Cation trapping by biochar reduces carbon removal efficiency

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Abstract

Biochar may be a scalable and cost-effective means of atmospheric carbon dioxide removal. However, frameworks for quantifying the effectiveness of this carbon removal pathway are still under development. Here, we quantify an initial carbon dioxide removal inefficiency associated with biochar's inherent ability to lock away cations and nitrogen that would otherwise be released back into the environment. Our analysis shows that this decreased flux of cations to soil water systems associated with the formation of biochar leads to a broad range of carbon dioxide removal inefficiency, anywhere from having no impact up to ~40% inefficiency. We argue that biochar's inherent ability to sequester cations and nitrogen and linked changes in carbon fluxes will need to be incorporated into monitoring, reporting, and verification frameworks when biochar is being sold as a means of durable carbon removal.

Keywords

Major cations. Nitrogen. CDR efficiency. Monitoring, reporting, and verification.

Main Text

1. INTRODUCTION

Carbon dioxide removal (CDR) is viewed as an essential part of meeting international climate goals (Intergovernmental Panel On Climate Change (Ipcc), 2023; Lehmann et al., 2021). Most pathways that keep peak climate warming below 2°C will require a dramatic and rapid increase in CDR deployment in the coming decades as a supplement to aggressive decarbonization(Intergovernmental Panel On Climate Change (Ipcc), 2023; Lehmann et al., 2021). Although there is an increasing focus on government procurement programs, to date most CDR projects have been developed and funded through voluntary carbon markets (VCMs) (*Exploring the Future of the Voluntary Carbon Market | Shell Global*). However, there have recently been a series of articles strongly critiquing the efficacy of VCMs (Gill-Wiehl et al., 2024; West et al., 2023). Projects aiming to scale organic carbon storage (e.g., forest and soil management) have proven particularly contentious (Wu et al., 2023). In step with a reevaluation of the efficacy of VCMs and a crash in prices for carbon credits (L, 2023), there have been more vocal calls for investment in "durable" CDR - pathways for which carbon is removed for timescales of at least hundreds of years. There has been a particular focus on the production of biochar (Lefebvre et al., 2023; Lehmann et al., 2021), the persistent form of solid, carbonaceous residue of anoxically pyrolyzed organic matter.

Biochar projects can be implemented in most working lands and potentially deployed at scale. For instance, it has been proposed that biochar has the potential to account for 3 gigatons (Gt = 10^9 tons) of CDR annually (Lefebvre et al., 2023), out of roughly 5-10 Gt/year of CDR necessary by 2050 to meet climate goals (Intergovernmental Panel On Climate Change (Ipcc), 2023). Assuming a nominal price of $100/ton of biochar, this process could rapidly become a >$100 billion dollar/year industry. As carbon removal marketplaces grow, there has been a proliferation of companies aiming to remove carbon via biochar application to soil. Currently, there are more than 250 biochar suppliers listed on the largest CDR supplier database (*CDR Leaderboards — Top Carbon Removal Suppliers, Buyers & Services | CDR.Fyi*, June, 2026), and as of May 2026, these companies have pledged to remove ~16 million tons of carbon dioxide via biochar with more than 1.4 million tons of CDR having already been delivered (*CDR Leaderboards — Top Carbon Removal Suppliers, Buyers & Services* | *CDR.Fyi*, June, 2026). Furthermore, biochar carbon removal sales increased nearly three orders of magnitude between 2020 through 2025 (*CDR Leaderboards — Top Carbon Removal Suppliers, Buyers & Services* | *CDR.Fyi*, June, 2026).

1.1 Definition of biochar

Biochar is produced by pyrolyzing biomass, an anoxic thermochemical process that increases the proportion of organic carbon locked in stable structures (e.g., fused, aromatic rings) resistant to oxidation and degradation (Joseph et al., 2021). There is evidence that biochar can directly benefit farmers as a soil amendment by increasing soil fertility, modulating soil pH, improving water retention, and increasing crop yields, among other benefits (Huang et al., 2023; Joseph et al., 2021; Lehmann et al., 2021). Besides agronomic benefits, biochar can contribute to climate change mitigation—carbon in biochar can persist unmineralized in soil on timescales orders of magnitude longer than biomass carbon. Biochar is also shown to decrease mineralization rates of existing soil organic matter (J. Wang et al., 2016) and ameliorate emissions of greenhouse gasses such as methane and nitrous oxide (Van Zwieten et al., 2015) by increasing total soil pore space and affecting other soil properties.

Existing carbon removal crediting protocols frame biochar as a carbon removal strategy based upon the comparison of two scenarios. In the first scenario, biomass waste is pyrolyzed to produce biochar and amended to soil as an alternative to disposal, meaning organic carbon is transformed into stable, recalcitrant, structures. In the second (counterfactual) scenario, biomass waste is left to decompose back into the soil as a method of disposal; the organic carbon is released back into the environment and natural waters (which, when biochar is being sold as a means of CDR, is assumed to be rapid). Thus the current verifications of carbon removal consider only the fate of organic carbon (Etter et al., 2025; Schimmelpfennig & Glaser, 2012).

1.2 Biochar chemistry in aqueous systems

Studies focusing on the physical structure and characteristics of biochar have observed that cations (e.g. Na, K, Ca, Mg) and anions (e.g. N, S, P, Cl) from the original biomass transform during pyrolysis, depending on biomass feedstock type and pyrolysis temperature, to bond with and embed within the biochar matrix, either through forming dense organometallic complexes, forming protective layers of oxides and carbonates, embedding directly between stable, covalently linked, carbon layers (Buss et al., 2022; Nan et al., 2021; Xu et al., 2017), or electrostatically trapping in micropores of the biochar itself (Joseph et al., 2021). These species are likely to be inert for as long as the biochar is stable, and in fact, have been shown to increase carbon retention during pyrolysis as well as enhance the stability of the biochar itself post pyrolysis (Buss et al., 2022; Nan et al., 2021).

The presence of bound cations and nonmineral species in the biochar matrix is unquestioned (Buss et al., 2022; Nan et al., 2021; Xu et al., 2017) and these trapped species are distinguished from charged mineral species adsorbed onto ion exchange sites of biochar, the presence and concentration of which are affected by the characteristics of the surrounding aqueous medium (e.g., soil porewater (Joseph et al., 2021)). These exchangeable cations and anions are not trapped in the biochar matrix and therefore can interact with other charged species in the soil porewater (Joseph et al., 2021). They are water-soluble and can be leached out of the biochar during laboratory procedures that aim to quantify the 'non-leachable' or entrapped ion content of biochar.

In this study, we compare the same two scenarios of biomass transformation described above but explicitly consider the fate of ions within the original biomass. The fate of ions is of particular interest because of the impact of these ions on charge balance in surface waters—and thus the carbonic acid system and ecosystem-scale carbon fluxes. Depending on metabolic and structural needs, living plants maintain charge balance within their tissue by absorbing and releasing cations and anions (Cunningham, 1964; Dewit & Andjcnoggle, 1963). These species become constituent parts of the biomass. When plants uptake cations, acidity is released from plant roots. When plants uptake anions, mainly nitrogen in the form of nitrate (NO_3^-), bicarbonate is released to maintain charge balance (Cunningham, 1964; Dewit & Andjcnoggle, 1963). In the scenario of biomass degradation, the constituent ions are electroneutral when reentering the biogeochemical cycle and therefore don't induce large-scale charge disturbances in the soil water system. In the scenario of biochar production, a percentage of the biomass's constituent parts, including nitrogen, are lost through volatilization or during quenching, and the biochar can have preferential accumulation of formerly plant-bound cations. The ratio of cations and nitrogen remaining as a part of the biochar will depend on feedstock characteristics and pyrolysis conditions.

Since the exchange of cations and anions from plants takes place in a soil-aqueous system that maintains charge balance via the bicarbonate buffer system,

$$CO_2\,(g) + H_2O\,(l) \leftrightarrow H_2CO_3\,(aq) \leftrightarrow HCO_3^-\,(aq) + H^+\,(aq) \quad (1)$$

an influx of positive charge (cations) is balanced by the increased formation of negatively charged bicarbonate (and carbonate ion) from carbonic acid (Drever, 1988; Zeebe & Wolf-Gladrow, 2001), effectively removing atmospheric carbon. An influx of negative change (anions) is balanced with a shift of the buffer system away from bicarbonate and towards formation of acidic protons, leading to the emission of carbon dioxide (Drever, 1988; Zeebe & Wolf-Gladrow, 2001). Since bicarbonate is exported from soil into the oceans to remain stable for thousands of years (DeVries, 2022; Drever, 1988), the change in concentration of bicarbonate due to the change in cation to anion ratio present in the soil system represents a change in transfer of carbon from a pool that will exchange with the atmosphere to a pool that will be exported in surface waters (Brady et al., 2010; Zeebe & Wolf-Gladrow, 2001).

The comparison of the two biomass use scenarios described above functionally represents a change in the ratio of cations to anions present in an agroecosystem over the lifetime of biochar. By the charge balance principle described above, cation uptake by biochar during pyrolysis would mean that those cations are removed from the biogeochemical cycle, functionally translating to an increase in negative charge in the soil porewater, compelling charge balance to be maintained by the formation of acidic protons – a carbon emitting process. Similarly, nitrogen (from biomass nitrate) uptake by biochar during pyrolysis means that nitrogen is essentially removed from the nitrogen cycle, which functionally translates to an increase in positive charge in the soil porewater. This would foster charge balance to be maintained through carbonate formation—a carbon negative process. However, in the counterfactual scenario, nitrate will eventually be released into the atmosphere via denitrification within biological timescales (a timeframe that varies from days to decades depending on the site), eventually leading to more extensive bicarbonate and carbonate ion formation. Therefore, the potential gain in system level accounting from nitrate uptake by biochar during pyrolysis compared to the biomass degradation scenario is not permeant and the time frame of this effect may be difficult to estimate.

1.2.1 The geochemistry implications of biochar

Comparing the effect of ion entrapment in biochar with ion release during biomass degradation within agroecosystems helps us better understand the long-term carbon and cation storage potential of biochar. As described above, the varying fate of the nitrogen and cations in the two biomass use scenarios will have a divergent effect on carbon removal. A drop in the alkalinity flux from soil—lower soil bicarbonate export—in a full carbon accounting scheme represents a reduction in biochar's overall CDR efficiency. Although biochar cation and nitrogen entrapment and charge balance in soil waters are both well-established concepts (Brady et al., 2010; Buss et al., 2022; Drever, 1988; Nan et al., 2021; Xu et al., 2017; Zeebe & Wolf-Gladrow, 2001), there has not yet been a consideration of how these processes affect the efficiency of biochar as a means of carbon dioxide removal.

We explore how biochar's carbon removal efficiency changes when considering the geochemical side of biochar by comparing two scenarios of biomass transformation—biochar production and biomass decay—with regards to the aqueous system, assuming all other aspects of the background aqueous systems, such as sources of acidity (HNO_3, H_2SO_4) and anionic charge from fertilization activity (NO_3^-, SO_4^{2-}, Cl^-), remain consistent. In other words, the only difference between the two scenarios is the ratio of cations and nitrogen present in the system. Our initial survey is built from a new database of peer-reviewed literature that pairs biochar's recalcitrant carbon stocks with trapped cation and nitrogen content. We focus on trapped cation and nitrogen values that are derived from procedures that have had exchangeable ions removed, ensuring that biochar-associated cations and nitrogen are structurally bound. This analysis is grounded in several underlying assumptions: (1) charge balance in soils, in the absence of shifts in conservative anions, is maintained by the carbonic acid system. To further simplify we assumed charge balance through bicarbonate formation (instead of carbonate ion and bicarbonate ion); (2) cations and nitrogen entrapped in the biochar matrix would have, without pyrolysis, been released into the environment through biomass decay, and would go on to impact the aqueous acid-base balance in the stoichiometrically appropriate ratio (i.e. 1 mol of a doubly charged cation charge balances 2 mol of singly charged anion (e.g., bicarbonate)); (3) between 60% (low recalcitrance rate) and 82% (high recalcitrance rate) of organic carbon in biochar is recalcitrant (stable on a 100+ year timescale (15)).

Building from this framework and our compilation of the chemical composition of biochar, we quantify the impacts of cation and nitrogen trapping on the overall carbon removal inefficiency of biochar when added to soil. Lastly, we build on this analysis with a discussion of the long-term fate of cations and nitrate in soils and surface waters. We do not provide any direct recommendations for how these effects should be incorporated into carbon removal accounting protocols. However, this work supports the notion that the CDR inefficiency we identify can be significant and provides impetus for monitoring the geochemical side of biochar to optimize investment in this process for carbon removal potential.

2. MATERIALS AND METHODS

Based on a literature review of diverse types of biochar (see SI), we collated information about elemental composition of base cations (i.e. Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}), anions (i.e. NO_3^{-} and SO_4^{2-} (when provided)), and the biochar's percent organic carbon. Chlorine and phosphate are not included in this database because of persistent lack of reporting.

Charge stoichiometry was used to determine the amount of bicarbonate affected by the cation to anion ratio present in biochar. Change in bicarbonate flux (mol/kg) associated with the biochar was converted to CO_2 emissions by assuming a 1:1 ratio of bicarbonate to CO_2 loss. For example, biochar containing 1 mole per kilogram of cationic charge would affect 1 mole of bicarbonate, leading to the emission of 1 mole of CO_2, when compared to the scenario of no biochar production. After converting cationic charge data given in percent concentration to units of grams of CO_2 eq emitted per kilogram of biochar and percent organic carbon to grams of CO_2 eq removed per kilogram of biochar, percent CDR inefficiency was calculated using the following equation:

$$\%\, CDR\ inefficiency = 1 - \left[\frac{CO_2 eq\ removed - CO_2\ eq\ emitted}{CO_2 eq\ removed} * 100\right]$$

Biochar's cation concentrations in the database are from studies that first leached out the exchangeable fraction of cations and then carried out elemental analysis of the biochar. Elemental data was derived from either X-ray fluorescence analysis or experimentally determined by digesting and analyzing biochar. We avoided older manuscripts (<2005). However, this had a small effect on database size given the increase in biochar work in recent years. Since Woolf et al. (2021) determines that carbonaceous material containing less than 10% organic carbon does not constitute as biochar, we also did not include low organic carbon pyrolysis products.

3. RESULTS

Our analysis suggests that cation trapping during biochar production from waste biomass feedstock can have a non-negligible impact on the overall carbon removal associated with biochar amendment to soil. Our database comprises of forty studies, some of which are review papers embedded with additional studies. Comparison of reductions in carbon export from soils driven by biochar cation trapping relative to the counterfactual scenario with durable carbon removal driven by recalcitrant carbon storage across our dataset yields a mean carbon removal inefficiency of 4.2% and 3.1% and a median of 1.3% and

0.94% at a biochar recalcitrance of 60% and 82%, respectively (**Fig. 1**). Additionally, we find that calculated CDR inefficiency covers a broad range within the two recalcitrance categories, from -45.6% to 43.6% at a recalcitrance of 82% and from -62.3% to 59.7% at a recalcitrance of 60%. Taken together, about ~30% of biochar in our database have a CDR inefficiency greater than 5%.

A biochar containing more anion charge than cation charge, reflected by a negative carbon removal inefficiency value, would remove more carbon than initially calculated by solely considering recalcitrant organic carbon storage, relative to the counterfactual scenario. In our database, ~20% of biochar contains more anion charge, i.e. has trapped more nitrogen from the feedstock biomass than cation charge (**Fig. 2**). Only ~7% of biochar within our database had less than -5% inefficiency (**Fig. 2**), meaning those biochar remove more carbon than calculated by solely considering recalcitrant organic carbon storage.

For a specific example, biochar from grapevine residue consisting of 77% organic carbon removes 2,319 gCO_2 eq per kilogram of biochar when solely considering the biochar's recalcitrant organic carbon content at a recalcitrance of 80%. However, this biochar also contains 162 moles of base cation charge per kilogram of biochar and 28 moles of anion charge per kilogram of biochar. If we assumed the cations would have been rapidly recycled back to soil and charge balanced by bicarbonate export when the wood rapidly decayed (the central assumption behind selling biochar as a form of carbon removal), this overall cation trapping has thus reduced soil bicarbonate export relative to the counterfactual scenario by 588 gCO_2 eq per kilogram of biochar, representing an overall carbon removal inefficiency of ~25% relative to that calculated solely by consideration of recalcitrant organic carbon storage. In contrast, biochar from eucalyptus wood consisting of 70% organic carbon, 6.5 moles of base cation charge per kilogram of biochar, and 2 moles of anion charge per kilogram of biochar removes 2,094 gCO_2 eq per kilogram of biochar as recalcitrant carbon at a biochar recalcitrance of 80% but reduces bicarbonate export relative to the counterfactual by only 20 gCO2 eq per kilogram of biochar—a much smaller carbon removal inefficiency of ~1%.

4. DISCUSSION

We present a data compilation and a simple framework to demonstrate that consideration of cation and nitrogen uptake by biochar can affect the overall CDR efficiency estimates of biochar deployments. This indicates that estimates of long term carbon removal in existing frameworks can be incorrect. However, it is already common to overestimate long-term biochar CDR rates—in cases where biochar preferentially binds Ca and Mg ions. Our data compilation allows us to provide an initial assessment of the impact of base cation trapping in biochar on carbon removal effectiveness at the moment of biochar deployment and payment transfer between biochar credit buyers and suppliers.

A process not explored in this study is the potential impact of biochar's cation and anion exchange capacity (CEC) on base cation cycling and bicarbonate production. Depending on how biochar is aged prior to deployment and ages after deployment, additional cation adsorption at biochar exchange sites and thus a decreased cation flux could further reduce overall carbon removal efficiency (Li et al., 2019; L. Wang et al., 2020). Additionally, the long-term (>100 years) aging of the recalcitrant biochar matrix will eventually release the stored carbon, cations, and nitrogen back into the environment, a consideration also not included in this analysis. While we know that cations can form secondary phases in porewater upon release and that nitrate will enter the aqueous system in the form of nitrate and eventually undergo denitrification, little to no data describing the mechanisms and timescales of the release of these species from biochar exist in the literature. Constraining changes in cation sorption as biochar ages within compost or soil also represents an important area of future work and should be further investigated in projects in which biochar is being used to credit carbon removal.

Carbon crediting and the verification provided by carbon removal crediting platforms (e.g., Verra, Isometric, and Puro) represent the currency of VCMs, allowing purchasers to pay carbon removal suppliers at set prices determined by the life cycle analysis of biochar projects. Although current verification methodologies used to issue biochar carbon credits consider greenhouse gases emitted during feedstock transport, biochar production, transport, and application, and changes to carbon removal permanence as biochar ages (Etter et al., 2025; Schimmelpfennig & Glaser, 2012), no current verification methodologies consider the CDR inefficiency introduced by cationic charge trapping after biochar has been added to soil and the fate of the cations is unaccounted for. The life cycle assessment of these projects may be robust, but this represents a flaw in the carbon accounting of this system (Nordahl et al., 2024). Ultimately, assuming the goal of CDR is carbon removal from the atmosphere, the costs of CDR from biochar have been underestimated and CDR potentials correspondingly overestimated. However, the magnitude of this effect will likely vary considerably between projects, with limited effect on many projects. Therefore, we suggest that biochar CDR quantification frameworks should be updated to consider base cation trapping. Additional research on the long-term effect of this process will be critical for accurate and responsible scaling of carbon removal through biochar amendment to soil.

Figures

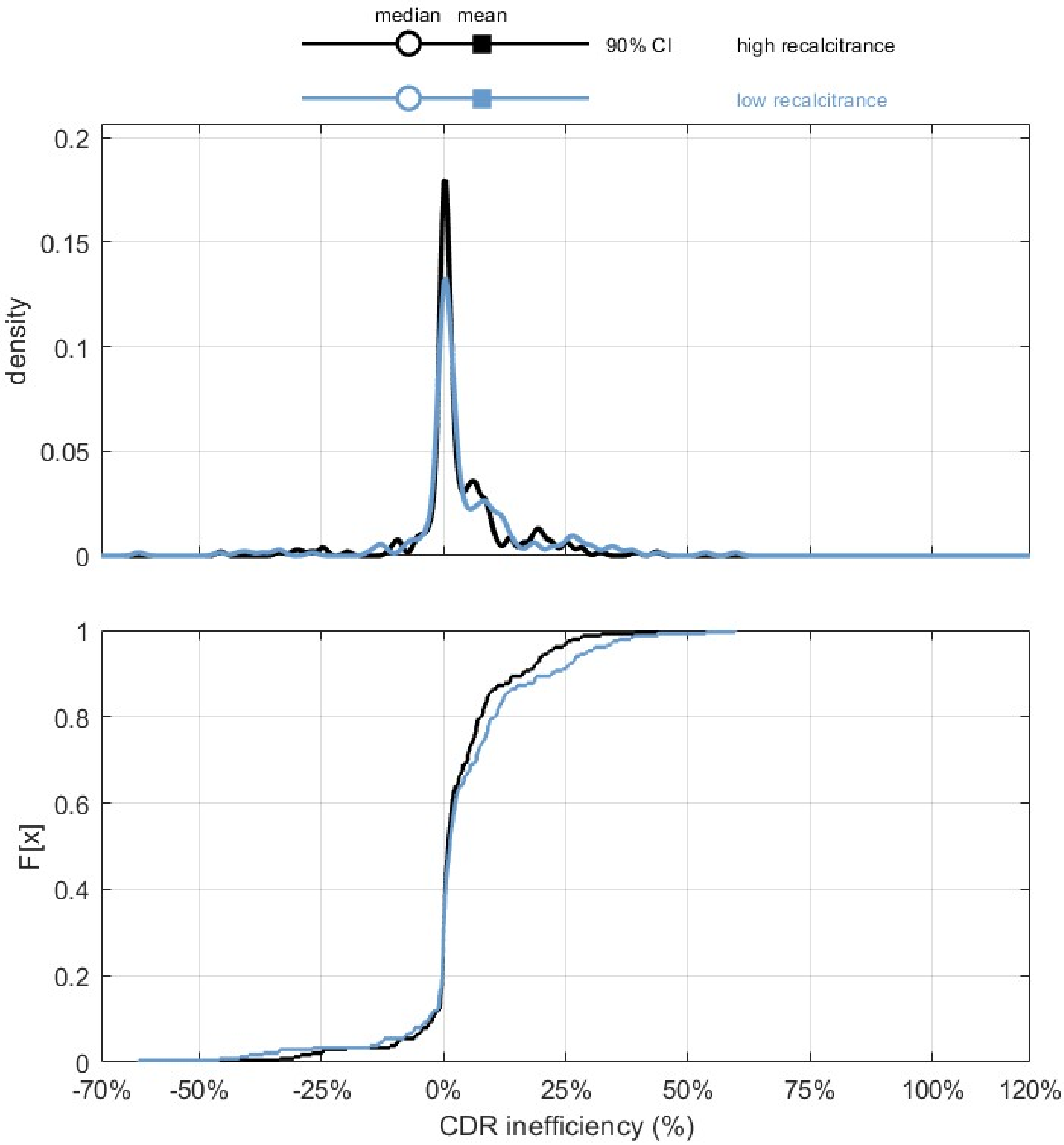

Fig. 1. Kernel density distributions (A) and cumulative frequency distributions (B) for carbon dioxide removal inefficiency linked to cation entrapment for a wide range of

biochar types. Low recalcitrance assumes 60% durability and high recalcitrance assumes 82% durability over a 100-year period.

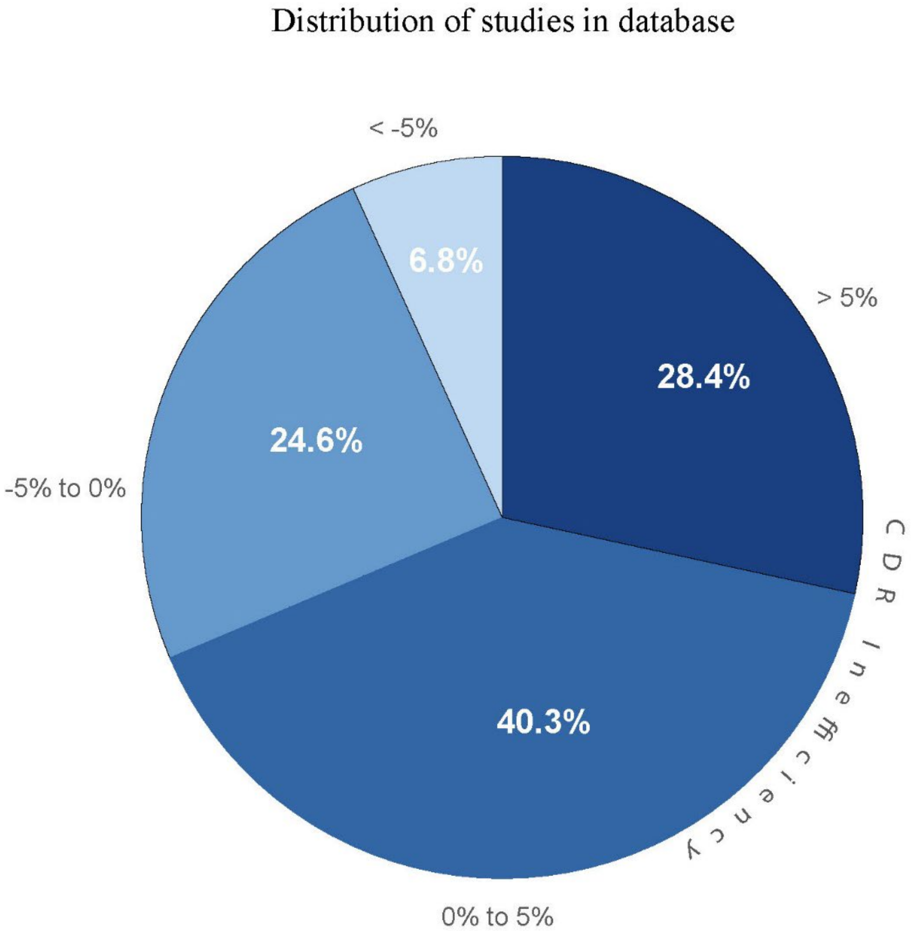

Fig. 2: Pie chart shows the distribution of biochar entries in the database according to CDR inefficiency. For example, 28.4% of biochar in the database have an entrapped cation driven CDR inefficiency of greater than 5%.

Acknowledgments

We acknowledge funding from Yale Center for Natural Carbon Capture and the Grantham Foundation. NJP acknowledges support from Environmental Defense Fund.

Author Contributions

All authors designed research. A.A.A. performed research. A.A.A. and N.J.P. analyzed data. A.A.A, N.J.P. and C.T.R. wrote the paper. T.J.S. and C.T.R edited and provided feedback. C.T.R. drafted final figures.

Conflict of Interest

Authors declare no competing interests.

Data and Supplementary Information

Biochar major cation and nitrogen content database in the form of a table is included in the supplementary information.

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