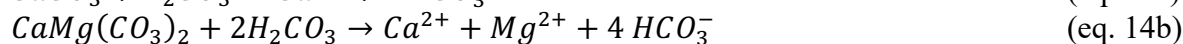
Although the direction and magnitude of the climate correction depend on the hydrologic proxy used, none of the assessed scenarios fully explains the observed increase in riverine alkalinity export through hydroclimate-driven changes in background weathering alone. Instead, the correction defines an envelope of plausible climate effects. While hydroclimate variability can influence the estimated baseline and contributes to uncertainty in the magnitude of excess alkalinity export, the long-term increase in riverine alkalinity fluxes still requires additional drivers such as agricultural lime addition. Because the direction and magnitude of the correction depend strongly on methodological choices, we treat the climate-adjusted estimates explored here as a sensitivity analysis rather than implementable correction factors. Accordingly, main-text **Figure 3b** and the associated discussion are based on excess riverine alkalinity fluxes calculated relative to the unadjusted pre-1935 baseline; the uncertainty shown for this central estimate reflects propagated measurement and baseline uncertainty but does not include additional uncertainty from potential climate-driven changes in background weathering.

Furthermore, we explicitly note that, in this framework, we cannot fully partition increases in non-lime carbonate weathering that are themselves driven by strong-acid inputs (e.g., fertilizer- and deposition-derived acidity, see Supplement S4). Such acid-enhanced dissolution of native carbonates would also contribute to riverine alkalinity export, although this effect is likely minor (see Supplement S4). Nevertheless, our analysis is not strictly causal with respect to lime being the only factor driving increases in MRB alkalinity fluxes, and we interpret the agreement between river-flux and reactive-transport estimates as convergence rather than exact attribution. Instead, the river record shows an excess alkalinity export comparable to the modeled alkalinity release resulting from liming in the SCEPTER simulations. This convergence indicates that the basin-scale hydrologic system effectively exports the soil acid–base perturbation on multi-decadal timescales, while not demonstrating that liming is the sole cause of the observed riverine trend.

S2 Acidity as a driver of CO₂ emissions from agriculture

This section provides the chemical basis for the central counterfactual used in the main text: CO₂ emissions from soil and riverine acid–base reactions are driven by the reaction of acidity with bicarbonate alkalinity, whereas lime addition changes the amount and source of alkalinity available to neutralize that acidity.

Carbonate dissolution in soils consumes acidity. Depending on soil conditions, dissolution may be driven predominantly by carbonic acid—particularly at pH values above approximately 5–6²⁴—or by stronger acids, including nitric and sulfuric acid^{3,5}. With carbonic acid (H₂CO₃), calcite or limestone (CaCO₃) and dolomite (CaMg(CO₃)₂) react to produce bicarbonate (HCO₃[−]) and dissolved Ca²⁺ and Mg²⁺.

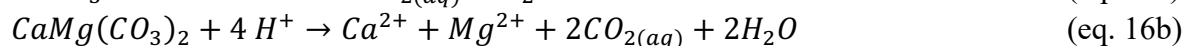


In the presence of protons derived from strong acids, bicarbonate alkalinity neutralizes acidity, shifting carbonate-system speciation toward dissolved CO₂ and potentially driving CO₂ degassing:



At circumneutral pH, where bicarbonate is the dominant component of carbonate alkalinity, titration of one mole of bicarbonate by one mole of H⁺ generates approximately one mole of dissolved CO₂. If this CO₂ subsequently equilibrates with the atmosphere during soil and river transport, up to approximately one mole of CO₂ may be emitted per mole of H⁺ added.

Alternatively, calcite and dolomite in soils can react directly with protons derived from strong acids, producing dissolved Ca²⁺ and Mg²⁺ and converting carbonate carbon to dissolved CO₂, which may subsequently degas. The corresponding strong-acid anions remain in solution but are omitted from the reactions for clarity:



Equations 14–16 illustrate why lime addition and carbonate dissolution alone is not a sufficient basis for attributing CO₂ emissions. Carbonate dissolution by carbonic acid generates bicarbonate alkalinity, with half of the resulting dissolved inorganic carbon derived from atmospheric or soil CO₂. In contrast, protonation of bicarbonate by stronger acids shifts the carbonate system toward carbonic acid and CO₂, converting pre-existing alkalinity into a potential atmospheric CO₂ source. The extent to which this process leads to net CO₂ release depends on carbonate-system equilibrium, soil *p*CO₂, pH, and hydrologic export²⁵. Nevertheless, the underlying driver of CO₂ generation is the input of acidity and its reaction with bicarbonate alkalinity or carbonate minerals, rather than the presence of lime itself.

This distinction is obscured in conventional lime-based accounting frameworks. Direct reaction of carbonate minerals with strong acids, as represented by equations 16a and 16b, provides a stoichiometric endmember under which carbonate carbon is released as CO₂. The default IPCC

approach effectively applies this endmember by assuming that all carbon contained in applied lime is emitted to the atmosphere²⁶. In contrast, U.S. national GHG reporting applies a lower emission factor, assuming that approximately half of the carbon in carbonate soil amendments is emitted as CO₂. Previous work similarly suggests that liming can range from a net CO₂ source to a net sink depending on the balance among carbonate dissolution, acidity neutralization, and bicarbonate export^{3,5,27,28}.

However, assigning emissions to lime inputs alone applies an incomplete counterfactual. If anthropogenic acidity were added without agricultural lime, that acidity would still react with native alkalinity pools, including bicarbonate in pore waters, naturally occurring carbonates, and alkalinity generated by mineral weathering, producing CO₂ even in the absence of liming²⁹. Lime addition changes the amount and source of alkalinity available to neutralize this acidity; it does not by itself define whether the system is a net CO₂ source or sink. Consequently, the relevant carbon-budget question is whether lime-derived alkalinity increases or decreases CO₂ emissions relative to the counterfactual scenario with anthropogenic acidity but without lime addition. This chemical framing underlies both the acid–alkalinity inventory discussion in Supplement S5 and the counterfactual reactive-transport simulations discussed in the main text, where our analysis shows that lime addition reduces CO₂ emissions relative to a counterfactual scenario with anthropogenic acidity inputs but no agricultural liming.

S3 Reactive transport model details (SCEPTER)

S3.1 SCEPTER set up

SCEPTER^{30–32} is spun up for $1^\circ \times 1^\circ$ grid cells for the US considering a soil depth of 0.5 m. The initial and spin-up boundary conditions for the reactive transport code are based on a variety of gridded data products, including runoff/infiltration³³, mean annual air temperature³⁴, aboveground net primary productivity (NPP)³⁵, soil organic matter (SOM)³⁶, topsoil pH³⁶, soil cation exchange capacity (CEC)³⁷, and soil base saturation³⁸. SCEPTER is initialized by tuning four key parameters:

1. a reference soil cation exchange coefficient ($K_{H/Na}$)
2. dissolved Ca^{2+} concentration at the upper boundary, representing carbonate weathering and agricultural liming
3. input of soil organic carbon (J_{org})
4. soil organic carbon (SOC) turnover time (τ_{org}).

These parameters are adjusted to reproduce four site-specific observational parameters: soil pH, soil base saturation, soil organic carbon content, and soil pCO_2 , which is estimated from soil temperature and net primary productivity³⁹. The model is forced by other boundary conditions, such as runoff and air temperature. Before start of the simulations, the model is spun up for 10^5 years to ensure processes are initially at steady state. 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). 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. There are locations where the model failed to initialize through the tuning/spinup procedure described by Kanzaki et al. (2025)³² (~5 sites out of 468 cropland sites with $>10\%$ cropland and ~20 sites out of all CONUS 825 sites) and these were excluded from the analysis here. SCEPTER outputs shown were derived from time-integrated fluxes (i.e., mass transfer fluxes through transport and reaction integrated across all time steps taken by the SCEPTER from the initialization up to any given prescribed timestamp for output-recording) because these avoid losing numerically solved mass-transfer information between the prescribed output timestamps. Where annual fluxes are shown, they are calculated as the difference between time-integrated fluxes in adjacent years.

We transfer the acidity and alkalinity fluxes into the Mississippi River catchment (**Figure 2**) into corresponding mass fluxes for each grid cell (see **Figure S20** to **Figure S25**). The fraction of N pollution that remains as acidity pollution (i.e., leaches from soils, see online methods and **Figure S29**) 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 (or any other N-component considered here), 1 mol of acidity is released per mol of N over the relevant system boundaries. Lime is introduced in the model as a 80:20 (by mass) mix of $CaCO_3$ and dolomite $CaMg(CO_3)_2$. SO_2 pollution is inserted into the model domain as H_2SO_4 . Example outputs of spatially explicit model outputs are shown in **Figure S8** (acidity only), **Figure S9** (acidity + lime, showing that some pixels become net- CO_2 sinks over time even without considering the acidity-only counterfactual scenario), and **Figure S10** (acidity-only minus acidity-plus-lime; positive values indicate a net CO_2 -removal effect of lime). All annual output layers including data for P simulations can be found in the linked Zenodo directory.

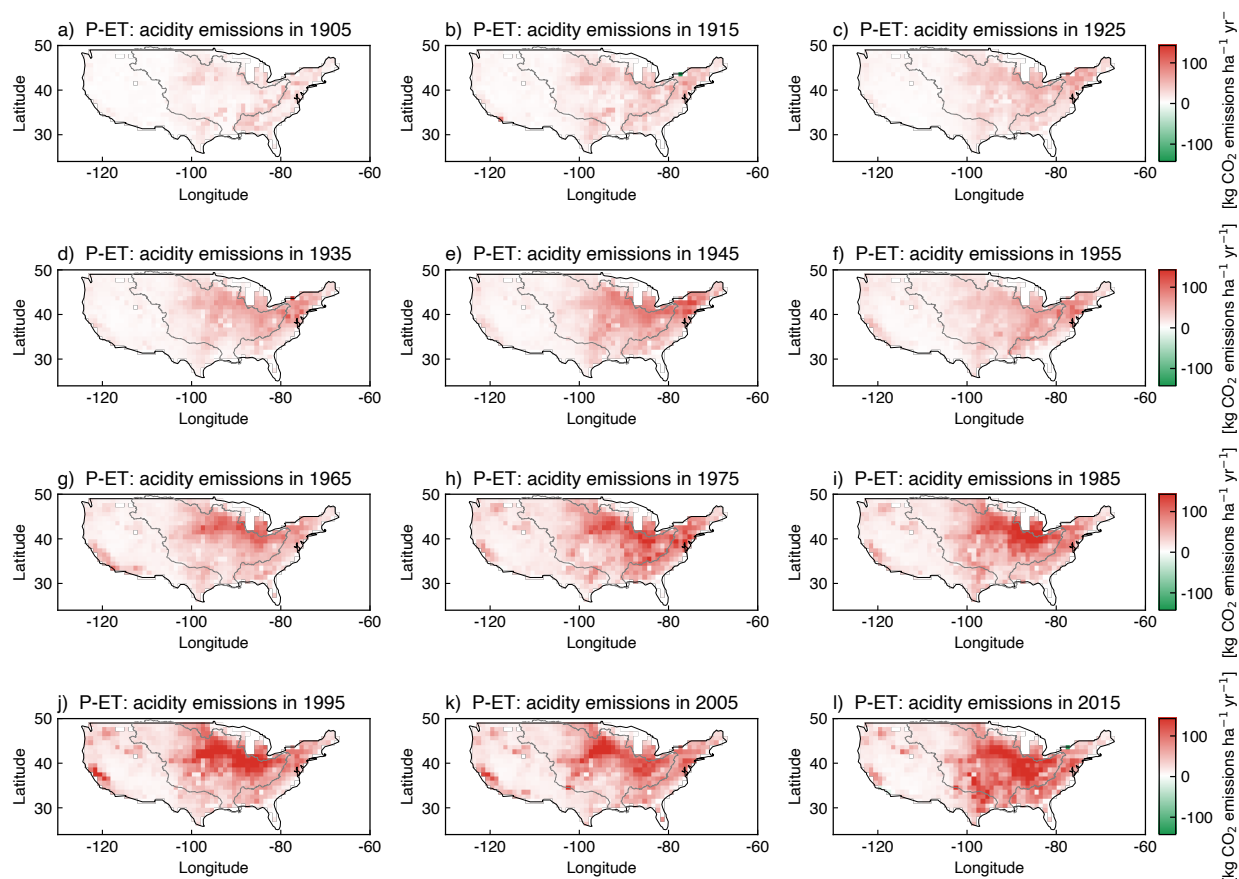


Figure S8: Area normalized CO₂ emissions for SCEPTER P-ET simulations considering only acidity inputs, no lime. Outputs are converted to kg CO₂ emissions ha⁻¹ yr⁻¹ from SCEPTER outputs in eq m⁻² yr⁻¹, with the eq corresponding to mol H reacting with HCO₃⁻, assumed to produce CO₂ at a 1:1 molar ratio.

We suppress carbonate precipitation in the SCEPTER runs because (1) there is considerable uncertainty for the threshold oversaturation required for such precipitation to occur⁴⁰; (2) SIC formation as a response to agriculture predominantly occurs in arid and semi-arid regions⁴¹, i.e., not the corn belt where most of the lime inputs occur (**Figure S20**); and (3) that studies in the Corn Belt and adjacent agricultural regions document substantial dissolved inorganic carbon and soil inorganic carbon losses through drainage^{42,43}. 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.

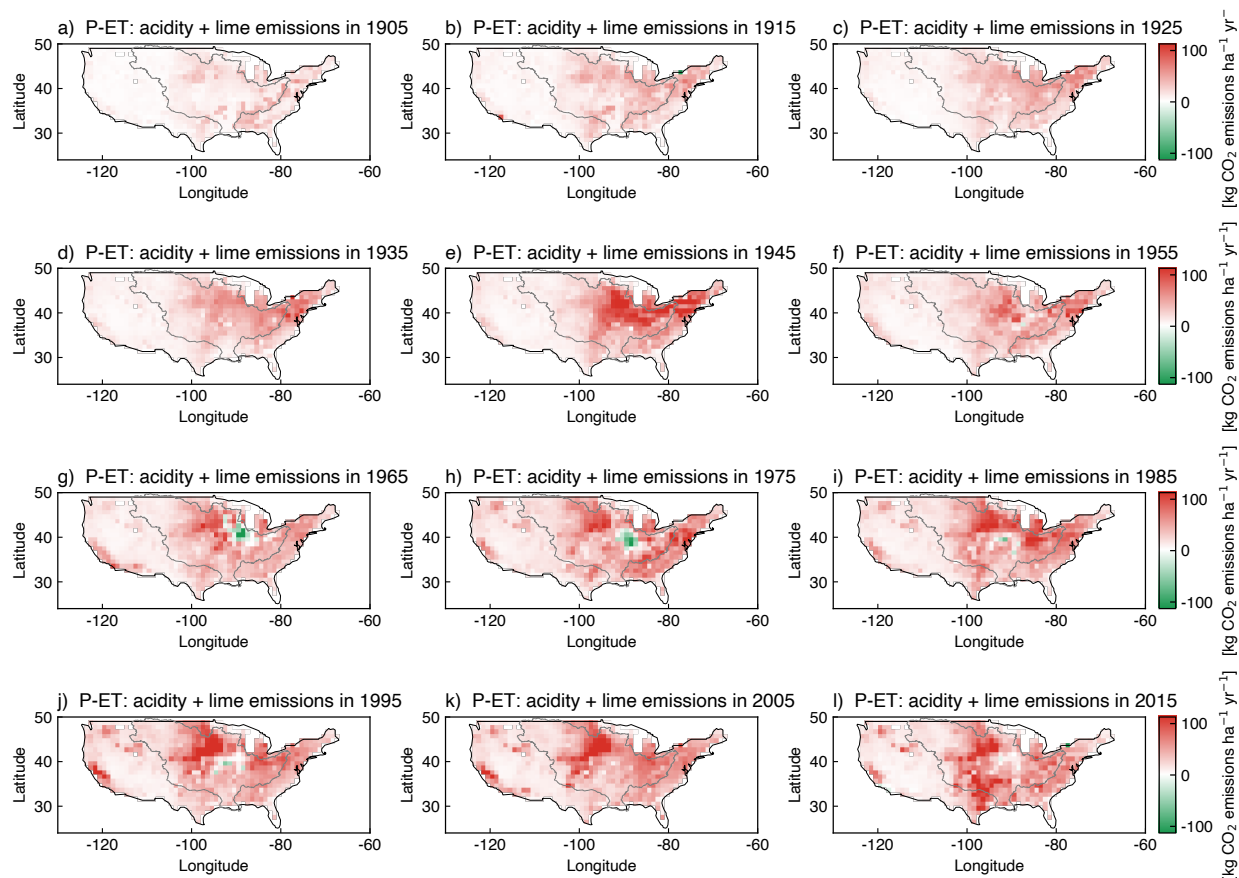


Figure S9: Area normalized CO₂ emissions for SCEPTER P-ET simulations considering acidity and lime inputs. Outputs are converted to kg CO₂ emissions ha⁻¹ yr⁻¹ from SCEPTER outputs in eq m⁻² yr⁻¹, with the eq corresponding to mol H reacting with HCO₃⁻, assumed to produce CO₂ at a 1:1 molar ratio.

Note that we compare SCEPTER-derived solute fluxes at the lower boundary of the 0.5-m soil columns directly with riverine fluxes and do not explicitly simulate groundwater transport. As acknowledged in the main text, estimated MRB-wide groundwater residence times are on the order of ~10 years⁴⁴ and are therefore shorter than the uncertainty ranges associated with both the SCEPTER-derived and empirically inferred riverine lag times.

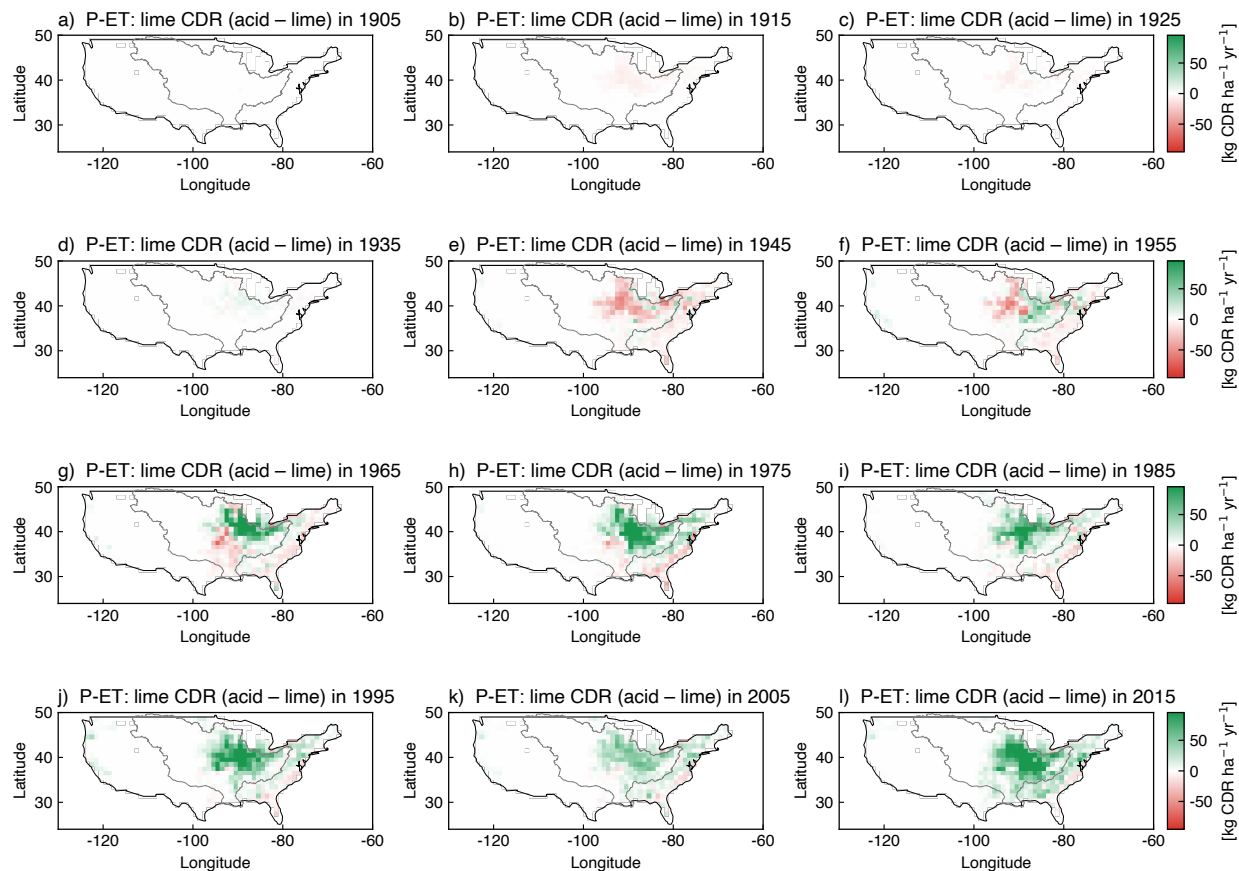


Figure S10: Area-normalized CO₂ removal in the SCEPTER P-ET simulations, calculated as CO₂ emissions in the counterfactual acidity-only scenario minus those in the acidity-plus-lime scenario, thereby isolating the effect of liming. Positive values correspond to a decrease in emission due to lime addition. SCEPTER outputs in eq m⁻² yr⁻¹ were converted to kg CO₂ emissions ha⁻¹ yr⁻¹, with one equivalent representing one mol H⁺ reacting with HCO₃⁻, assumed to produce CO₂ at a 1:1 molar ratio.

S3.2 Temporal dynamics of cation exchange processes in SCEPTER simulations

The temporal dynamics of proton and base-cation exchange with the soil cation exchange complex are strongly land-use history-dependent (**Figure S11**). In the acid-only simulations, representing the counterfactual case with anthropogenic acidity inputs but no agricultural liming, cation exchange acts as a persistent proton sink and base-cation source. In this case, added protons increasingly exchange onto CEC sites and displace base cations into solution, although the magnitude of this sink changes through time. The acidity sink strengthens during periods of increasing excess acidity inputs (see main-text **Figure 2a**), because additional proton loading drives the exchange complex further from equilibrium and promotes the replacement of base cations on exchange sites by protons. By contrast, when excess acidity inputs remain relatively stable, the sink gradually weakens as proton–cation exchange approaches a new quasi-equilibrium.

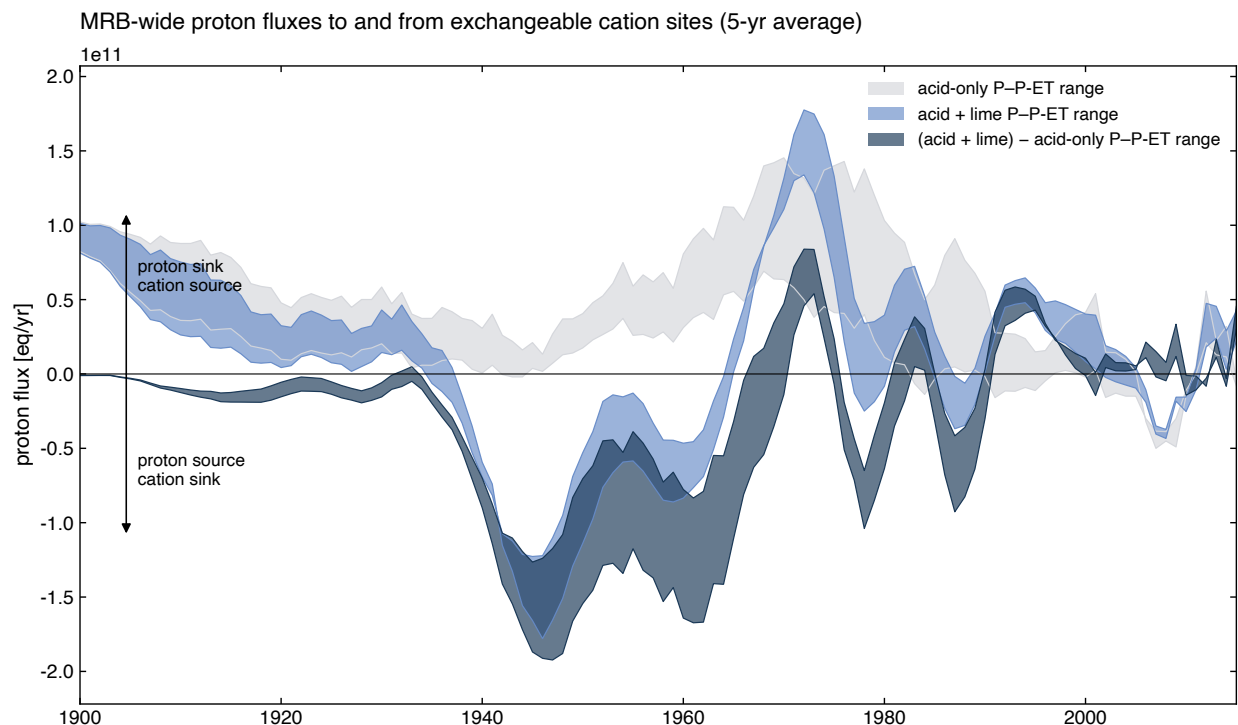


Figure S11: Five-year running mean of simulated proton fluxes onto cation exchange sites in the MRB. Shaded ranges show simulations forced by acid inputs only, acid + lime inputs, and the difference between acid + lime and acid-only simulations, with bounds defined by P- and P-ET-based SCEPTER flux estimates. Positive values indicate net proton uptake by the CEC and base-cation release, whereas negative values indicate net proton release and base-cation retention. Annual values show greater year-to-year variability because of changes in the imposed inputs, but the overall temporal trends are unchanged; five-year running means are therefore shown to improve visual clarity.

In the acid + lime simulations, lime application alters both the direction and magnitude of exchange fluxes. As liming begins at scale in the late 1930s, it releases base cations to soil pore waters and reduces, or locally reverses, the prevailing acidity–alkalinity imbalance. These base cations exchange onto CEC sites and displace previously stored protons, causing the exchange complex to act as a net proton source and base-cation sink for approximately three decades. This response is particularly pronounced after roughly 35 years of elevated excess acidity inputs, during which substantial legacy acidity had accumulated on exchange sites. The simulations therefore illustrate a counterintuitive non-steady-state effect: alkalinity addition through liming can transiently increase proton release to pore waters by mobilizing legacy acidity stored on the exchange complex. This transient release of legacy acidity also affects the CO₂ balance: by consuming bicarbonate and shifting dissolved inorganic carbon toward CO₂, it can generate a temporary pulse of CO₂ emissions (see discussion in the main text). In the 1960s, liming rates remain relatively constant while acidity inputs increase, causing the exchange flux to reverse and the CEC to become a proton sink once again. From approximately 1980 onward, exchange fluxes approach a near-steady state, consistent with the subsequent period of comparatively stable excess acidity inputs.

The difference between the acid + lime and acid-only simulations isolates the effect of liming on exchange reactions. This difference is predominantly negative, indicating that lime addition shifts the exchange complex toward greater base-cation retention and proton release relative to the acid-only counterfactual. Consistent with earlier findings, this implies that part of the lime-derived

cation flux is temporarily stored on exchange sites that had been progressively acidified since the start of the simulations³². These CEC dynamics contribute to the lag between lime application and downstream alkalinity export, because some lime-derived base cations are initially retained in soils while legacy exchangeable acidity is released. Toward the end of the record, the liming effect approaches a near-steady state, reflecting equilibration between the composition of the exchange complex and the relatively stable magnitude and spatial distribution of excess acidity and alkalinity inputs.

S3.3 Uncertainty propagation within SCEPTER simulations

The main-text figures represent uncertainty in the SCEPTER simulations using two alternative hydrological parameterizations, precipitation (P) and precipitation minus evapotranspiration (P–ET). These scenarios bracket a plausible range of water availability for reaction with lime in surface soils. Here, we examine how uncertainty in the reconstructed acidity and alkalinity inputs propagates into the modelled carbon balance, with the full range across these simulations displayed in main-text **Figure 3**.

We evaluate this sensitivity in three complementary ways. First, we hold lime-derived alkalinity inputs constant while varying acidity inputs by adding or subtracting the spatially explicit 1-SD uncertainty layers from their respective best estimates. This analysis reflects our assessment that lime inputs are better constrained than acidity inputs. Lime application rates are derived directly from county- and national-level agricultural census data and therefore have a comparatively strong empirical basis, although uncertainty remains in their spatial distribution during periods for which county-level observations are unavailable. Furthermore, the conversion of applied lime mass to alkalinity input is comparatively well constrained by mineral composition and reaction stoichiometry. However, uncertainties are substantially larger for acidity inputs, particularly those associated with N cycling. Agricultural BNF and SON mineralization must be reconstructed indirectly, and all N and S inputs require additional assumptions to translate elemental fluxes into acidity generation. These translations rely on first-order representations of N and S cycling and therefore do not capture the full complexity of the underlying biogeochemical processes.

The uncertainty estimates should consequently be interpreted as first-order sensitivity ranges rather than comprehensive probabilistic confidence intervals. They are primarily linked to uncertainty in the reconstructed N and S input fluxes, including the temporal distance from the nearest observational or model-data anchor year, and capture uncertainty in their conversion to acidity only incompletely. Total acidity is also calculated by aggregating several processes and input components. If errors among these components are at least partly independent, aggregation may result in partial cancellation of positive and negative deviations, such that uncertainty in total acidity is smaller than the combined uncertainty of the individual components.

We first combine the best-estimate lime inputs with acidity inputs adjusted by ± 1 SD. The resulting SCEPTER simulations are shown in **Figure S12**. As expected, varying acidity substantially changes the absolute CO₂ emissions in both the acidity-only and acidity-plus-lime simulations. The cumulative acidity-only emissions by 2015 vary by approximately $\pm 8\%$ around the best estimate under both hydrological forcings. However, most of this response occurs in both members of the matched counterfactual and therefore cancels when the contribution of liming is calculated as the difference between the acidity-only and acidity-plus-lime simulations. Consequently,

holding lime constant while varying acidity changes the estimated cumulative lime-associated sink by less than 1% under P forcing and by approximately 4% under P–ET forcing (**Figure S12b**).

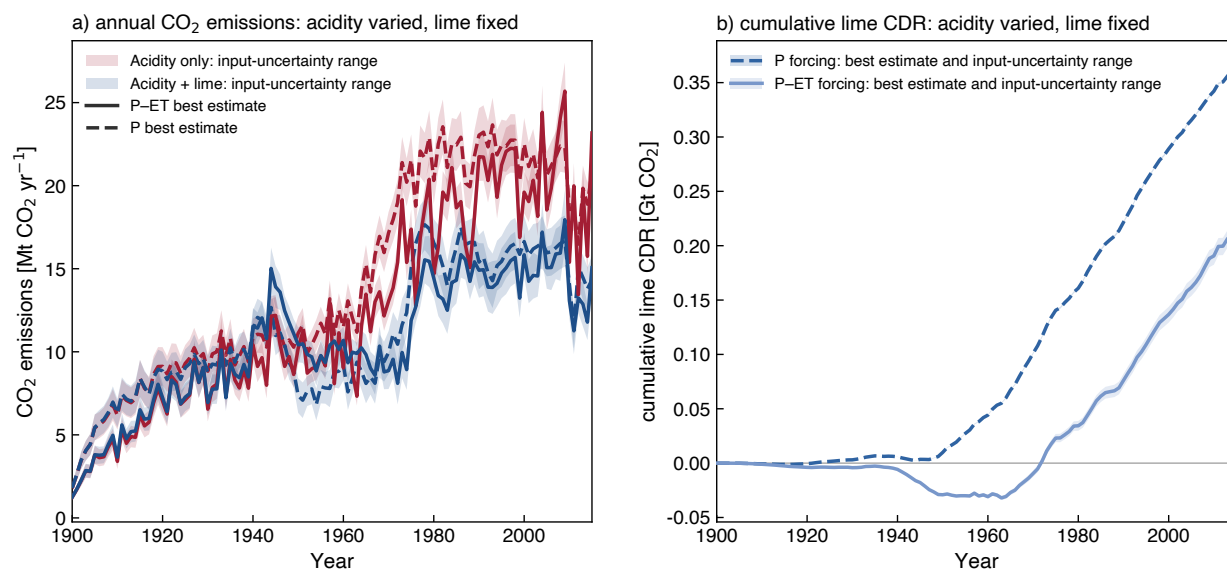


Figure S12: Sensitivity of modelled CO₂ emissions and lime-induced CDR to reconstructed acidity inputs while lime inputs are held constant. (a) Annual MRB-integrated CO₂ emissions in acidity-only (red) and acidity-plus-lime (blue) SCEPTER simulations. Solid and dashed lines show the best-estimate P–ET and P hydrological forcings, respectively. Shaded ranges are calculated separately for each forcing and span simulations using acidity inputs adjusted by +1 and –1SD, with lime retained at its best-estimate reconstruction. (b) Cumulative lime-induced CDR, calculated within each matched forcing and acidity branch as the difference between acidity-only and acidity-plus-lime emissions. Shading spans the acid+1SD and acid–1SD matched CDR branches.

This result demonstrates that uncertainty in reconstructed acidity primarily affects the absolute acid–base CO₂ balance while having a much smaller effect on the inferred contribution of lime application. In other words, the counterfactual difference is considerably more robust than either simulated emissions trajectory considered individually. The somewhat greater sensitivity under P–ET forcing indicates that the response to acidity uncertainty depends on hydrological conditions. A plausible explanation is that, under lower water inputs, the same absolute change in elemental flux produces a larger change in porewater concentration, although the simulations do not uniquely resolve the mechanism responsible.

We next vary acidity and alkalinity inputs in phase. This scenario assumes that, if actual acidity inputs were higher or lower than reconstructed, lime inputs may also have been correspondingly higher or lower as farmers responded to differences in soil acidification. Such covariation is plausible because acidity and alkalinity inputs are approximately balanced in many limed areas toward the end of the record (**Figure S27**). We represent this possibility by pairing the acidity +1-SD scenario with the lime +1-SD scenario and the acidity –1-SD scenario with the lime –1-SD scenario under both P and P–ET forcing. The results are shown in **Figure S13**.

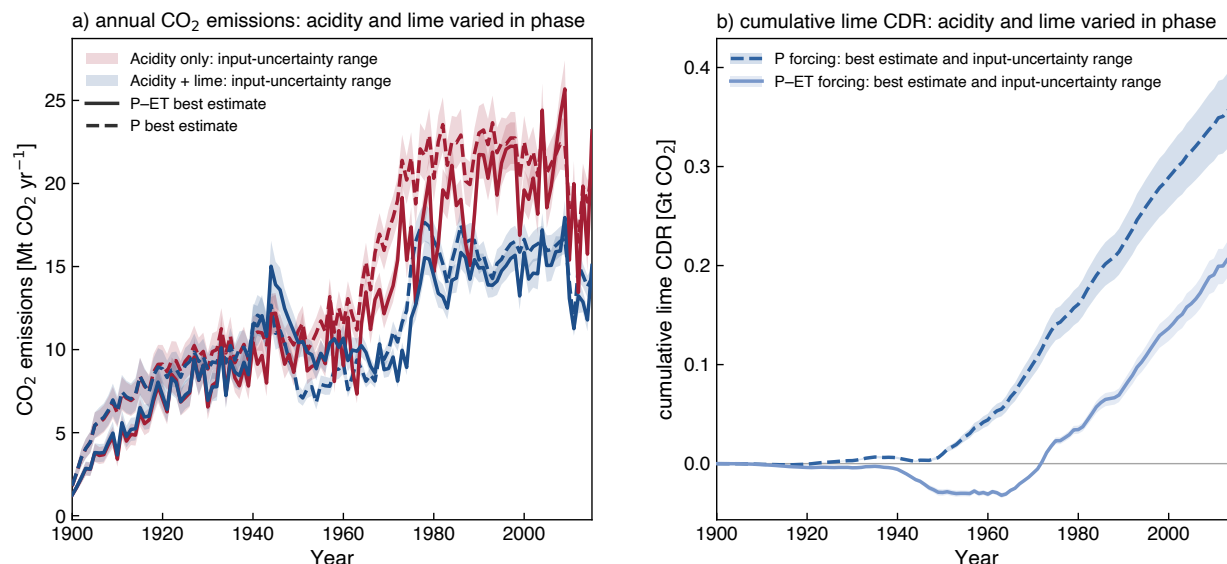


Figure S13: Sensitivity of modelled CO₂ emissions and lime-induced CDR when reconstructed acidity and lime inputs are varied in phase. (a) Annual MRB-integrated CO₂ emissions in acidity-only (red) and acidity-plus-lime (blue) SCEPTER simulations. Solid and dashed lines show the best-estimate P-ET and P hydrological forcings, respectively. Shaded ranges are calculated separately for each forcing and pair acidity+1 SD with lime+1 SD and acidity-1 SD with lime-1 SD. (b) Cumulative lime-induced CDR for the corresponding matched branches, calculated as acidity-only minus acidity-plus-lime emissions and cumulatively summed through time.

For the absolute acidity-plus-lime emissions, the in-phase perturbation produces a narrower range than varying acidity while keeping lime constant over much of the simulation. This likely occurs because the two perturbations partly compensate: greater acidity tends to increase CO₂ emissions, whereas the accompanying increase in lime tends to reduce the longer-term emissions relative to the corresponding high-acidity simulation with standard lime. Similarly, lower acidity is paired with lower lime inputs, which partly offsets the reduction in emissions caused by the lower acidity. This compensation is evident in the absolute acidity-plus-lime simulations, but importantly this does not translate into reduced uncertainty on the impact of lime on CO₂ emissions.

For the matched lime effect, the opposite is true. Once lime inputs vary among scenarios, the lime perturbation occurs only in the acidity-plus-lime member of the counterfactual pair and therefore does not cancel in the subtraction. The resulting cumulative CDR range is substantially wider than in the lime-constant analysis, reaching approximately ± 9 –11% around the best estimate by 2015. The response is close to symmetric around the best estimate, with the +1-SD and -1-SD perturbations producing changes of similar magnitude but opposite sign.

Finally, we consider an out-of-phase perturbation in which acidity and alkalinity inputs vary in opposite directions (**Figure S14**). In one bounding scenario, acidity inputs are increased while lime inputs are decreased; in the other, acidity inputs are decreased while lime inputs are increased. These combinations produce the largest perturbations to the reconstructed acid–base balance within the uncertainty ranges considered and are likely less representative of the actual covariation between soil acidification and farmer responses.

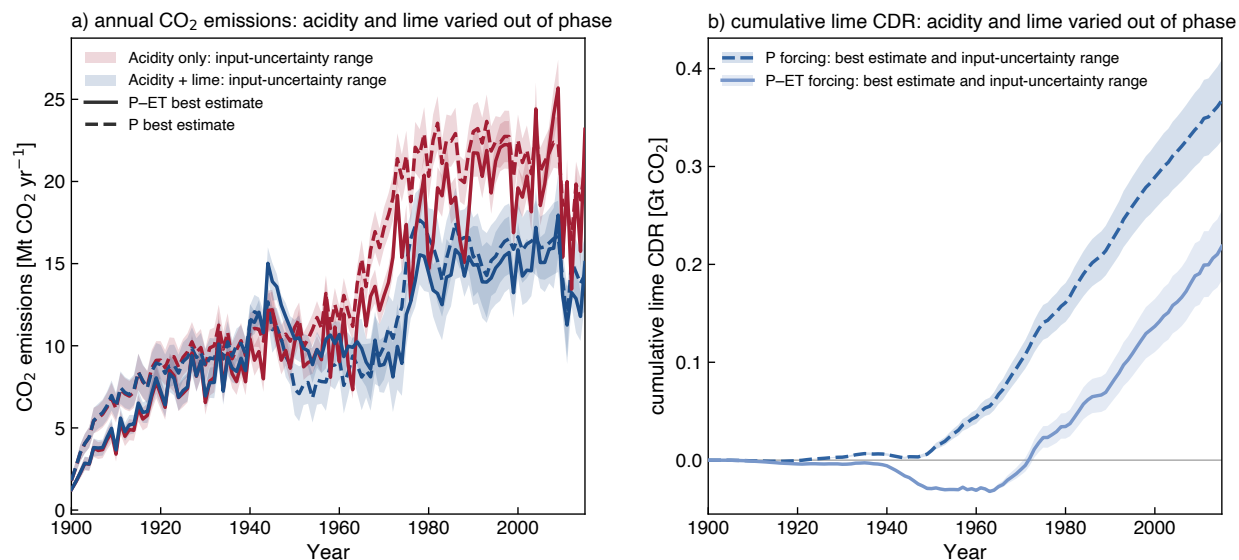


Figure S14: Sensitivity of modelled CO₂ emissions and lime-induced CDR when reconstructed acidity and lime inputs are varied out of phase. (a) Annual MRB-integrated CO₂ emissions in acidity-only (red) and acidity-plus-lime (blue) SCEPTER simulations. Solid and dashed lines show the best-estimate P-ET and P hydrological forcings, respectively. Shaded ranges are calculated separately for each forcing and pair acidity+1 SD with lime-1 SD and acidity-1 SD with lime+1 SD. (b) Cumulative lime-induced CDR for the corresponding matched branches, calculated as acidity-only minus acidity-plus-lime emissions and cumulatively summed through time.

As expected, the out-of-phase simulations generally produce the widest range of model outcomes because the acidity and lime perturbations reinforce rather than compensate for one another. By 2015, the cumulative lime-associated sink varies by approximately $\pm 11\%$ under P forcing and by approximately $\pm 16\%$ under P-ET forcing. The larger response under P-ET forcing is consistent with the greater sensitivity to acidity uncertainty observed in the lime-constant analysis.

Despite these differences in magnitude, the qualitative temporal evolution is robust. All simulations exhibit an initial period during which lime application increases CO₂ emissions relative to the acidity-only counterfactual, followed by a transition to net annual CO₂ removal. More importantly, the cumulative effect of liming is positive by 2015 in every matched simulation considered, including the out-of-phase bounding cases. The uncertainty constructions therefore affect the estimated magnitude and, to a lesser extent, the timing of the lime-associated carbon sink, but not the conclusion that liming reduced cumulative CO₂ emissions over the study period.

Figure S15 compares the three uncertainty constructions directly and highlights an important distinction between uncertainty in absolute emissions and uncertainty in the counterfactual effect of lime application. Uncertainty in reconstructed acidity strongly affects the absolute level of simulated acid-base CO₂ emissions. However, when lime inputs are held constant, the same acidity perturbation affects both the acidity-only and acidity-plus-lime simulations and therefore largely cancels when the lime effect is calculated as the difference between them (**Figure S12**). As a result, even substantial uncertainty in the individual acidity components has only a limited influence on the inferred contribution of liming.

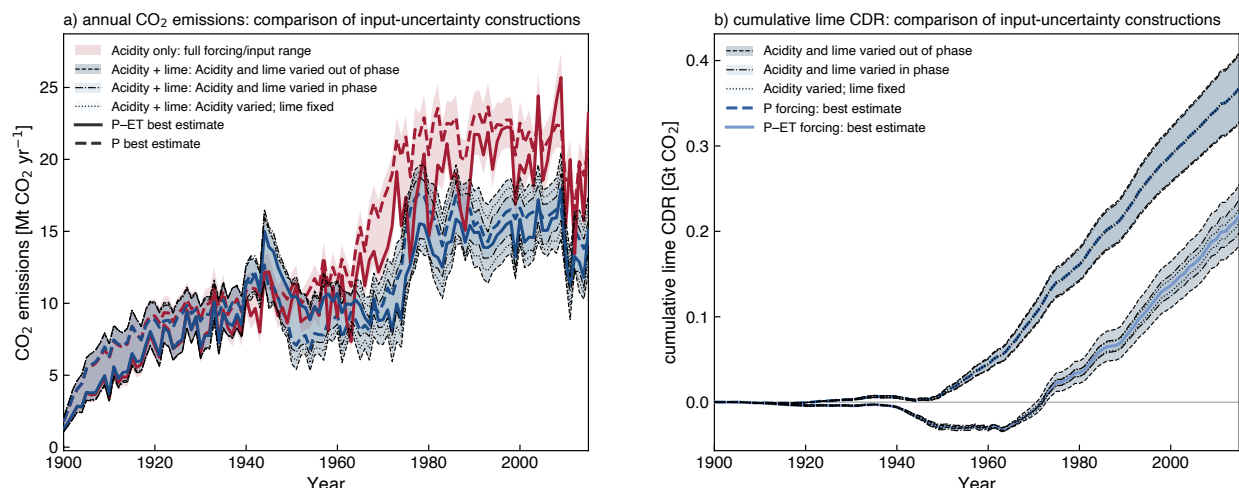


Figure S15: Comparison of the three input-uncertainty constructions. (a) Annual MRB-integrated CO₂ emissions. Red shading shows the common pointwise range across acidity-only simulations using best, +1-SD, and -1-SD acidity inputs under both P and P-ET forcing. Blue bands of increasing darkness show the corresponding pointwise ranges for acidity-plus-lime simulations when lime is held constant, varied in phase with acidity, or varied out of phase with acidity. (b) Cumulative lime-induced CDR. Each shaded band is the pointwise minimum-to-maximum range across the best, acid+1-SD, and acid-1-SD matched branches under both hydrological forcings for one uncertainty construction. Solid and dashed lines show the common best-estimate P-ET and P simulations, respectively.

The uncertainty in the magnitude of the lime-associated sink is instead driven primarily by uncertainty in the reconstructed lime inputs (**Figure S13** and **Figure S14**). Once lime inputs are allowed to vary, their effect is present only in the acidity-plus-lime simulation and therefore does not cancel in the counterfactual subtraction. This produces a substantially wider range in cumulative lime-attributable CDR, with the widest bounds obtained when acidity and lime are varied out of phase. From a counterfactual perspective, the effect of lime application is therefore considerably more robust than the absolute magnitude of either the reconstructed acid-base balance or the simulated emissions in individual scenarios. The sensitivity analysis shows that uncertainty in acidity inputs primarily determines the absolute level of simulated emissions, whereas uncertainty in lime inputs primarily determines the magnitude of the inferred lime-associated sink. Crucially, neither source of uncertainty changes the conclusion that agricultural liming produced a net cumulative reduction in CO₂ emissions over the study period.

S4 Increased weathering of natural carbonate minerals due to anthropogenic acidity input

Anthropogenic acidity inputs may enhance background mineral weathering beyond that associated with agricultural liming⁴⁵. Quantifying this effect is inherently uncertain⁴⁶, as it depends on poorly constrained interactions between acidity fluxes, mineral availability, and hydrologic flow paths. Direct observational constraints that would allow for estimates of the fraction of added excess acidity being neutralized are limited. In particular, the absence of basin-wide river pH data prior to ~1955¹³ precludes quantification of long-term proton export relative to pre-industrial conditions. Hence, here we assess the magnitude of this potential flux by combining spatially explicit estimates of excess acidity after lime addition (see main text; **Figure 2**) with spatially explicit constraints on limestone and dolomite availability in soils. Using a gridded soil geochemistry dataset⁴⁷, average dolomite + calcium carbonate concentrations in topsoils were interpolated onto a 0.1° grid using inverse-distance weighting, and the resulting surface was aggregated to area-weighted mean values for each 1° SCEPTER grid cell (IDW; **Figure S16a**). For each grid cell and year, negative excess-acidity values (see **Figure 2**), representing net alkalinity, are set to zero before the remaining positive excess acidity is multiplied by the local soil carbonate fraction. This carbonate-fraction-weighted acidity flux provides a first-order estimate for the magnitude of reaction of acidity inputs with carbonates naturally available in soils.

This assumption represents a pragmatic middle-ground estimate. On the one hand, because carbonates dissolve orders of magnitude faster than silicates⁴⁸, rapid carbonate dissolution and preferential flow may allow carbonates to neutralize a larger fraction of added acidity than implied by soil carbonate content. On the other hand, reactions between acidity and dissolved bicarbonate in pore waters will be extremely rapid^{49,50}. Therefore, excess acidity will not largely be expressed through additional solid-phase carbonate dissolution and even the carbonate-availability constrained estimate adopted here could therefore still be viewed as conservative to moderately upper-bound in CDR-equivalent terms.

To remain consistent with the framework in **Figure 3** (main text), alkalinity fluxes are expressed in CDR equivalents assuming carbonate weathering by carbonic acid. This corresponds to a stoichiometric conversion in which 50% of the bicarbonate carbon (assuming charge balance with released cations) is attributed to atmospheric CO₂ uptake. Expressing this term as CDR potential does not imply that strong-acid-driven carbonate dissolution itself removes atmospheric CO₂. Rather, it represents a counterfactual CDR-equivalent: acidity that is neutralized by carbonate cannot subsequently react with bicarbonate and drive CO₂ release—but the dissolution of carbonate via acidity has added alkalinity compared to this counterfactual.

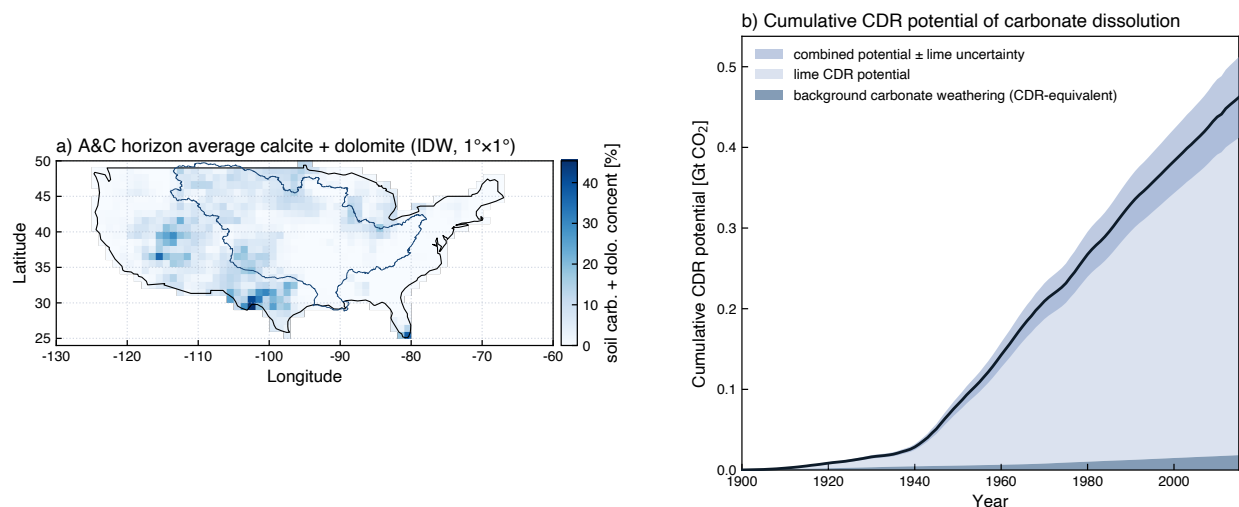


Figure S16: Spatial distribution of soil carbonate content and its implication for cumulative CDR potential in the Mississippi River Basin (MRB). Panel (a) shows the inverse-distance-weighted interpolation of average A- and C-horizon dolomite + calcite content from a semi-gridded soil geochemistry database⁴⁷, regridded to the $1^\circ \times 1^\circ$ spatial resolution used in the SCEPTER simulations. Panel (b) shows cumulative CDR potential associated with carbonate dissolution in the MRB when conventional lime CDR is combined with the estimated contribution of additional background carbonate weathering driven by excess acidity inputs. The dark blue shaded area in the bottom represents the cumulative CDR-equivalent associated with the fraction of the MRB-wide excess acidity budget that overlaps with carbonate-bearing soils, while the light blue shaded area above it represents cumulative lime CDR potential, such that the upper boundary gives the sum of both terms. The line traces this cumulative sum, and the surrounding uncertainty band applies the original uncertainty in cumulative lime CDR potential to that upper boundary. Expressing the acidity-driven carbonate dissolution term as CDR does not imply that dissolution of carbonate by strong acids itself constitutes atmospheric CO_2 removal. Rather, it is shown as a counterfactual CDR-equivalent: acidity neutralized via carbonate dissolution cannot subsequently react with pore water bicarbonate which releases CO_2 , yet this dissolution still generates additional alkalinity relative to the counterfactual in which that carbonate dissolution did not occur.

Using this carbonate-availability constrained approach, the effect of anthropogenic acidity inputs reacting with naturally occurring soil carbonates appears to be minor relative to the cation and alkalinity fluxes added via agricultural lime (b). By 2015, the cumulative CDR-equivalent associated with this process is only 0.018 GtCO_2 , compared with 0.444 GtCO_2 from lime, such that acidity-driven increases in background carbonate weathering contribute just 3.8% of the combined total in this framework. This is also qualitatively consistent with the underlying spatial data: carbonates are absent in $\sim 77\%$ of soil samples across the conterminous United States⁴⁷ and are likewise relatively sparse across much of the MRB (**Figure S16a**), limiting the extent to which excess acidity can be neutralized by natural carbonate phases in soils.

Nevertheless, a larger contribution from acidity-enhanced weathering of naturally occurring carbonates cannot be excluded. Agricultural lime addition compensated for only approximately half of the cumulative anthropogenic acidity input across the MRB (see main text), leaving a considerable excess-acidity flux that could have been neutralized through reactions with native minerals. A basin-wide proton mass balance cannot be constructed because river pH observations are unavailable for the pre-liming baseline period, while added acidity may also be retained temporarily on soil cation-exchange sites or exported through hydrologic pathways not resolved by the available observations. Documented changes in lower Mississippi River pH over recent decades further demonstrate that the acid–base state of the basin has evolved through time¹³. We

SI to “Agricultural liming is a carbon sink in the Mississippi River Basin”, Suhrhoff et al. (2026)

therefore cannot uniquely determine what fraction of excess acidity reacted with native carbonates, bicarbonate alkalinity, silicate minerals, or exchangeable soil pools.

If acidity-enhanced background carbonate weathering was larger than estimated here and an important cation and alkalinity source in the MRB, part of the observed increase in riverine alkalinity would reflect native carbonate dissolution rather than agricultural lime alone. This would reduce the fraction of the observed alkalinity increase attributable specifically to lime and could lower the inferred fraction of lime-derived alkalinity exported from the basin. It could also affect estimated lag times because the riverine signal would integrate alkalinity generated by both lime dissolution and changes in background weathering. Conversely, it would imply a larger total carbonate-derived alkalinity source and would not negate the broader inference that carbonate weathering has constituted a net CO₂ sink at the basin scale. In addition to this process, uncertainty in total excess cation release relative to the pre-1935 baseline is influenced by climate variability and long-term hydrologic change (Supplementary S1.3).

Rather than claiming that lime application alone causally explains the observed shifts in MRB carbon chemistry, we present multiple, internally consistent lines of evidence indicating that liming—and carbonate weathering more generally—has contributed to net CO₂ uptake at the basin scale. This conclusion is supported by (i) process-based model results, (ii) the magnitude and trajectory of increasing alkalinity export, and (iii) evolving cation-to-bicarbonate relationships³, which together indicate a progressive shift of the MRB toward enhanced net CO₂ uptake over time.

S5 Improved GHG inventory emissions factor for soil acid-base reactions

Existing inventory approaches recognize that liming-related CO₂ emissions arise from reactions between carbonate minerals and soil acidity, but operationalize these emissions using the amount of limestone and dolomite applied and associated emission factors, rather than an explicit measure of the acidity being neutralized^{26,28}. The IPCC Tier 1 method multiplies limestone and dolomite application by emission factors equal to their carbonate-carbon contents and therefore assumes that all carbonate C is emitted as CO₂ in the year of application²⁶. Higher-tier methods may apply lower, country-specific emission factors that account for secondary carbonate formation and the hydrological transport of lime-derived dissolved inorganic carbon²⁶. The U.S. national inventory follows such a Tier 2 approach: its country-specific factors, equivalent to approximately 49% of the IPCC estimate, are based on a framework that considers the relative importance of strong- and carbonic-acid dissolution and the hydrological export of bicarbonate^{26,28}. Thus, lime application serves as an activity-based proxy for the acid-base processing and subsequent fate of added carbonate C.

However, the acidity driving these reactions remains implicit, and emissions are attributed only to the carbon contained in applied lime. Lime-based approaches therefore do not explicitly account for the CO₂ that anthropogenic acidity would release by titrating natural background alkalinity in the absence of liming, including in unmanaged soils or where lime application is insufficient to offset acidification, nor for the gross atmospheric CO₂ uptake associated with carbonic-acid dissolution of lime. The Tier 1 approach may therefore be conservative with respect to the acid base-reaction of the fraction of acidity that does react with added lime or background alkalinity more broadly, but not necessarily with respect to the broader landscape-scale CO₂ emissions caused by anthropogenic acidification reacting with alkalinity pools beyond the applied lime. An inventory based only on lime application can therefore misestimate not only the magnitude of liming-related CO₂ fluxes (**Figure 3**), but also, over sufficiently large spatial and temporal scales, the sign of liming’s net climate effect. By assigning a positive emission to lime while leaving the underlying anthropogenic acidity outside the explicit accounting boundary, such an approach may also create incentives that discourage soil-pH management even where liming reduces net CO₂ emissions.

An alternative, still simplified, inventory approach based on acidity and alkalinity inputs would be:

$$CO_2 emissions [t\ yr^{-1}] = (J_{acidity} - 0.5 J_{carbonate\ alkalinity}) \frac{M_{CO_2}}{10^6} \quad (eq. 17)$$

where $J_{acidity}$ is the annual anthropogenic acidity flux, expressed as mol H⁺ equivalents yr⁻¹, $J_{carbonate\ alkalinity}$ is the annual stoichiometric alkalinity capacity supplied by carbonate addition, expressed as mol alkalinity equivalents yr⁻¹, and M_{CO_2} is the molar mass of CO₂ in g mol⁻¹ (and the 10⁶ is the conversion factor of g to t). Here, $J_{carbonate\ alkalinity}$ represents two alkalinity equivalents per mole of carbonate carbon added via lime rather than only the alkalinity remaining in solution after reaction with strong acid. With this definition, strong-acid dissolution of lime does not require a separate term: it is algebraically equivalent to carbonic-acid dissolution followed by proton titration of the generated bicarbonate, such that the $J_{acidity}$ term offsets the atmospheric CO₂ uptake term for the fraction of carbonate weathered by strong acid.

The first term represents the potential CO₂ release associated with proton-driven titration of bicarbonate alkalinity, assuming that one mole of acidity can ultimately convert one mole of bicarbonate to CO₂. The second term represents the ideal atmospheric CO₂ uptake associated with carbonate dissolution by carbonic acid: because each mole of carbonate-derived alkalinity contains carbon from both the carbonate mineral and the atmosphere, only half of the generated bicarbonate alkalinity corresponds to atmospheric CO₂ removal. This simplified formulation therefore estimates net CO₂ emissions as acidity-driven CO₂ release minus the atmospheric CO₂ uptake potential of carbonate alkalinity inputs. Based on the data compiled here, we estimate CO₂ emissions for the MRB using eq. 17 in **Figure S17**.

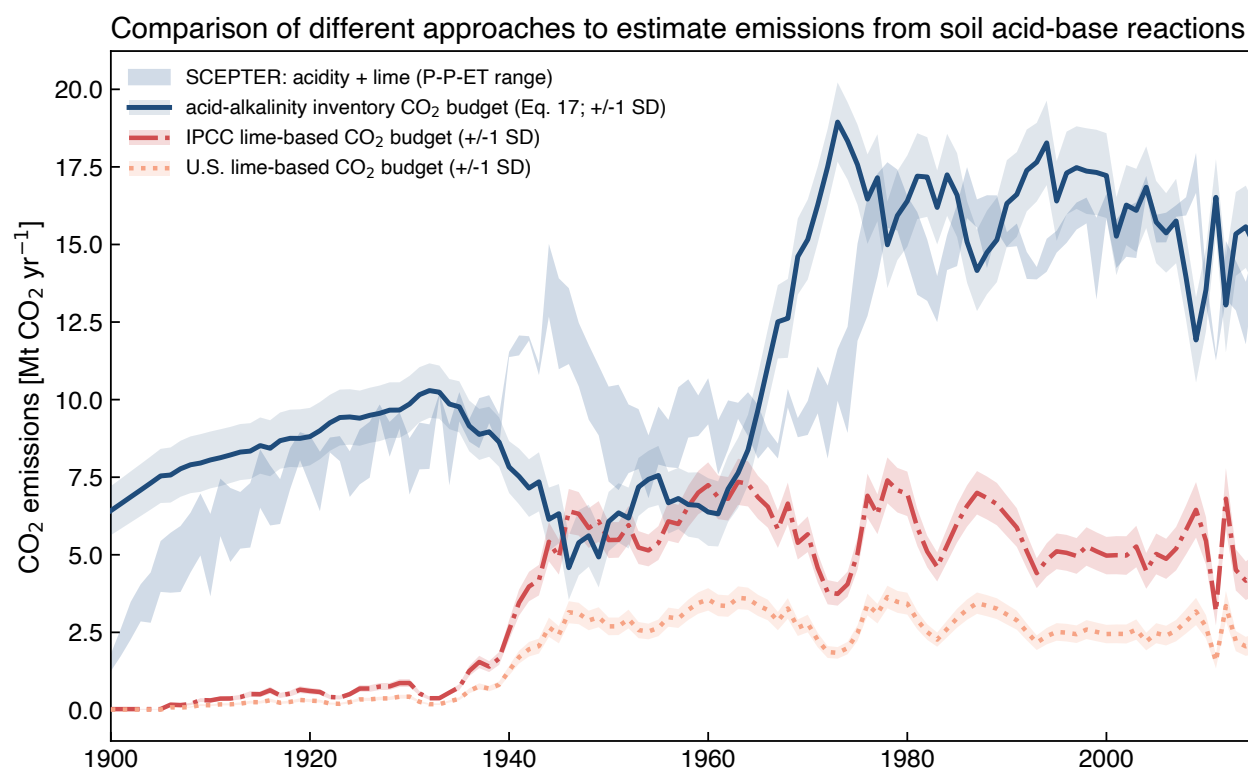


Figure S17: Comparison of acid–alkalinity inventory and existing liming-related CO₂ emissions estimates. Annual CO₂ emissions estimated using the acid–alkalinity inventory approach introduced in eq. 17 are compared with the liming-related CO₂ budgets discussed in the main text: conventional lime-based estimates following the default IPCC and U.S. inventory approaches, and SCEPTEr reactive transport simulations forced with historical anthropogenic acidity and agricultural lime inputs. The acid–alkalinity inventory estimate is calculated from MRB-wide total anthropogenic acidity inputs and lime-derived carbonate alkalinity inputs; total acidity includes fertilizer, manure, atmospheric N and S deposition, SON mineralization, and agricultural BNF. Shaded bands indicate propagated ± 1 SD uncertainty.

The acid–alkalinity inventory approach introduced in eq. 17 provides a simple alternative to lime-based emissions factors that more directly reflects the acid–base chemistry controlling CO₂ release from soils and surface waters. In contrast to the IPCC and U.S. lime-based approaches, which scale emissions to the amount of carbonate carbon added as lime, eq. 17 estimates net CO₂ emissions from the balance between anthropogenic acidity inputs and lime-derived carbonate alkalinity capacity. Applied to the MRB, this approach yields emissions estimates that are much closer in magnitude and temporal evolution to the SCEPTEr reactive transport simulations than either lime-

SI to “Agricultural liming is a carbon sink in the Mississippi River Basin”, Suhrhoff et al. (2026)

based inventory approach. This agreement suggests that an acidity-based counterfactual captures an important control on basin-scale CO₂ fluxes associated with soil acid–base reactions. The approach therefore provides a more complete basin-scale approximation than lime-mass-based emission factors because it assigns emissions to the underlying acid–alkalinity imbalance rather than to lime application alone.

However, eq. 17 should still be interpreted as a simplified inventory approximation rather than a full process model. Because it is based on annual acidity and alkalinity input fluxes, it implicitly assumes that acid–base reactions and associated CO₂ fluxes occur without explicit storage or delay. It therefore does not capture the initial pulse of CO₂ emissions following lime addition (**Figure 3**), nor the lag between lime application and net carbon removal. In the reactive transport simulations, both effects arise primarily from non-steady-state interactions with the soil cation exchange pool and legacy acidity: lime-derived base cations can be retained on exchange sites while previously stored protons are released to pore waters, and solute export can be delayed by exchange and transport processes. These non-steady-state effects could potentially be approximated in future inventory methods using additional terms that depend on the relative rates of change in acidity and alkalinity inputs, thereby representing transient disequilibrium between external forcing and soil exchange pools. Thus, while Eq. 17 may improve on entirely lime-based emissions factors, reactive transport modeling and empirical constraints will likely remain necessary to explicitly resolve upfront emissions, storage, and lag times associated with cation exchange and solute transport dynamics.

The condition under which eq. 17 gives the same numerical estimate as the default IPCC approach can be shown by simple rearrangement. If carbonate alkalinity capacity is expressed in mol alkalinity equivalents yr^{−1}, the default IPCC approach effectively estimates CO₂ emissions as 0.5 × $J_{\text{carbonate alkalinity}}$, whereas eq. 17 estimates emissions as $J_{\text{acidity}} - 0.5 J_{\text{carbonate alkalinity}}$. Setting these expressions equal gives $J_{\text{acidity}} = J_{\text{carbonate alkalinity}}$. Thus, within this simplified framework, the conventional IPCC estimate and the acid–alkalinity inventory estimate coincide numerically when anthropogenic acidity inputs are exactly balanced by carbonate alkalinity inputs from lime, and the system is sufficiently close to steady state that transient effects associated with cation exchange, legacy acidity release, and solute-transport lags have largely dissipated. Under these conditions, lime addition approximately neutralizes the acidity that would otherwise generate CO₂, and no substantial net storage or delayed release of acidity or alkalinity occurs through exchange reactions, hydrologic transport, or other transient pools. This provides the basis for the statement in the main text that the conventional IPCC estimate and the acid–alkalinity estimate coincide when alkalinity addition through liming matches overall anthropogenic acidity inputs to the system. Such conditions may occur locally or over limited time intervals, but are unlikely to be generally satisfied across large heterogeneous catchments or over historical timescales (cf., **Figure 2** and associated discussion in the main text).

This acid–alkalinity framework could also be extended to silicate-based Enhanced Weathering by adding a silicate-derived alkalinity term. In that case, eq. 17 could be generalized to:

$$CO_2 \text{ emissions } [t \text{ yr}^{-1}] = (J_{\text{acidity}} - J_{\text{silicate alkalinity}} - 0.5 J_{\text{carbonate alkalinity}}) \frac{M_{CO_2}}{10^6} \quad (\text{eq. 18})$$

where $J_{\text{silicate alkalinity}}$ represents realized alkalinity generation from silicate mineral weathering. This term should be multiplied by 1 rather than 0.5 because, unlike carbonate dissolution, alkalinity generated by carbonic-acid weathering of silicate minerals is charge-balanced by dissolved inorganic carbon derived entirely from atmospheric or soil CO_2 . In practice, $J_{\text{silicate alkalinity}}$ would need to represent realized rather than idealized silicate weathering, accounting for incomplete mineral dissolution, cation retention in soils, secondary mineral formation, and the fraction of weathering driven by non-carbonic acids. This is conceptually consistent with emerging ERW inventory approaches^{51,52}, which estimate CDR from rock application using mineralogical carbonation potential corrected for kinetic limits, cation retention, and alternate-acid effects.

S6 Additional supplementary figures main text & online methods

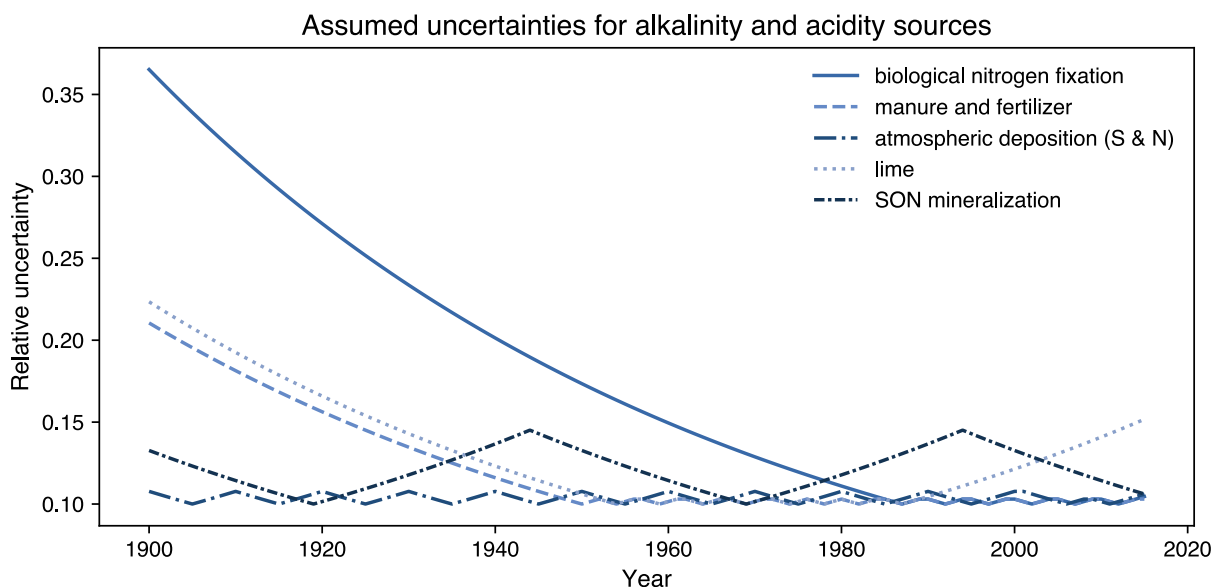


Figure S18: Timeseries of assumed uncertainty for spatially explicit alkalinity and acidity source layers. These factors were used to modulate raster layers, and where sums were used as inputs into SCEPTER model the uncertainties were propagated accordingly.

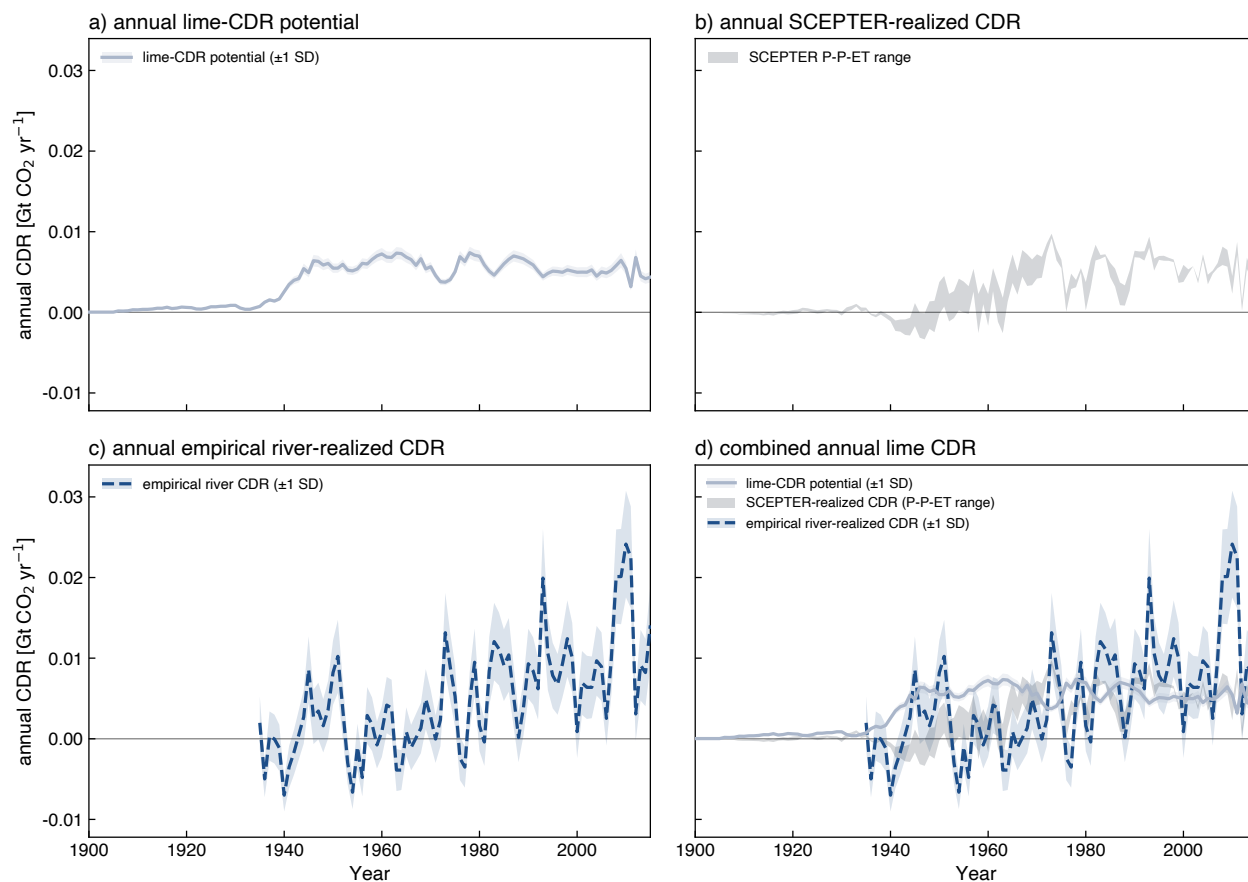


Figure S19: Annual carbon sink resulting from agricultural liming in the Mississippi River Basin (MRB). Annual CDR fluxes are shown for (a) the ideal lime-CDR potential, calculated from lime application rates and carbonate reaction stoichiometry; (b) realized CDR estimated using the SCEPTER reactive transport model; (c) realized CDR estimated from empirical excess riverine alkalinity fluxes; and (d) all three estimates shown together. Shaded envelopes represent ± 1 SD where available, or the range between the P- and P-ET-forced SCEPTER simulations. Based on carbonate reaction stoichiometry, the empirical riverine estimate assumes that half of the carbon in excess bicarbonate alkalinity is derived from lime and half from the atmosphere.

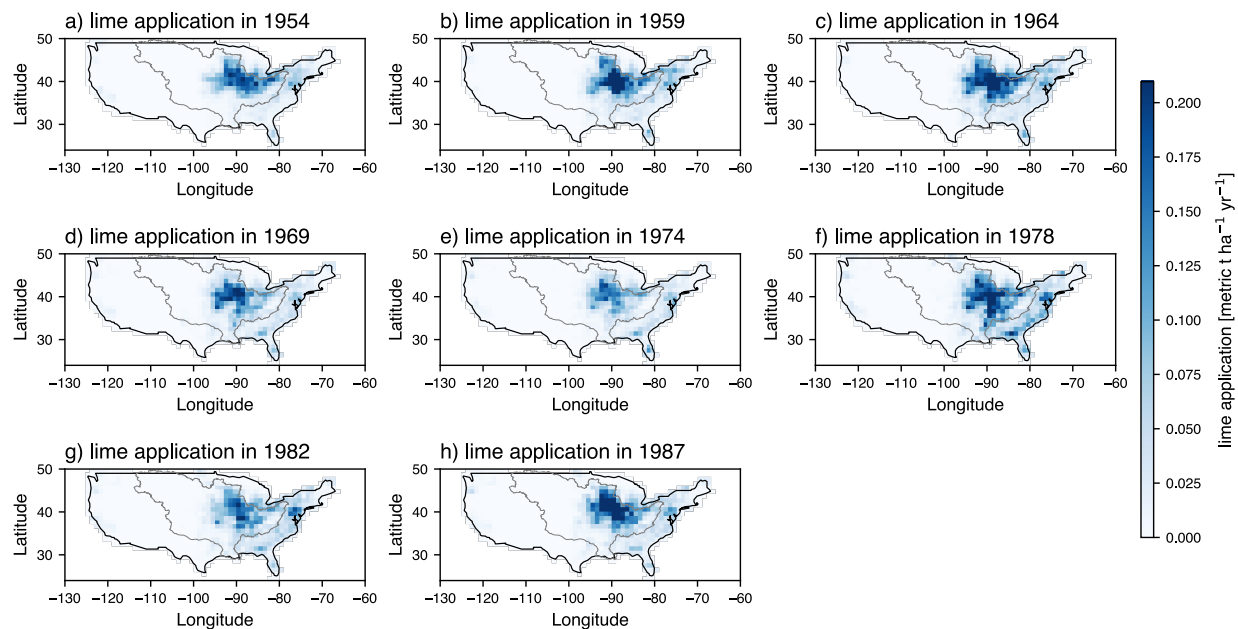


Figure S20: Spatially explicit lime data based on county level liming data for years with reference data. Outside these periods, spatial patterns are extra- and interpolated based on country level liming data.

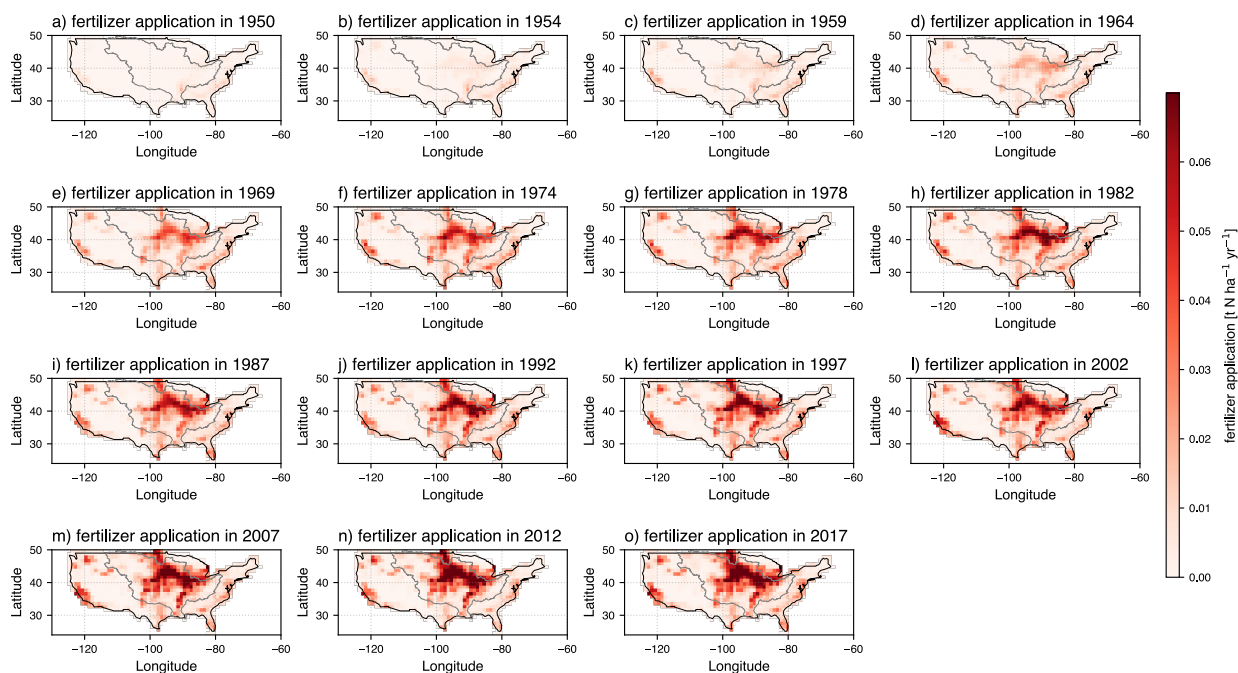


Figure S21: Spatially explicit fertilizer data based on county level data for years with reference data. Outside these periods, spatial patterns are extra- and interpolated based on spatially explicit model-derived fertilizer application rates⁵³.

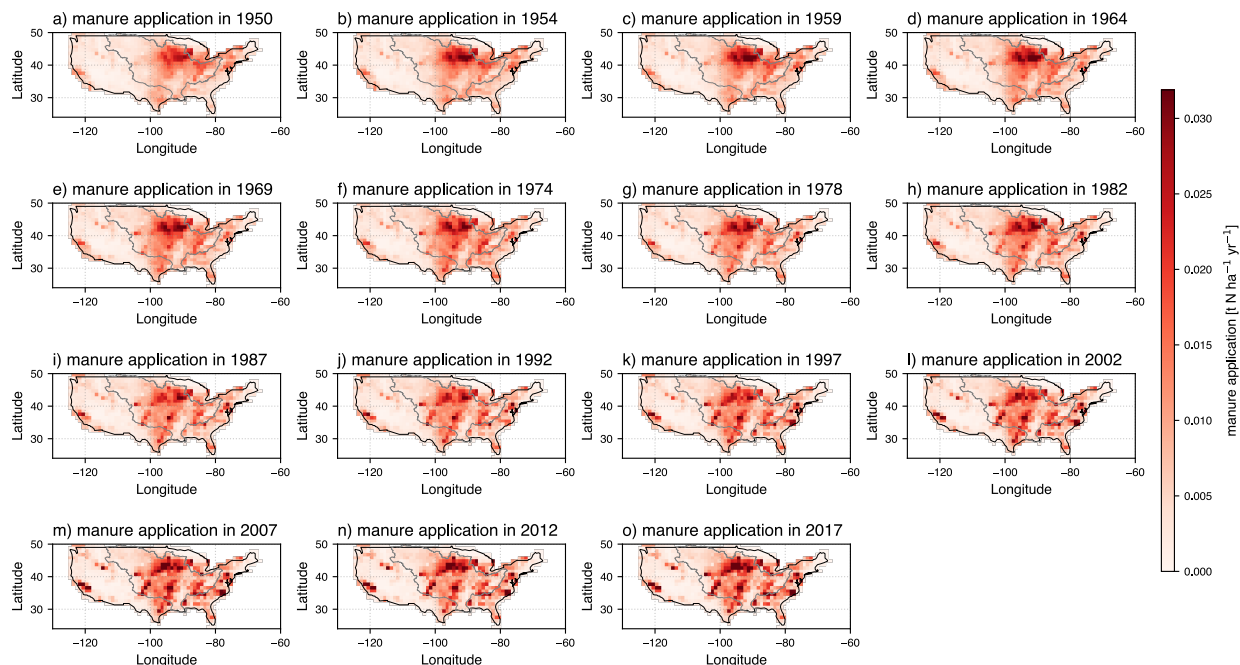


Figure S22: Spatially explicit manure data based on county level data for years with reference data. Outside these periods, spatial patterns are extra- and interpolated based on country-wide application amounts⁵⁴.

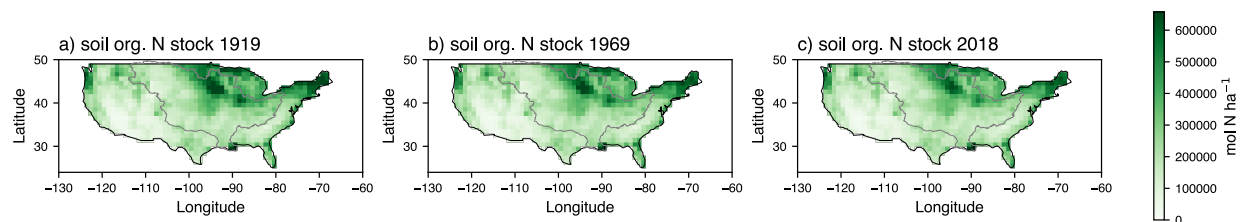


Figure S23: Stocks of soil organic N based on interpolated SOC stocks⁵⁵ as well as soil C:N ratios of 14.3⁵⁶. Negative values for derived acidity sources occur in a limited number of grid cells where inferred SOC-derived organic N stocks increase between reference periods. In the acid–base accounting framework used here, these negative SON–mineralization terms were retained as local reductions in N-derived acidity, consistent with net N immobilization/storage. However, negative SON terms were only allowed to offset other N-derived acidity sources; the summed N-derived acidity forcing was not allowed to become a net acidity sink due to SON dynamics alone. This treatment affects only a small number of grid cells and has negligible influence on MRB-scale acidity budgets.

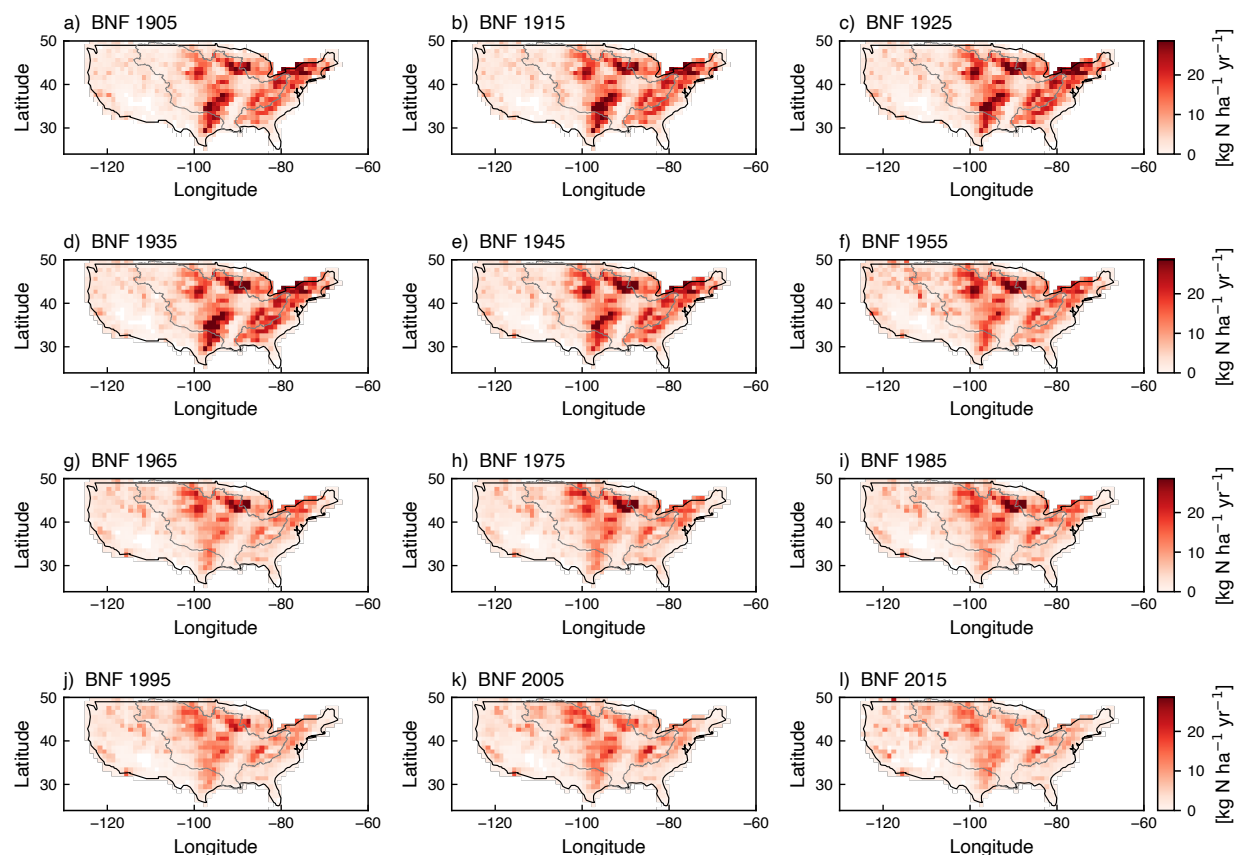


Figure S24: Changes in agricultural biological N fixation (BNF) over time. Estimates derived from county-level crop distributions of alfalfa, non-alfalfa hay, cropland pasture, snap peas, and peanuts and their N fixation rates using the NANI framework⁵⁷, re-gridded to the 1° analysis grid. For the acid-base budget, these are converted to acidity fluxes using the same assumptions as for soil organic N mineralization (eq. 10). Soybean-derived fixation was excluded because harvested soybean seed commonly exports as much or more N than is fixed biologically⁵⁸, making soybean BNF a poor proxy for net retained, acidity-generating topsoil N. Other minor harvested legume categories, such as peanuts and snap beans, may be affected by similar harvest-removal effects, but they represent much smaller contributions to the considered non-soybean BNF terms, for example <2% (of non-soybean BNF) for the last available census data in 2012⁵⁷. The resulting BNF-derived acidity term should therefore be interpreted as a likely upper-bound estimate of BNF-derived N available for soil N cycling and acidity generation.

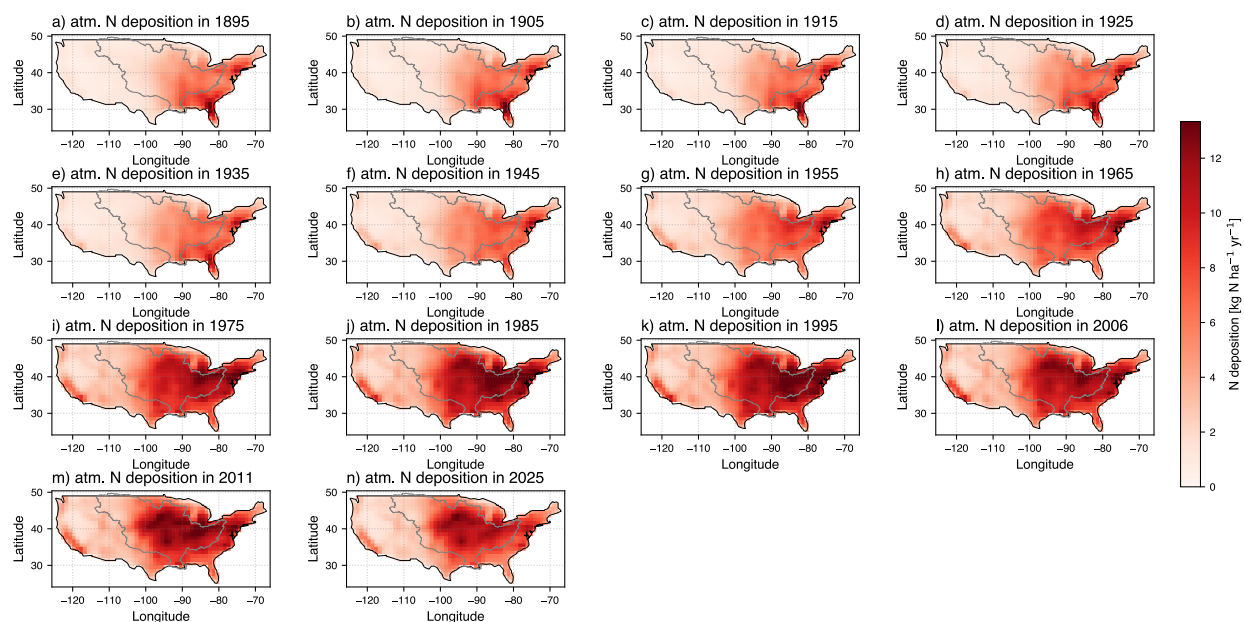


Figure S25: Atmospheric wet+dry N deposition for years with TDep model output⁵⁹.

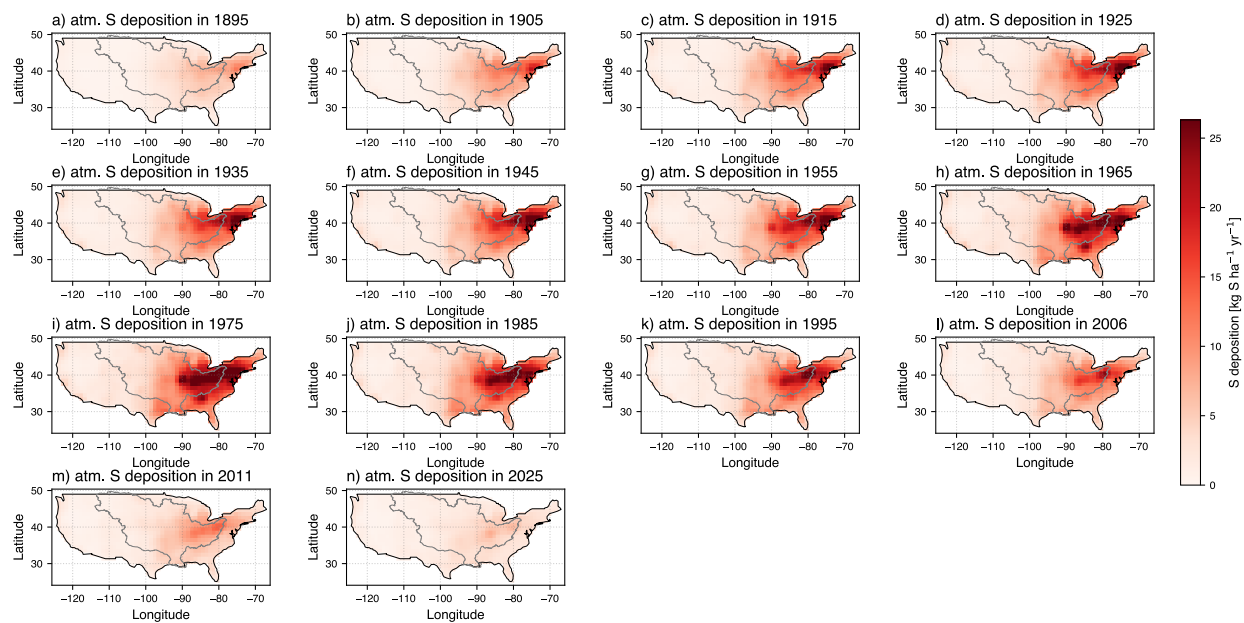


Figure S26: Atmospheric wet+dry S deposition for years with TDep model output⁵⁹.

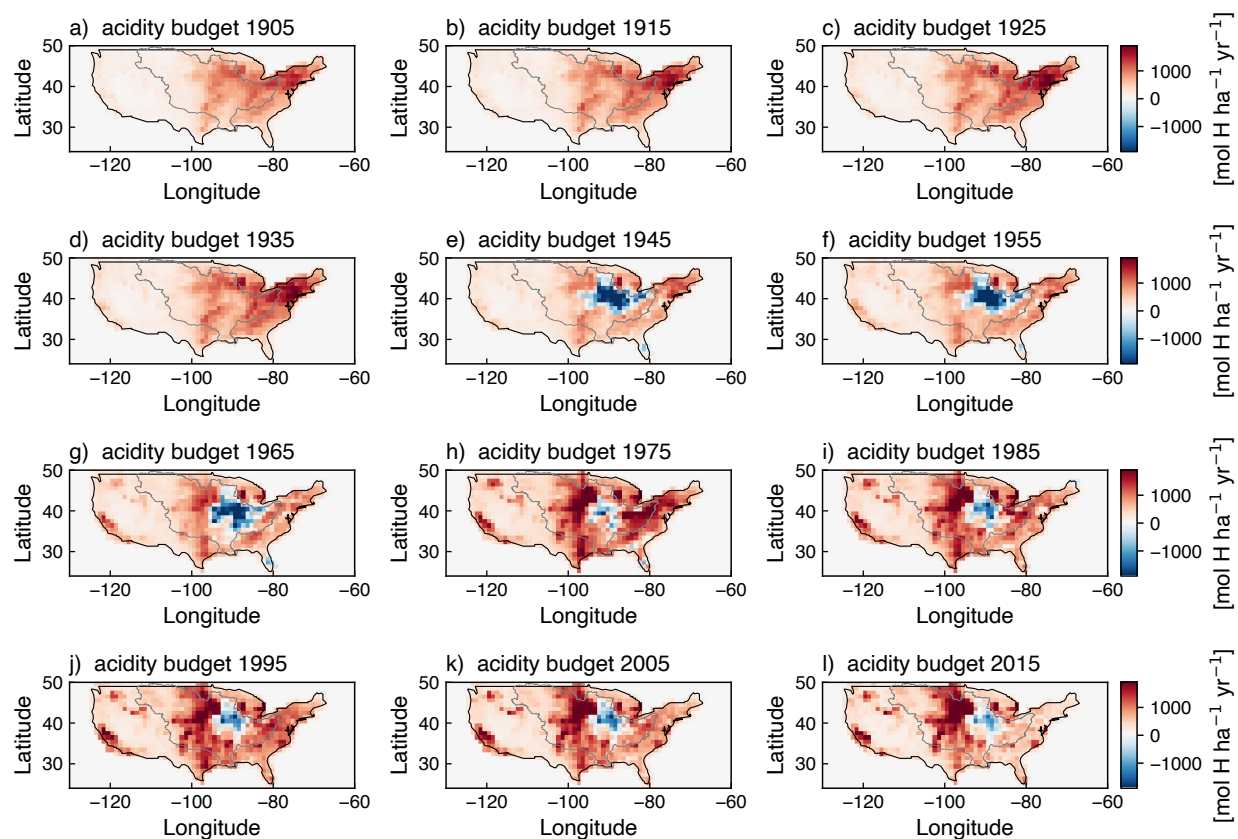


Figure S27: Spatial distribution of the net acid–base balance across all considered acidity sources and agricultural lime inputs. Positive values indicate net excess acidity, whereas negative values indicate net excess alkalinity.

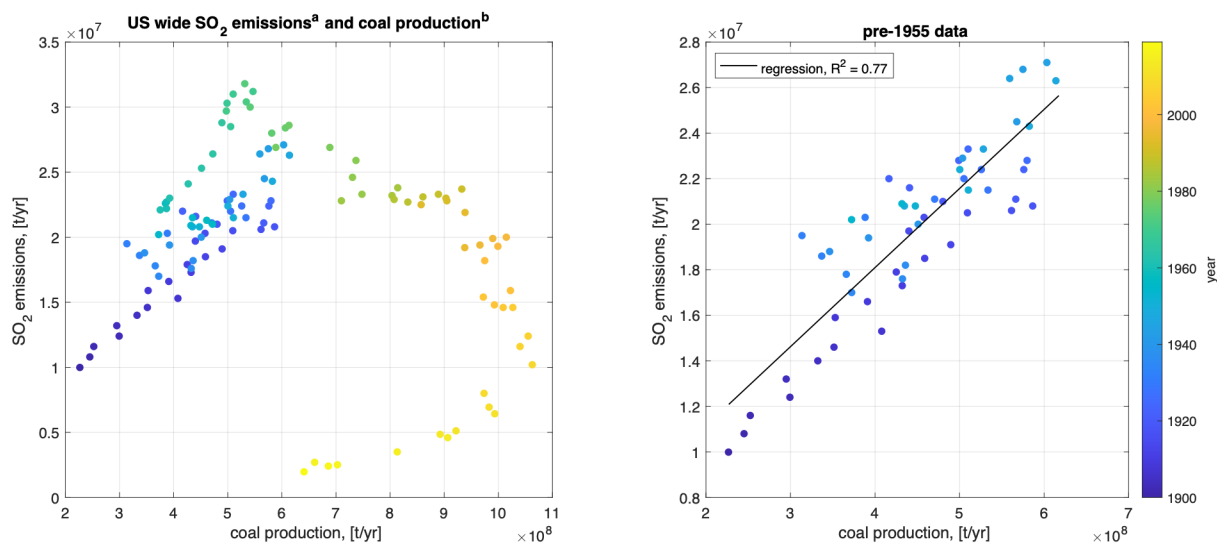


Figure S28: Panel (a) shows how SO₂ emissions^{14,15} and coal production⁶⁰ have changed since 1900, and panel (b) shows the correlation between both parameters for the pre-1955 period where the SO₂ data was used to modulate $f_{\text{strong acid}}$ to demonstrate that to a large extent, in that period, dynamics in SO₂ emissions reflect changes in coal production. After this period SO₂ emissions decreased although coal production still increased (a), likely due to switching to coal with lower S content as well as the advent of industrial flue gas desulfurization technologies (1970 Clean Air Act). After ~2000, both coal production and SO₂ emissions have decreased, following a new regression line with a lower slope (i.e., less SO₂ emissions at same coal production).

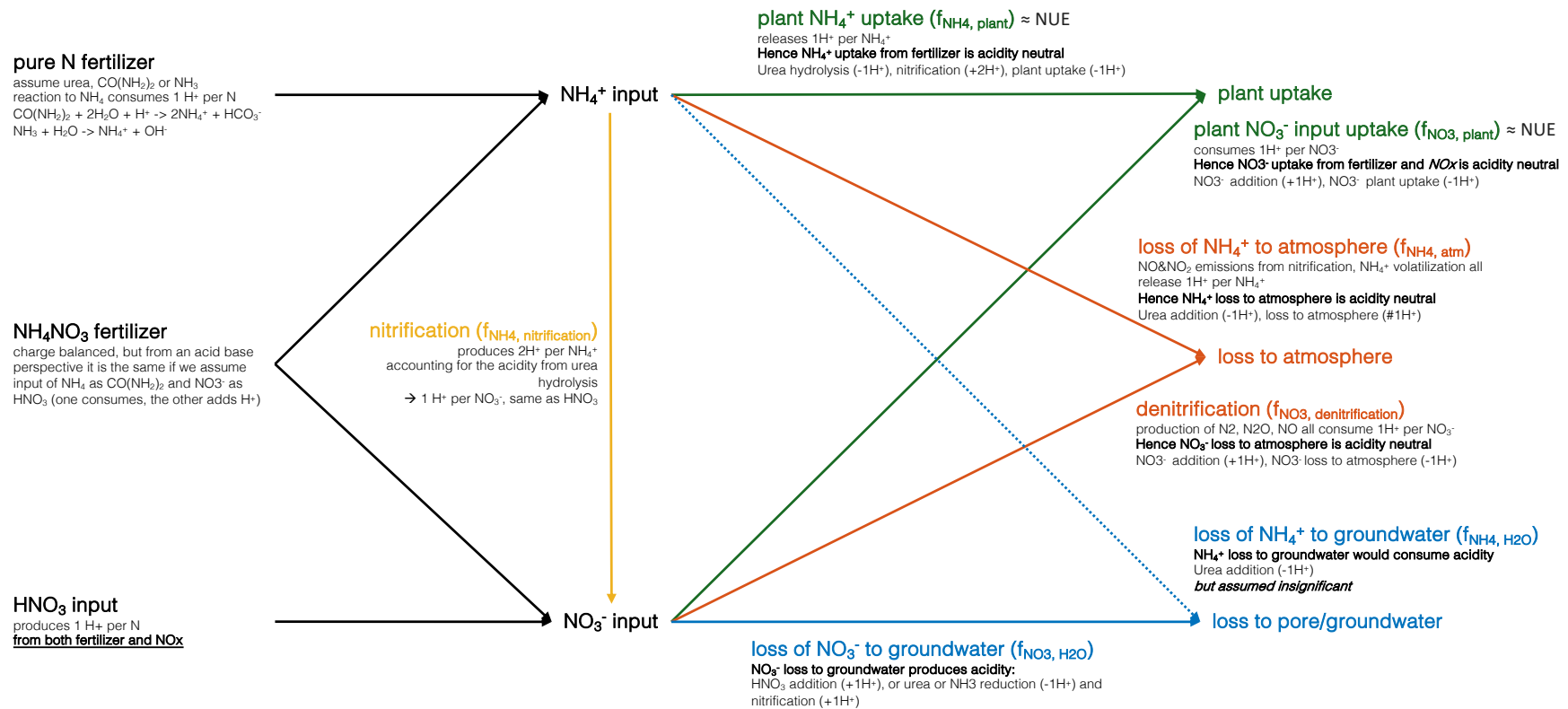


Figure S29: Sketch of the N-cycle processes considered in this study. The pathways assumed to dominate the net proton balance and parameterized for the different N sources are shown in Figure S30. The simplified accounting assumes that (1) irrespective of its original input form, each mole of N ultimately leached as NO_3^- contributes one mole of retained H^+ to the system; (2) N taken up, immobilized, denitrified, or lost through other gaseous pathways makes no net contribution to retained acidity over the relevant system boundary (including generation of NH_4^+ in soils); and (3) dissolved NH_4^+ loss is negligible relative to NO_3^- leaching because of efficient nitrification, plant uptake, and retention on soil exchange sites.

- 1) Reactive N can enter soils as nitrate, ammonium/ammonia, urea, ammonium nitrate (NH_4NO_3), manure-derived organic N, biologically fixed N, atmospheric deposition, or mineralized soil organic N. Neutral reduced-N and mineralizable organic-N precursors are represented as entering the NH_4^+ pool, followed by oxidation to NO_3^- under efficient nitrification. Nitrification releases two moles of H^+ per mole of NH_4^+ oxidized, while the preceding formation of NH_4^+ from neutral reduced-N precursors offsets part of this proton release. NH_4NO_3 contains both reduced and oxidized N and is treated consistently within the same proton balance. Hence, irrespective of the original input form, the fraction ultimately leached as NO_3^- , rather than taken up, immobilized, denitrified, or otherwise removed, is assigned a net acidity contribution of one mole H^+ equivalent per mole N.
- 2) Both plant uptake pathways as well as loss to the atmosphere neutralize the initial addition of acidity. As examples production of N_2 , N_2O , and NO during denitrification all consume 1H^+ per NO_3^- . Similarly, production of NO and NO_2 from nitrification and NH_4^+ volatilization all consume 1 H^+ per mol N, at which point the process is acidity neutral as production of NH_4 consumes one proton per N. Plant uptake is either acidity balanced by direct fluxes of protons, or assumed to balance through charge balance and re-equilibration of the carbonate system.

- 3) In the simplified N-cycle calculations, we assume that mobile NH_4^+ loss is negligible relative to NO_3^- loss for the well-drained agricultural soils considered here. This reflects efficient plant uptake, microbial nitrification, and retention of NH_4^+ on soil exchange sites. While NH_4^+ accumulation or loss can occur locally under waterlogged, strongly nitrification-limited, or high-loading conditions, we treat NO_3^- leaching as the dominant dissolved N pathway contributing to net acidity export at the spatial and temporal scales of this analysis.

a) estimation of acid generation from manure and fertilizer input

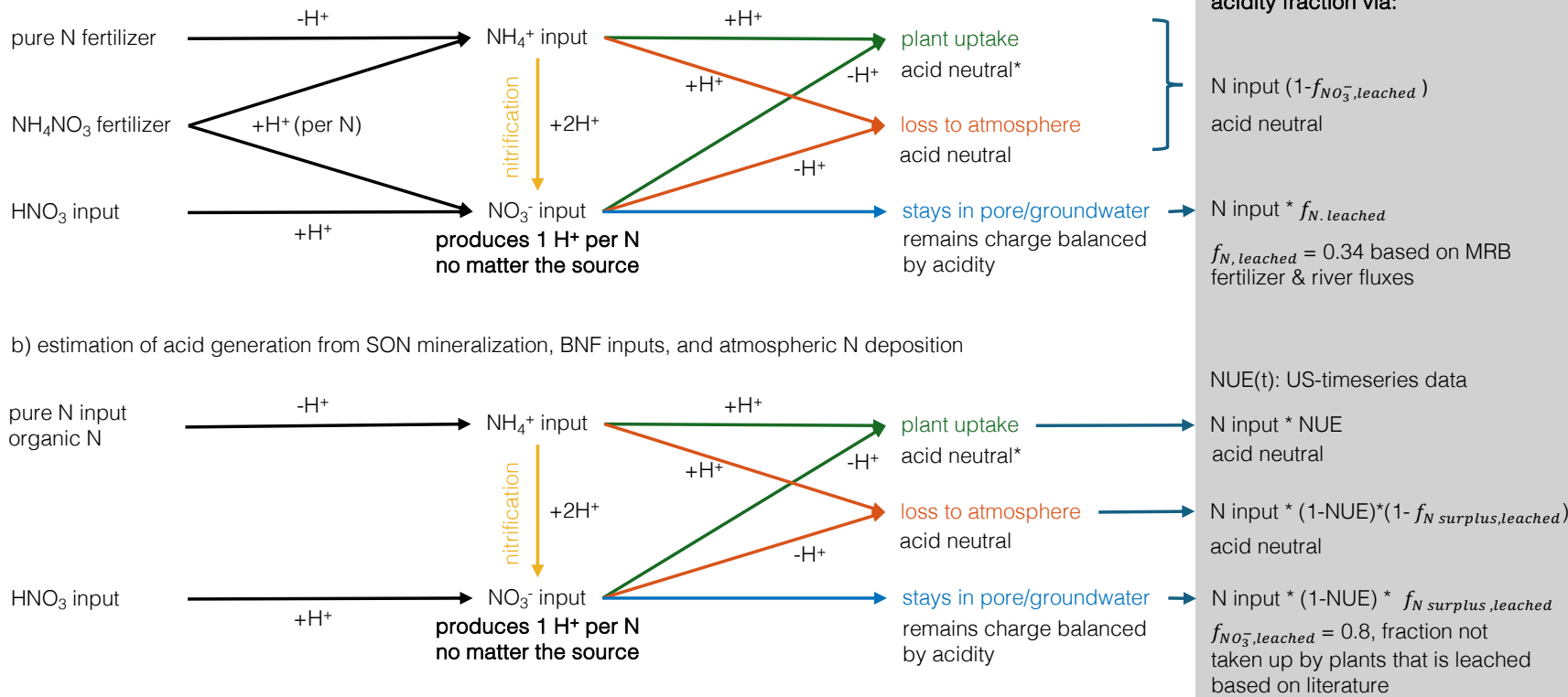


Figure S30: Simplified proton-balance parameterization used to estimate first-order net acidity associated with fertilizer and manure inputs (a), and with SON mineralization, agricultural BNF, and atmospheric N inputs (b), over century and continental scales. Individual arrows indicate proton release or consumption during the represented transformations, whereas only N ultimately leached as NO_3^- is assigned a retained acidity contribution in the integrated accounting. Derived values are intended as first-order estimates that capture spatial patterns and the approximate magnitude of N-derived acidity fluxes over the full spatial and temporal domain considered. Although N removal in harvested biomass could be represented explicitly as an acidity sink, it is already accounted for implicitly because retained acidity is assigned only to the fraction of N not removed through plant uptake and ultimately leached as NO_3^- .

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