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Parameter-Minimal Analysis of Carbon Dioxide Removal through Direct Air Capture

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Abstract

In detailed Earth models that require extensive computation time, it is difficult to make an a priori prediction of the possibility of multistationarity. The potential for multistationarity, or the existence of steady-state multiplicity, in the Earth System raises concerns that the planet could reach a climatic 'tipping point,' rapidly transitioning to a warmer steady-state from which recovery may be practically unattainable. In this study, we demonstrate Chemical

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Reaction Network Theory (CRNT) analysis of a simple heuristic box model of the Earth System carbon cycle with the human intervention of Direct Air Capture. CRNT leverages parameter-minimal analysis, relying primarily on the graphical and kinetic structure of the reaction network system, to identify necessary conditions for steady-state multiplicity. The analysis reveals necessary conditions for the combination of system parameters where steady-state multiplicity may exist. Moreover, the analysis provides insights into key system properties, such as absolute concentration robustness and some conditions for atmospheric carbon reduction.

1 Introduction

As researchers explore the intricate dynamics of climate change, the notion of climate tipping points has emerged as a key area of interest [1, 2, 5, 9]. These tipping points represent moments when the climate system reaches a threshold and undergoes self-perpetuating changes, leading to profound and possibly irreversible impacts on our planet. Understanding and anticipating these tipping points is essential to formulate successful approaches for lessening the impact of climate change. Researchers have developed sophisticated models, primarily utilizing numerical simulations, to simulate the intricate dynamics of multistationarity in the global carbon system [5]. However, the challenge lies in pinpointing the precise conditions that can trigger multistationarity within the system [2, 20, 23, 24].

In this study, we explore the possibility of a global carbon system to exhibit multiple steady states by employing a methodology based on reaction networks. The process entails constructing a reaction network that mirrors the dynamic behavior and properties of the global carbon system. By applying chemical reaction network theory (CRNT), key characteristics, including the system's potential for multiple steady states, are efficiently identified. In addition, the analysis offers valuable insights into essential system characteristics, such as absolute concentration robustness, along with specific conditions for the reduction of atmospheric carbon.

Specifically, we analyze a global carbon cycle system that involves carbon dioxide removal (CDR) technology. CDR technologies encompass a variety of methods such as afforestation, reforestation, direct air capture, and bioenergy with carbon capture and storage [12, 18]. Implementing CDR technologies is seen as vital in achieving the goals set out in the Paris Agreement, which aims to keep the global mean surface temperature well below 2°C and target 1.5°C [16].

Our analysis focuses on a global carbon system with Direct Air Capture (DAC) intervention. In this technology, carbon dioxide is directly captured from the atmosphere using chemical absorbents. The captured carbon is securely stored in geological formations, preventing its release back into the atmosphere [18, 23].

The proposed CRNT approach provides a unique advantage by focusing on the topological features and kinetics of the network itself, eliminating the need to define system rate constants. This feature is especially beneficial when studying systems where such parameter values are unknown. By enabling a rate-constant-minimal analysis, CRNT promises to be a useful tool for revealing the intricacies of systems with uncertain rate-constant data, thereby providing critical insights into the dynamic behavior of the global carbon system.

This paper continues with the following structure: Section 2 establishes the necessary background by reviewing preliminary concepts in CRNT. Section 3 presents the global carbon cycle model and elaborates on the process of obtaining its dynamically equivalent power-law kinetic representation. Section 4 discusses the relevant dynamical properties of the system, using the kinetic representation derived in Section 3 and tools from CRNT. Lastly, Section 5 synthesizes the key results from the preceding analysis and points towards future research directions.

2 Fundamentals of reaction networks and kinetic systems

As preparation for the paper's analysis, we outline some foundational concepts pertaining to chemical reaction networks and chemical kinetic systems.

Notation

We denote the real numbers by $\mathbb{R}$, the non-negative real numbers by $\mathbb{R}_{\geq 0}$ and the positive real numbers by $\mathbb{R}_{>0}$. Objects in reaction systems are viewed as members of vector spaces. Suppose $\mathscr{I}$ is a finite index set. By $\mathbb{R}^{\mathscr{I}}$, we mean the usual vector space of real-valued functions with domain $\mathscr{I}$. If $x \in \mathbb{R}^{\mathscr{I}}_{>0}$ and $y \in \mathbb{R}^{\mathscr{I}}$, we define $x^y \in \mathbb{R}_{>0}$ by $x^y = \prod_{i \in \mathscr{I}} x_i^{y_i}$. Let $x \wedge y$ be the component-wise minimum, $(x \wedge y)_i = \min(x_i, y_i)$. The vector $\log x \in \mathbb{R}^{\mathscr{I}}$,where $x \in \mathbb{R}^{\mathscr{I}}_{>0}$, is given by $(\log x)_i = \log x_i$, for all $i \in \mathscr{I}$. The *support* of $x \in \mathbb{R}^{\mathscr{I}}$, denoted by supp x, is given by supp $x := \{i \in \mathscr{I} \mid x_i \neq 0\}$.

2.1 Fundamentals of chemical reaction networks

A chemical reaction network or CRN is a finite set of interdependent reactions that happen simultaneously. In an abstract sense, it can serve as a representation of any system whose evolution is driven by the transformation of its elements into different elements. The fundamental element of a chemical reaction is the *species.* The chemical species can encompass a range of entities, including chemical elements, molecules, or proteins. In this study, the species represent various carbon pools involved in the system. A *complex* is a nonnegative linear combination of the species. Put another way, a complex is the set of species with associated nonnegative coefficients (called *stoichiometric coefficients*). A chemical reaction is typically written as

$$\text{Reactant complex} \rightarrow \text{Product complex},$$

where the set of species on the left side of the equation (*reactant complex*) are consumed or transformed to form the set of species on the right side (*product complex*).

Formally, we define a CRN as follows.

Definition 1. A **chemical reaction network** or CRN is a triple $\mathscr{N} := (\mathscr{S}, \mathscr{C}, \mathscr{R})$ of nonempty finite sets $\mathscr{S}$, $\mathscr{C}$, and $\mathscr{R}$, of m **species**, n **complexes**, and r **reactions**, respectively, where $\mathscr{C} \subseteq \mathbb{R}^{\mathscr{S}}_{\geq 0}$ and $\mathscr{R} \subset \mathscr{C} \times \mathscr{C}$

satisfying the following properties:

(i) $(y, y) \notin \mathscr{R}$ for any $y \in \mathscr{C}$;

(ii) for each $y \in \mathscr{C}$, there exists $y' \in \mathscr{C}$ such that $(y, y') \in \mathscr{R}$ or $(y', y) \in \mathscr{R}$.

For $y \in \mathscr{C}$, the vector

$$y = \sum_{A \in \mathscr{S}} y_A A,$$

where y_A is the **stoichiometric coefficient** of the species A. In lieu of $(y, y') \in \mathscr{R}$, we write the more suggestive notation $y \to y'$. In this reaction, the vector y is called the **reactant complex** and y' is called the **product complex**.

We can view every complex in a CRN as a vector in a vector space called **species space** $\mathbb{R}^{\mathscr{S}}$, whose coordinates refer to the coefficients or stoichiometry of the different species. In this way, every reaction may also be associated with a vector, called **reaction vector**, which is formed by subtracting the reactant complex vector from the product complex vector.

Example 1. Consider the following CRN with five species, A_1, A_2, A_3, A_4, A_5, and seven reactions.

Reaction	**Reactant**	**Product**	**Reaction vector**
$A_1 + 2A_2 \to 2A_1 + A_2$	$[1, 2, 0, 0, 0]^\top$	$[2, 1, 0, 0, 0]^\top$	$[1, -1, 0, 0, 0]^\top$
$2A_1 + A_2 \to A_1 + 2A_2$	$[2, 1, 0, 0, 0]^\top$	$[1, 2, 0, 0, 0]^\top$	$[-1, 1, 0, 0, 0]^\top$
$A_2 \to A_3$	$[0, 1, 0, 0, 0]^\top$	$[0, 0, 1, 0, 0]^\top$	$[0, -1, 1, 0, 0]^\top$
$A_3 \to A_2$	$[0, 0, 1, 0, 0]^\top$	$[0, 1, 0, 0, 0]^\top$	$[0, 1, -1, 0, 0]^\top$
$A_4 \to A_2$	$[0, 0, 0, 1, 0]^\top$	$[0, 1, 0, 0, 0]^\top$	$[0, 1, 0, -1, 0]^\top$
$A_2 \to A_5$	$[0, 1, 0, 0, 0]^\top$	$[0, 0, 0, 0, 1]^\top$	$[0, -1, 0, 0, 1]^\top$
$A_5 \to A_4$	$[0, 0, 0, 0, 1]^\top$	$[0, 0, 0, 1, 0]^\top$	$[0, 0, 0, 1, -1]^\top$

From a dynamic perspective, every reaction $y \to y' \in \mathscr{R}$ leads to a change in species concentrations proportional to the reaction vector $(y' - y) \in \mathbb{R}^{\mathscr{S}}$. The overall change induced by all the reactions lies in a subspace of $\mathbb{R}^{\mathscr{S}}$ such that any trajectory in $\mathbb{R}^{\mathscr{S}}_{>0}$ lies in a coset of this subspace.

Definition 2. The **stoichiometric subspace** of a network $\mathscr{N}$ is given by

$$\mathcal{S} := \text{span}\ \{y' - y \in \mathbb{R}^{\mathscr{S}} \mid y \to y' \in \mathscr{R}\}.$$

The **rank** of the network is defined as $s := \dim \mathcal{S}$. For $x \in \mathbb{R}^{\mathscr{S}}_{>0}$, its **stoichiometric compatibility class** is defined as $(x + \mathcal{S}) \cap \mathbb{R}^{\mathscr{S}}_{\geq 0}$. Two vectors $x^*, x^{**} \in \mathbb{R}^{\mathscr{S}}$ are **stoichiometrically compatible** if $x^{**} - x^* \in \mathcal{S}$.

Definition 3. A CRN with stoichiometric subspace $\mathcal{S}$ is said to be **conservative** if there exists a positive vector $x \in \mathbb{R}^{\mathscr{S}}_{>}$ such that $S^{\perp} \cap \mathbb{R}^{\mathscr{S}}_{>} \neq \emptyset$.

The stoichiometric subspace $\mathcal{S}$ of the CRN is Example 1 is spanned by the following vectors:

$$\left\{ \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 0 \\ 0 \\ 1 \end{bmatrix} \right\}.$$

Since $\mathcal{S}$ has 4 basis vectors, the rank of the CRN is 4. Moreover, it is conservative since there exists a positive vector, say $[k, k, k, k, k]^{\top}$ with $k \in \mathbb{R}$, that is orthogonal to all reaction vectors.

CRNs can be viewed as directed graphs where the complexes are vertices and the reactions are arcs. A group of complexes that are connected by arrows is referred to as a **linkage class**. Hence, in Example 1 there two linkage classes: $\{A_1 + 2A_2 \rightleftarrows 2A_1 + A2\}$ and $\{A_2 \rightleftarrows A_3, A_4 \to A_2, A_2 \to A_5, A_5 \to A_4\}$.

The strongly connected components of a CRN are precisely the **strong linkage classes** of the CRN. A strong linkage class is a **terminal strong linkage class** if there is no reaction from a complex in the strong linkage class to a complex outside the given strong linkage class.

Definition 4. A CRN with n complexes, n_r reactant complexes, ℓ linkage classes, $s\ell$ strong linkage classes, and t terminal strong linkage classes is

(i) **weakly reversible** if $s\ell = \ell$;

(ii) ***t*-minimal** if $t = \ell$;

(iii) **point terminal** if $t = n - n_r$; and

(iv) **cycle terminal** if $n - n_r = 0$.

Clearly, the CRN in Example 1 is weakly reversible, t-minimal, and cycle terminal.

An important structural index of a CRN, called *deficiency*, provides one way to classify networks.

Definition 5. The **deficiency** δ of a CRN with n complexes, ℓ linkage classes, and rank s is defined as $\delta := n - \ell - s$.

This index, independent of network size, measures the "linear independence" of reactions: higher deficiency indicates less linear independence. Even large or complex CRNs can have a deficiency of zero [28].

Example 1 provides a deficiency-zero CRN since it has 6 complexes, 2 linkage classes, and its rank is 4.

2.2 Fundamentals of chemical kinetic systems

It is generally assumed that the rate of a reaction $y \to y' \in \mathscr{R}$ depends on the concentrations of the species in the reaction. The exact form of the non-negative real-valued rate function $K_{y \to y'}$ depends on the underlying *kinetics.*

The following definition of kinetics is expressed in a more general context than what one typically finds in CRNT literature.

Definition 6. A **kinetics** for a network $\mathscr{N} = (\mathscr{S}, \mathscr{C}, \mathscr{R})$ is an assignment to each reaction $y \to y' \in \mathscr{R}$ a rate function $K_{y \to y'} : \Omega_K \to \mathbb{R}_{\geq 0}$, where Ω_K is a set such that $\mathbb{R}^{\mathscr{S}}_{>0} \subseteq \Omega_K \subseteq \mathbb{R}^{\mathscr{S}}_{\geq 0}$, $x \wedge x^* \in \Omega_K$ whenever $x, x^* \in \Omega_K$, and $K_{y \to y'}(x) \geq 0$ for all $x \in \Omega_K$. A kinetics for a network $\mathscr{N}$ is denoted by $K : \Omega_K \to \mathbb{R}^{\mathscr{R}}_{\geq 0}$ ([36]). A **chemical kinetics** is a kinetics K satisfying the condition that for each $y \to y' \in \mathscr{R}$, $K_{y \to y'}(x) > 0$ if and only if $\operatorname{supp} y \subset \operatorname{supp} x$. The pair $(\mathscr{N}, K)$ is called a **chemical kinetic system** ([4]).

The system of ordinary differential equations that govern the dynamics of a CRN is defined as follows.

Definition 7. The **ordinary differential equation (ODE)** associated with a chemical kinetic system $(\mathscr{N}, K)$ is defined as $\dfrac{dx}{dt} = f(x)$ with **species formation rate function**

$$f(x) = \sum_{y \to y' \in \mathscr{R}} K_{y \to y'}(x)(y' - y). \tag{1}$$

A **positive equilibrium** or **steady state** x is an element of $\mathbb{R}^{\mathscr{S}}_{>0}$ for which $f(x) = 0$.

Definition 8. The **set of positive equilibria** or **steady states** of a chemical kinetic system $(\mathscr{N}, K)$ is given by

$$E_+(\mathscr{N}, K) = \{x \in \mathbb{R}^{\mathscr{S}}_{>0} \mid f(x) = 0\}.$$

For brevity, we also denote this set by E_+. The chemical kinetic system is said to be **multistationary** (or has the capacity to admit **multiple steady states**) if there exist positive rate constants such that $\mid E_+ \cap \mathcal{P} \mid \geq 2$ for some positive stoichiometric compatibility class $\mathcal{P}$. On the other hand, it is **monostationary** if $\mid E_+ \cap \mathcal{P} \mid \leq 1$ for all positive stoichiometric compatibility class $\mathcal{P}$.

Definition 9. The reaction vectors of a CRN $(\mathscr{S}, \mathscr{C}, \mathscr{R})$ are **positively dependent** if for each reaction $y \to y' \in \mathscr{R}$, there exists a positive number $k_{y \to y'}$ such that $\sum_{y \to y' \in \mathscr{R}} k_{y \to y'}(y' - y) = 0$.

Remark. In view of Definitions 7 and 8, a necessary condition for a chemical kinetic system to admit a positive steady state is that its reaction vectors are positively dependent.

To reformulate the species formation rate function in Eq. (1), we consider the natural basis vectors $\omega_i \in \mathbb{R}^{\mathscr{I}}$ where $i \in \mathscr{I} = \mathscr{C}$ or $\mathscr{R}$ and define

(i) the **molecularity map** $Y : \mathbb{R}^{\mathscr{C}} \to \mathbb{R}^{\mathscr{S}}$ with $Y(\omega_y) = y$;

(ii) the **incidence map** $I_a : \mathbb{R}^{\mathscr{R}} \to \mathbb{R}^{\mathscr{S}}$ with $I_a(\omega_{y \to y'}) = \omega_{y'} - \omega_y$; and

(iii) the **stoichiometric map** $N : \mathbb{R}^{\mathscr{R}} \to \mathbb{R}^{\mathscr{S}}$ with $N = YI_a$.

Hence, Eq. (1) can be rewritten as $f(x) = YI_aK(x) = NK(x)$. The positive steady states of a chemical kinetic system that satisfies $I_aK(x) = 0$ are called *complex balancing equlibria.*

Definition 10. The **set of complex balanced equilibria** of a chemical kinetic system $(\mathscr{N}, K)$ is the set

$$Z_+(\mathscr{N}, K) = \{x \in \mathbb{R}^{\mathscr{S}}_{>0} \mid I_aK(x) = 0\} \subseteq E_+(\mathscr{N}, K).$$

A chemical kinetic system is said to be **complex balanced** if it has a complex balanced equilibrium.

We define power law kinetics through the $r \times m$ **kinetic order matrix** $F = [F_{ij}]$, where $F_{ij} \in \mathbb{R}$ encodes the kinetic order the jth species of the reactant complex in the ith reaction. Further, consider the **rate vector** $k \in \mathbb{R}^{\mathscr{R}}_{>0}$, where $k_i \in \mathbb{R}_{>0}$ is the rate constant in the ith reaction.

Definition 11. A kinetics $K : \mathbb{R}^{\mathscr{S}}_{>0} \to \mathbb{R}^{\mathscr{R}}$ is a **power law kinetics** or **PLK** if

$$K_i(x) = \kappa_i x^{(F_{i,*})^\top} \quad \text{for all } i \in \mathscr{R},$$

where $F_{i,*}$ is the row vector containing the kinetic orders of the species of the reactant complex in the ith reaction.

Definition 12. A PLK system has **reactant-determined kinetics** (or of type **PL-RDK**) if for any two **branching reactions** i, $j \in \mathscr{R}$ (i.e., reactions sharing a common reactant complex), the corresponding rows of kinetic orders in F are identical. That is, $F_{ih} = F_{jh}$ for all $h \in \mathscr{S}$.

Definition 13. The $m \times n$ matrix $\widetilde{Y}$ defined by Müller and Regensburger [22] is the matrix $(\widetilde{Y})_{ij} = F_{ki}$ if j is a reactant complex of reaction k and $(\widetilde{Y})_{ij} = 0$, otherwise. The $m \times n_r$ ***T*-matrix** is the truncated $\widetilde{Y}$ where the non-reactant columns are deleted and n_r is the number of reactant complexes.

2.3 Independent decomposition of a CRN

Decomposition theory was initiated by M. Feinberg in his 1987 review paper [7]. He introduced the general concept of a network decomposition of a CRN as a union of subnetworks whose reaction sets form a partition of the network's set of reactions. He also introduced the so-called *independent decomposition* of chemical reaction networks.

Definition 14. A decomposition of a CRN $\mathscr{N}$ into k subnetworks of the form $\mathscr{N} = \mathscr{N}_1 \cup \cdots \cup \mathscr{N}_k$ is **independent** if its stoichiometric subspace is equal to the direct sum of the stoichiometric subspaces of its subnetworks, i.e., $\mathcal{S} = \mathcal{S}_1 \oplus \cdots \oplus \mathcal{S}_k$. Equivalently, the decomposition is independent if $s = s_1 + \cdots + s_k$.

For an independent decomposition, Feinberg concluded that any positive equilibrium of the "parent network" is also a positive equilibrium of each subnetwork.

Theorem 1 (Rem. 5.4, [7])**.** *Let* $(\mathscr{N}, K)$ *be a chemical kinetic system with partition* $\{\mathscr{R}_1, \ldots, \mathscr{R}_k\}$*. If* $\mathscr{N} = \mathscr{N}_1 \cup \cdots \cup \mathscr{N}_k$ *is the network decomposition generated by the partition and* $E_+(\mathscr{N}_i, K_i) = \{x \in \mathbb{R}^{\mathscr{S}}_{>0} \mid N_i K_i(x) = 0, i = 1, \ldots, k\}$*, then* $\bigcap_{i=1}^{k} E_+(\mathscr{N}_i, K_i) \subseteq E_+(\mathscr{N}, K)$*. If the network decomposition is independent, then equality holds.*

2.4 Absolute concentration robustness in PLP systems

A chemical kinetic system is said to be *absolute concentration robust* in the species $A \in \mathscr{S}$ if c^*_A does not depend on the initial conditions and attains the same value in every positive equilibrium concentration $c^* \in \mathbb{R}^{\mathscr{S}}_{>}$.

Definition 15. A CKS $(\mathscr{N}, K)$ has **absolute concentration robustness** (ACR) in a species $A \in \mathscr{S}$ if there exists $c^* \in E_+(\mathscr{N}, K)$ and for every other $c^{**} \in E_+(\mathscr{N}, K)$, we have $c^{**}_A = c^*_A$.

Lao et al. [19] developed the *Species Hyperplane Criterion* for absolute concentration robustness for a large class of chemical kinetic system called positive equilibria log-parametrized (PLP) kinetic system:

Definition 16. For a reaction network $\mathscr{N}$ with species $\mathscr{S}$, a **log-parameterized (LP) set** is a non-empty set of the form

$$E(P, x^*) = \{x \in \mathbb{R}^{\mathscr{S}}_{>0} \mid \log x - \log x^* \in P^{\perp}\},$$

where P (called the LP set's **flux subspace**) is a subspace of $\mathbb{R}^{\mathscr{S}}$, x^* (called the LP's **reference point**) is a given element of $\mathbb{R}^{\mathscr{S}}_{>0}$, and $P^{\perp}$ (called the LP set's **parameter subspace**) is the orthogonal complement of P. A chemical kinetic system $(\mathscr{N}, K)$ is **positive equilibria log-parametrized (PLP) system** if its set of positive equilibria is an LP set, i.e., $E_+(\mathscr{N}, K) = E(P_E, x^*)$ where P_E is the flux subspace and x^* is a given positive equilibrium.

Theorem 2 (Species Hyperplane Criterion, Theorem 3.12, [19])**.** *If $(\mathscr{N}, K)$ is a PLP system, then it has ACR in species S if and only if its parameter subspace $(P_E)^{\perp}$ is a subspace of the hyperplane $\{x \in \mathbb{R}^{\mathscr{S}} \mid x_S = 0\}$.*

Consequently, a simple method for evaluating ACR in a PLP system is obtained:

Corollary (Prop. 4.1, [19])**.** *Let $\{v_1, \ldots, v_E\}$ be a basis of the parameter subspace $(P_E)^{\perp}$ of a PLP system $(\mathscr{N}, K)$. The system has ACR is species S if and only if the coordinate corresponding to S in each basis vector $v_{i,S} = 0$ for each $i = 1, \ldots, E$.*

3 The DAC model and its kinetic representation

The global carbon cycle has been modeled with varying complexity. While sophisticated state-of-the-art models offer highly accurate Earth system predictions, they rely on complex networks (with an enormous number of equations) that are computationally expensive. Here, we focus on a simple heuristic box model, based on the spatial aggregation of carbon while focusing only on the processes that are most significant at a global

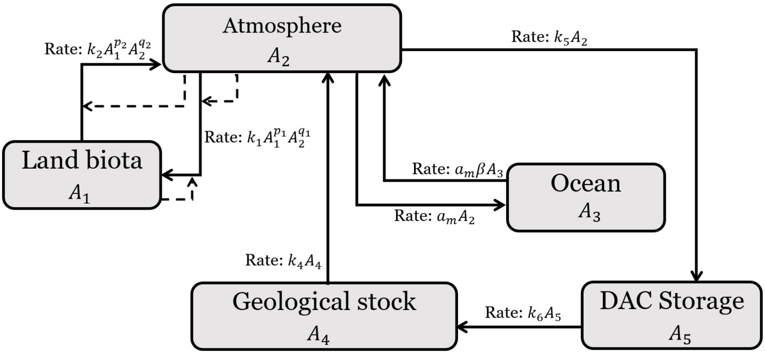

Figure 1. In the box model, the boxes represent the different pools, solid arrows indicate the transfer of carbon from one pool to another, and dashed arrows indicate the pools that influence a carbon transfer.

scale. Though box models of carbon cycle are not quantitatively precise, they provide reasonable accuracy and help reveal important interactions and feedback often obscured in more complex systems [1, 13, 27].

3.1 The DAC model

The pre-industrial system of Anderies et al. [1] forms the building block for developing and examining the global carbon cycle system with DAC intervention. The model extends the initial three-box model that considers carbon interactions in the land-atmosphere-ocean system of Anderies et al. [1], denoted by A_1, A_2 and A_3 respectively. The schematic diagram is shown in Figure 1. The modeling framework relies on ordinary differential equations where all processes are modeled by products of power law functions. More precisely, a Generalized Mass Action (GMA) system is an ODE system established by individually approximating each process in the system with a power-law term [25, 26, 32–35]. These terms are then aggregated, with incoming fluxes indicated by a plus sign and outgoing fluxes by a minus sign. The procedure for deriving power-law approximations of rate functions is based on Taylor linearization in logarithmic coordinates. For a detailed derivation of the power-law approximation of the process rates in the pre-industrial carbon cycle model of [1], refer to Appendix B of [10].

The current model incorporates the industrial carbon transfer activities (such as fossil fuel combustion) that lead to the linear transfer of carbon geological stock (A_4) to the atmosphere. DAC intervention is introduced by incorporating an extra box to store carbon (A_5) directly sequestered from the atmosphere. The rate of transfer is also assumed to be linear. The system also introduces a possible leak, which can be used to assess the CDR performance of the system even in the presence of such a leak.

Together with the power-law approximation of the transfer rates in the pre-industrial model and the linear functions of carbon transfer from A_4 to A_2, and A_5 to A_4, we form the system of ODEs of the carbon cycle system with DAC intervention:

$$\begin{aligned}
\dot{A}_1 &= k_1 A_1^{p_1} A_2^{q_1} - k_2 A_1^{p_2} A_2^{q_2} \\
\dot{A}_2 &= k_2 A_1^{p_2} A_2^{q_2} - k_1 A_1^{p_1} A_2^{q_1} - a_m A_2 + a_m \beta A_3 + k_4 A_4 - k_5 A_2 \\
\dot{A}_3 &= a_m A_2 - a_m \beta A_3 \\
\dot{A}_4 &= k_6 A_5 - k_4 A_4 \\
\dot{A}_5 &= k_5 A_2 - k_6 A_5
\end{aligned} \tag{2}$$

Table 1 provides a summary of the system parameters that will be referenced in the model's specification and analysis.

3.2 Power-law kinetic representation of the model of carbon cycle with DAC

The analysis of the model involves constructing a **power-law kinetic representation**. Such a representation involves a chemical reaction network (CRN) with power-law kinetics that is dynamically equivalent to the original system (i.e., they share the same ODEs). The goal is to identify important system dynamic properties through its power-law kinetic representation without the need for numerical computations or simulations typically required for nonlinear ODEs. With tools and insights from CRNT, the analysis is conducted with minimal reliance on specific parameters, as it treats rate constants symbolically and avoids dependence on their numerical values.

Symbol	Description
p_1 and p_2	Kinetic orders of land interaction p_1: Kinetic order of land photosynthesis interaction (p-interaction) p_2: Kinetic order of land respiration interaction (r-interaction)
q_1 and q_2	Kinetic orders of atmosphere interaction q_1: Kinetic order of atmosphere photosynthesis interaction (p-interaction) q_2: Kinetic order of atmosphere respiration interaction (r-interaction)
$p_2 - p_1$	Land r-p-interaction difference
$q_2 - q_1$	Atmosphere r-p-interaction difference
$R_p = \dfrac{p_2 - p_1}{q_2 - q_1}$	Land-atmosphere r-p-intearction difference ratio
$R_q = \dfrac{q_2 - q_1}{p_2 - p_1}$	Atmosphere-land r-p-intearction difference ratio

Table 1. Model parameters

In this section, we outline the process of constructing the CRN network for the model of interest and defining the power-law kinetics for this CRN.

3.2.1 CRN representation of the DAC model

Given a box model of a global carbon cycle, a corresponding **CRN representation** can be set up using the procedure proposed by Arceo et al. [3]. In this approach, one associates the reaction $A_i \to A_j$ to the carbon transfer from pool A_i to pool A_j. Moreover, if the carbon transfer is influenced by some carbon pools (as indicated by the dashed arrows in the schematic diagram), say $\sum A_k$, all these species are added to both sides of $A_i \to A_j$ to form the chemical reaction

$$\underbrace{A_i + \left(\sum A_k\right)}_{\text{reactant complex}} \to \underbrace{A_j + \left(\sum A_k\right)}_{\text{product complex}} \tag{3}$$

This process preserves the set of coordinates of the reaction vectors, which is important in describing the dynamics of the whole system (see Section 3.2.2).

In the current model of the carbon cycle with DAC (see Fig. 1), the transfer of carbon from the atmosphere A_2 to land A_1 is influenced by A_1 and A_2. According to (3), the reaction associated with this process is $A_2 + \{A_1 + A_2\} \rightarrow A_1 + \{A_1 + A_2\}$ or simply $A_1 + 2A_2 \rightarrow 2A_1 + A_2$. The carbon transfer from land to atmosphere is represented by the reaction $A_1 + A_2 \rightarrow 2A_2$ because the process is influenced by A_2. This reaction can be translated (as described in [17]), but without changing the stoichiometry, by adding A_1 to both sides of the reaction. The translation lowers the deficiency of the network from one (as done in [10]) into zero. Hence, the atmosphere-land carbon transfer is depicted by the reversible reaction $A_1 + 2A_2 \rightleftarrows 2A_1 + A_2$.

In summary, the CRN representation of the DAC model is precisely the network specified in Example 1 of Section 2.

3.2.2 Power-law kinetics of the DAC model

Given the CRN representation of the DAC model, we can associate the corresponding transfer power-law rates (provided in Figure 1) to each reaction:

$$\begin{array}{cc}
\textbf{Reaction} & \textbf{Reaction rates} \\
R_1 : A_1 + 2A_2 \rightarrow 2A_1 + A_2 & k_1 A_1^{p_1} A_2^{q_1} \\
R_2 : 2A_1 + A_2 \rightarrow A_1 + 2A_2 & k_2 A_1^{p_2} A_2^{q_2} \\
R_3 : A_2 \rightarrow A_3 & a_m A_2 \\
R_4 : A_3 \rightarrow A_2 & a_m \beta A_3 \\
R_5 : A_4 \rightarrow A_2 & k_4 A_4 \\
R_6 : A_2 \rightarrow A_5 & k_5 A_2 \\
R_7 : A_5 \rightarrow A_4 & k_6 A_5
\end{array} \tag{4}$$

Hence, the CRN representation of the DAC model must be endowed with power-law kinetics in order to reflect the ODE system in Equation (2). From Definition 11, the power-law functions of a CRN representation are encoded using the kinetic order matrix F, where entry F_{ij} encodes the kinetic order of the jth species in the ith reaction. Hence, given the power-law rates in (4), the kinetic order matrix of the current system is

$$F = \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array}\begin{array}{cccccc} A_1 & A_2 & A_3 & A_4 & A_5 & \\ \end{array}$$

$$F = \begin{array}{cc} & \begin{array}{ccccc} A_1 & A_2 & A_3 & A_4 & A_5 \end{array} \\ & \left[\begin{array}{ccccc} p_1 & q_1 & 0 & 0 & 0 \\ p_2 & q_2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{array}\right] \begin{array}{c} R_1 \\ R_2 \\ R_3 \\ R_4 \\ R_5 \\ R_6 \\ R_7 \end{array} \end{array}.$$

Let N be the stoichiometric matrix of the CRN representation of the DAC model. Then the system of ODEs can be rewritten as

$$\dot{x} = NK(x), \tag{5}$$

where $K(x)$ is the vector which contains the reaction rates. It can be easily checked that if the stoichiometric matrix for the CRN representation of the DAC model and the vector the containing the reaction rates are specified, the ODE system in (5) is precisely the system in (2), thereby verifying the dynamical equivalence of the power-law kinetic representation and the original system.

Remark. Henceforth, we refer to the power-law kinetic representation of the model of carbon cycle system with DAC as the **DAC system**.

4 Steady-state analysis of the DAC system

Since the power-law kinetic representation of the DAC system is weakly reversible and has zero deficiency, current theorems on power law kinetic systems on deficiency-zero networks [21,30] ensure the presence of a set of positive equilibria of the system.

Proposition 3. *The DAC system has a positive steady state.*

In fact, for a class of DAC system (later defined as positive and negative DAC systems), a parameterization of its steady state is provided in Proposition 11.

4.1 Multistationarity analysis

As expressed in Definition 8, a CRN is said to be multistationary or has the capability for multiple steady states if there is at least one stoichiometric compatibility class with at most two distinct positive steady states. Otherwise, the CRN is monostationary.

In the subsequent discussion, it is found that the capacity of the DAC system to admit multiple steady states depends on values of the kinetic orders p_1, p_2, q_1, and q_2. More precisely, the multistationarity property is quickly decided based on the sign of the ratio R_p or R_q defined in Table 1. The analysis centers around these two values due to the structure of the *kinetic flux subspace* $\widetilde{S}$ of the system. Essentially, the kinetic flux subspace of a system is the kinetic analogue of the stoichiometric subspace. If the stoichiometric subspace is the span of the reaction vectors, the kinetic flux subspace is the span of the fluxes in terms of the kinetic vectors. Interestingly, a mathematical description of the set of positive steady states of a chemical kinetic system can be written as a vector element of the space that is perpendicular (i.e., orthogonal complement) to the system's kinetic flux subspace: If the vector x^* is any positive equilibrium of a system, the set of positive equilibria consists of vectors x such that the vector $\log(x) - \log(x^*)$ resides in the orthogonal complement of kinetic flux subspace. (See Section 2.4.)

Proposition 4. *For the DAC system,*

$$(\widetilde{S})^{\perp} = span \left\{ \begin{bmatrix} -1 & R_p & R_p & R_p & R_p \end{bmatrix}^{\top} \right\} \text{ where } R_p := \frac{p_2 - p_1}{q_2 - q_1},\ q_2 \neq q_1.$$

Similarly,

$$(\widetilde{S})^{\perp} = span \left\{ \begin{bmatrix} -R_q & 1 & 1 & 1 & 1 \end{bmatrix}^{\top} \right\} \quad \text{where } R_q := \frac{q_2 - q_1}{p_2 - p_1},\ p_2 \neq p_1.$$

Proof. In a weakly reversible CRN, $\widetilde{S} = \operatorname{Im}\left(\widetilde{Y} I_a\right)$. For the DAC system,

$$\widetilde{Y} = \begin{array}{c} \\ A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{array} \begin{array}{c} \begin{array}{cccccc} A_1{+}2A_2 & 2A_1{+}A_2 & A_2 & A_3 & A_4 & A_5 \end{array} \\ \begin{bmatrix} p_1 & p_2 & 0 & 0 & 0 & 0 \\ q_1 & q_2 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array},$$

$$I_a = \begin{array}{c|ccccccc|} & R_1 & R_2 & R_3 & R_4 & R_5 & R_6 & R_7 \\ A_1{+}2A_2 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 2A_1{+}A_2 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ A_2 & 0 & 0 & -1 & 1 & 1 & -1 & 0 \\ A_3 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ A_4 & 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ A_5 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{array}.$$

Hence,

$$\widetilde{Y} I_a = \begin{bmatrix} p_2 - p_1 & p_1 - p_2 & 0 & 0 & 0 & 0 & 0 \\ q_2 - q_1 & q_1 - q_2 & -1 & 1 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix}.$$

So,

$$\widetilde{S} = \operatorname{Im}\left(\widetilde{Y} I_a\right) = \operatorname{span}\left\{ \begin{bmatrix} p_2 - p_1 \\ q_2 - q_1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ -1 \\ 1 \end{bmatrix} \right\}.$$

From here, it can be easily computed that

$$(\widetilde{S})^{\perp} = \operatorname{span}\left\{ \begin{bmatrix} -1 & R_p & R_p & R_p & R_p \end{bmatrix}^{\top} \right\}$$

or $(\widetilde{S})^\perp = \text{span}\left\{\begin{bmatrix}-R_q & 1 & 1 & 1 & 1\end{bmatrix}^\top\right\}$. ■

The ratio R_p was crucial in the analysis of the power-law kinetic representation of the pre-industrial model of Anderies et al. done by Fortun & Mendoza [11]. They identified and analyzed three distinct classes of Anderies systems, characterized by the sign of the ratio R_p. Here, the analysis of the DAC system will be largely characterized in a similar way. For convenience, we will call the different system classes of DAC as positive, negative, P-null and Q-null DAC systems:

Definition 17. We call the set of DAC systems with $R_p > 0$ (or $R_q > 0$) as **positive DAC systems**. The set of DAC systems where $R_p < 0$ (or $R_q < 0$) are termed **negative DAC systems**. DAC systems with $p_2 - p_1 = 0$ and $q_2 - q_1 \neq 0$ are ***P*-null DAC systems**. DAC systems with $q_2 - q_1 = 0$ and $p_2 - p_1 \neq 0$ are ***Q*-null DAC systems**.

Multistationarity of positive DAC systems

Müller & Regensburger [22] provided a simple criterion to assess the uniqueness of a (complex balanced) steady state in a deficiency zero network. This is done by analyzing the sign vector connections between the stoichiometric subspace and the orthogonal complement of the kinetic flux subspace.

Theorem 5. *(Proposition 3.2 of [22]) If for a weakly reversible generalized mass action system with* $\sigma(\mathcal{S}) \cap \sigma(\widetilde{\mathcal{S}})^\perp \neq \{0\}$, *then there is a stoichiometric class with more than one complex balanced equilibrium.*

Due to this, we have the following result:

Proposition 6. *A positive DAC system is multistationary.*

Proof. If $R_p > 0$, sign $(\widetilde{S})^\perp = \left\{\begin{bmatrix}-\\+\\+\\+\\+\end{bmatrix}, \begin{bmatrix}+\\-\\-\\-\\-\end{bmatrix}\right\}$. The stoichiometric subspace S is spanned by the following vectors:

$$\left\{ \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 0 \\ 0 \\ 1 \end{bmatrix} \right\}.$$

Let $x \in S$ where

$$x = a_1 \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix} + a_2 \begin{bmatrix} 0 \\ -1 \\ 1 \\ 0 \\ 0 \end{bmatrix} + a_3 \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 0 \end{bmatrix} + a_4 \begin{bmatrix} 0 \\ -1 \\ 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} a_1 \\ -a_1 - a_2 + a_3 - a_4 \\ a_2 \\ -a_3 \\ a_4 \end{bmatrix}.$$

Choose $a_1 > 0, a_2 < 0, a_3 > 0, a_4 < 0$, and $a_1 + a_2 > a_3 - a_4$ so that $\operatorname{sign}(x) = \begin{bmatrix} + & - & - & - & - \end{bmatrix}^\top$ and thus, $\operatorname{sign}(S) \cap \operatorname{sign}(\widetilde{S})^\perp \neq \{0\}$. Therefore, any positive DAC system is multistationary. ■

Figure 2 shows time-domain simulations for a positive DAC system with three stoichiometrically compatible initial conditions:

$$\begin{aligned} \text{IC1} &= \begin{bmatrix} 0.25 & 0.25 & 0.25 & 0.25 & 0 \end{bmatrix}^\top, \\ \text{IC2} &= \begin{bmatrix} 0.35 & 0.15 & 0.35 & 0.15 & 0 \end{bmatrix}^\top, \text{ and} \\ \text{IC3} &= \begin{bmatrix} 0.15 & 0.05 & 0.45 & 0.35 & 0 \end{bmatrix}^\top. \end{aligned} \tag{6}$$

The MATLAB code for the simulations and analyses presented in this study is available on GitHub at `https://github.com/morn-phil/Parameter-Minimal-Analysis-of-CDR-through-DAC`.

For the case where both the land respiration and photosynthesis interaction difference $(p_2 - p_1)$ and the atmosphere respiration and photosynthesis interaction difference $(q_2 - q_1)$ are positive, there exists a set of rate constants that leads to multiple equilibrium points. The simulations demonstrate that each initial condition converges to a distinct equilibrium,

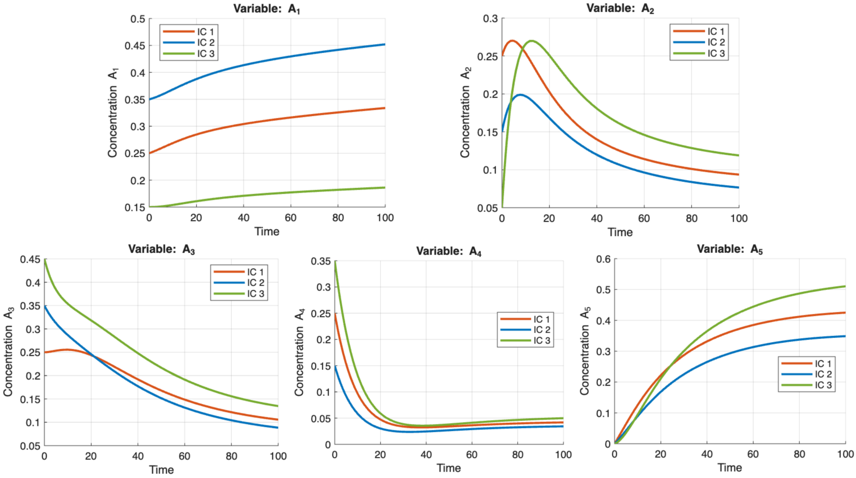

Figure 2. Time-domain simulations of a positive DAC system ($p_2 = 5$, $p_1 = 2$, $q_2 = 5$, and $q_1 = 2$). The rate constants assigned are $k_1 = 0.4$, $k_2 = 0.3$, $k_4 = 0.1$, $k_5 = 0.05$, $k_6 = 0.01$, $a_m = 0.05$, and $\beta = 1$. Here, three stochiometrically compatible initial conditions (ICs) lead to different equilibrium points.

confirming the capacity for multistationarity.

Generally, the presence of multistationarity in a carbon cycle system reveals the possibility of tipping points, which are critical thresholds beyond which a return to a previous state becomes difficult or prolonged. Although not all multistationary systems will exhibit crossed tipping points, their confirmed presence motivates a targeted numerical search. Once a tipping point is located, it transforms from a theoretical risk into a quantifiable target, allowing policymakers to define and enforce boundaries that keep the system within a 'safe operating space' [1, 13, 29].

Multistationarity of negative DAC systems

For a negative DAC system where $R_p < 0$, we have

$$\text{sign } (\widetilde{S})^{\perp} = \left\{ \begin{bmatrix} - & - & - & - & - \end{bmatrix}^{\top}, \begin{bmatrix} + & + & + & + & + \end{bmatrix}^{\top} \right\}.$$

In order for $x \in S$ to have similar signs for all its components, say positive, necessarily

$$a_1 > 0, a_2 > 0, a_3 < 0, a_4 > 0.$$

However, the second component $-a_1 - a_2 + a_3 - a_4 < 0$. Hence, it is not possible for a uniform positive sign for all components of x. Similarly, it is not possible to obtain a vector $x \in S$ with negative signs in all its components. Thus, sign $(S) \cap$ sign $(\widetilde{S})^{\perp} = \{0\}$ and Theorem 5 does not apply. For negative DAC systems, we turn to *injectivity* analysis.

Definition 18. ([8,36]) A CRN with stoichiometric matrix N is **injective** if for any distinct stoichiometrically compatible species vectors x and y, we have $NK(x) \neq NK(y)$ for all kinetics K endowed on the CRN.

Note that if a CRN is injective, then it is monostationary. In other words, an injective CRN cannot support multiple positive steady states for any rate constants. Wiuf and Feliu [8, 36] established a criterion to identify if a system is injective.

Let $M = N \cdot \mathrm{diag}(z) \cdot F\ \mathrm{diag}(k)$, where N represents the stoichiometric matrix and F is the kinetic order matrix of the PLK system. Consider the symbolic matrix M^* created by using symbolic vectors $k = (k_1, \ldots, k_m)$ and $z = (z_1, \ldots, z_r)$. Assume $\{\omega^1, \ldots, \omega^d\}$ forms a basis of the left kernel of N, and $i_1, \ldots, i_d$ represent row indices. Define the $m \times m$ matrix M^* by substituting the i_j-th row of M with ω^j.

Theorem 7. *([8, 36]) The interaction network with power law kinetics and fixed kinetic orders is injective if and only if the determinant of M^* is a non-zero homogeneous polynomial with all coefficients being positive or all being negative.*

We identify two subsets of negative DAC systems that are injective:

Proposition 8. *The DAC system is injective, and hence monostationary, if any of the following cases hold:*

(i) $p_1 < 0, p_2 > 0, q_1 > 0$, *and* $q_2 < 0$; *or*

(ii) $p_1 > 0, p_2 < 0, q_1 < 0$, *and* $q_2 > 0$.

For all other cases, the network is not injective.

Proof. Using the computational approach and Maple script provided by Feliu & Wiuf [8], we obtain the determinant of M^* for the DAC system:

$$\begin{aligned} det = &- p_1k_1k_2k_3k_4z_1z_4z_5z_6 - p_1k_1k_2k_3k_5z_1z_4z_6z_7 - p_1k_1k_2k_4k_5z_1z_3z_5z_7 \\ &- p_1k_1k_3k_4k_5z_1z_4z_5z_7 + p_2k_1k_2k_3k_4z_2z_4z_5z_6 + p_2k_1k_2k_3k_5z_2z_4z_6z_7 \\ &+ p_2k_1k_2k_4k_5z_2z_3z_5z_7 + p_2k_1k_3k_4k_5z_2z_4z_5z_7 + q_1k_2k_3k_4k_5z_1z_4z_5z_7 \\ &- q_2k_2k_3k_4k_5z_2z_4z_5z_7 \end{aligned}$$

Hence, for $p_1 < 0, p_2 > 0, q_1 > 0$, and $q_2 < 0$, all the terms are positive, and for $p_1 > 0, p_2 < 0, q_1 < 0$, and $q_2 > 0$, all the terms are negative. In both cases, the networks are injective by Theorem 7 and hence, monostationary. In all other cases, the systems are non-injective, which is a necessary condition for multistationarity. ■

Figure 3 presents time-domain simulations for a negative DAC system conforming to the conditions of Proposition 8, Case (i). The initial conditions used are the same stoichiometrically compatible initial conditions as Equation (6). The convergence of these initial conditions to a single equilibrium point indicates monostationarity.

Monostationarity of null DAC systems

For P-null and Q-null DAC systems, the analysis is based on an independent decomposition of the network. Feinberg [7] demonstrated that, in an independent decomposition, the intersection of the set of positive steady states of the subnetworks coincides with the set of positive steady states of the entire network (see Section 2.3). By examining an independent decomposition of the P-null and Q-null DAC systems, we observe that:

Proposition 9. *Any P-null or Q-null DAC system is monostationary.*

Proof. Consider the (finest) independent decomposition of DAC that contains two subnetworks:

$$\begin{aligned} \mathscr{N}_1 &= \{A_1 + 2A_2 \rightleftarrows 2A_1 + A_2, A_2 \rightleftarrows A_3\}, \\ \mathscr{N}_2 &= \{A_4 \rightarrow A_2, A_2 \rightarrow A_5, A_5 \rightarrow A_4\} \end{aligned}$$

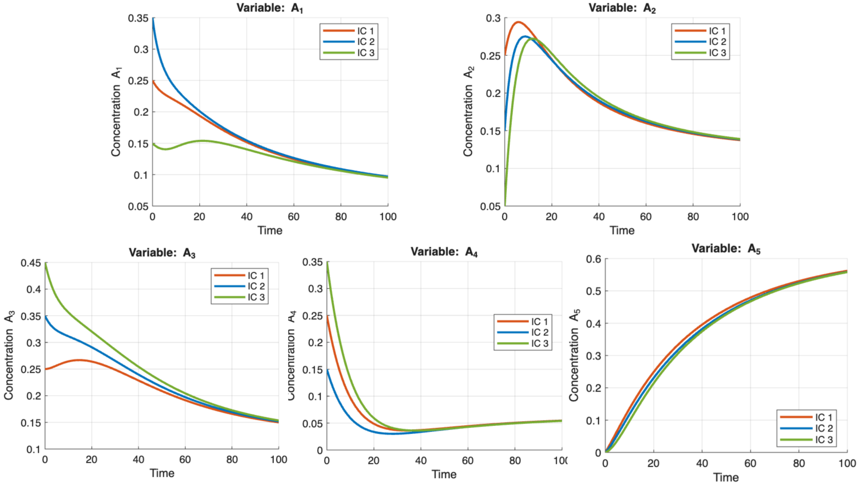

Figure 3. Time-domain simulations of a monostationary negative DAC system. Specifically, $p_2 = 3$, $p_1 = -0.2$, $q_2 = -0.5$, and $q_1 = 4$, which satisfy Case (i) of Proposition 8. The rate constants used are $k_1 = 0.4$, $k_2 = 0.3$, $k_4 = 0.1$, $k_5 = 0.05$, $k_6 = 0.01$, $a_m = 0.05$, and $\beta = 1$.

The subnetwork $\mathscr{N}_1$ is identical to the power-law kinetic representation of the pre-industrial system of the Anderies system studied by Fortun & Mendoza [11]. They showed that the null Anderies system cannot exhibit multiple steady-states or monostationary. The other subnetwork $\mathscr{N}_2$ is a mass action system that is weakly reversible and has zero deficiency. By the classic Deficiency Zero Theorem for mass action systems [6, 14, 15], $\mathscr{N}_2$ is monostationary. By Theorem 1, since both subsystems are monostationary, the whole system is also monostationary. ■

4.2 Absolute concentration robustness

Absolute concentration robustness or ACR refers to a condition in which the concentration of a species in a network attains the same value in every positive steady-state set by parameters and does not depend on initial conditions (see Definition 15). This implies that if an important variable, such as A_2 (representing atmospheric CO_2 concentration), exhibits ACR, its stability is guaranteed even when other variables fluctuate. Notably, conducting an ACR analysis for the DAC system is straightforward by examining the values of R_p and R_q and applying the *Species Hyperplane Criterion* introduced by Lao et al. [19]:

Proposition 10. *A DAC system that is a*

(i) positive or negative system has no ACR species;

(ii) P-null system has ACR species consisting precisely of A_2, A_3, A_4 and A_5; and

(iii) Q-null system has ACR in A_1.

Prior to the proof, we illustrate a case where the DAC system is a Q-null system. As shown in Figure 4, simulations from five different initial conditions (not necessarily stoichiometrically compatible) converge to a consistent steady-state value for A_1, suggesting ACR for this species. This property is not observed in the other system species.

We present the proof of the Proposition:

Proof. The *Species Hyperplane Criterion* (Theorem 2 and its Corollary) guarantees that a system has ACR species if and only if the vector coordinates corresponding to these species are zero for all basis vectors in space $(\widetilde{S})^{\perp}$. As noted earlier, for the DAC system,

$$\begin{aligned} (\widetilde{S})^{\perp} &= \text{span}\left\{\begin{bmatrix}-1 & R_p & R_p & R_p & R_p\end{bmatrix}^{\top}\right\} \\ \text{or} \quad (\widetilde{S})^{\perp} &= \text{span}\left\{\begin{bmatrix}-R_q & 1 & 1 & 1 & 1\end{bmatrix}^{\top}\right\} \end{aligned}$$

Hence, a DAC system with positive or negative R_p or R_q has no ACR species. The DAC system with $R_p = 0$ has ACR species consisting precisely of A_2, A_3, A_4 and A_5. If $R_q = 0$, the system has ACR in A_1. ■

This Proposition suggests that if we desire that A_2 or the CO_2 concentration in the atmosphere be stable irrespective of the initial conditions, we would like R_p to be equal to zero. To achieve this, p_1 (the kinetic order of land photosynthesis interaction) must be equal to p_2 (the kinetic order of land respiration interaction) but q_1 (the kinetic order of atmosphere

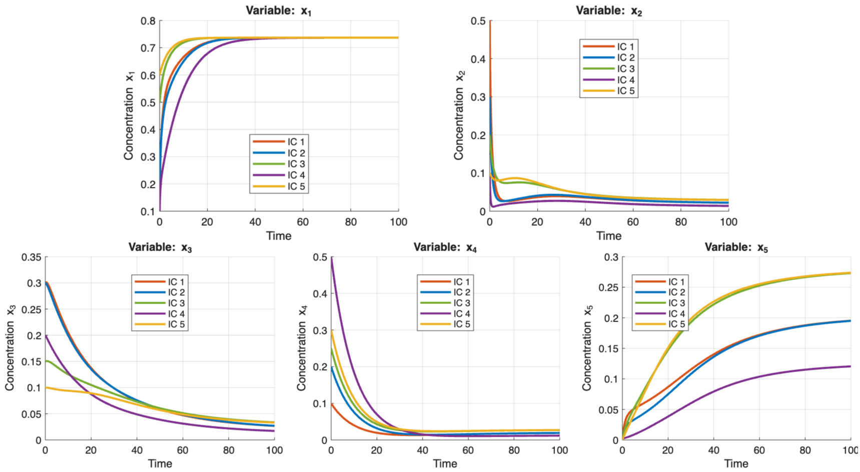

Figure 4. Time-domain simulations of a Q-null DAC system,where $p_2 = 2$, $p_1 = -1$, and $q_1 = q_2 = 0.6$. Morover, the rate constants used are $k_1 = 0.2$, $k_2 = 0.5$, $k_4 = 0.1$, $k_5 = 0.1$, $k_6 = 0.01$, $a_m = 0.05$, and $\beta = 1$.

photosynthesis interaction) must not be equal to q_2 (the kinetic order of atmosphere respiration interaction).

4.3 Conditions for atmospheric carbon reduction

Finally, we provide different conditions under which a set of initial conditions, along with all positive steady states within the corresponding stoichiometric classes, leads to a genuine reduction in the atmospheric carbon pool. That is, for a set of initial conditions $\mathcal{A}^0 = \{A_1^0, A_2^0, A_3^0, A_4^0, A_5^0\}$ and steady state $\mathcal{A}^* = \{A_1^*, A_2^*, A_3^*, A_4^*, A_5^*\}$ in the corresponding stoichiometric class, we have $A_2^* < A_2^0$.

The approach taken here is to use total amounts or conserved quantities (in the sense of Definition 3) in a kinetic system. Generally, for any element $w \in S^\perp$ and $x \in \Omega$,

$$wf(x) = w\frac{dx}{dt} = 0,$$

since $\operatorname{Im} f \subseteq S$. If $w = (w_1, \ldots, w_m)$ and $x = (x_1, \ldots, x_m)$, then

$$0 = \sum w_i \frac{dx_i}{dt} = \frac{d}{dt}\left(\sum w_i x_i\right),$$

which implies that $T := \sum w_i x_i$ is a constant—this is called a **conserved quantity**. Clearly, any two elements in a stoichiometric compatibility class have the same conserved quantity or total amount.

The DAC system is a conservative CRN since $(1, 1, 1, 1, 1)$ is a basis for $S^{\perp}$. This implies that for a set of initial conditions $\mathcal{A}^0$ and steady state $\mathcal{A}^*$ in the corresponding stoichiometric class,

$$A_1^0 + \cdots + A_5^0 = A_1^* + \cdots + A_5^*.$$

4.3.1 A necessary condition for A_2 reduction in positive/negative DAC systems

Observe that the set of positive equilibria of the positive or negative CDAC system can be described as follows:

Proposition 11. *The set of positive equilibria of the positive or negative CDAC system can be parametrized by A_2 as follows*

$$A_1 = \left(\frac{k_2}{k_1} A_2^{q_2 - q_1}\right)^{\frac{1}{p_1 - p_2}}, \quad p_1 \neq p_2$$

$$A_2 = A_2, \qquad A_3 = \frac{1}{\beta} A_2, \qquad A_4 = \frac{k_5}{k_4} A_2 \qquad A_5 = \frac{k_5}{k_6} A_2.$$

Proof. Set the equations in (2) to 0 and solve for A_2. For instance, setting the first equation in the system to 0, we get

$$A_1^{p_1 - p_2} = \frac{k_2}{k_1} A_2^{q_2 - q_1}$$

If $p_1 \neq p_2$, $A_1 = \left(\frac{k_2}{k_1} A_2^{q_2 - q_1}\right)^{\frac{1}{p_1 - p_2}}$. ■

Remark. If we let $P := p_2 - p_1$, the equilibrium value of A_1 can be written as

$$A_1 = \left(\frac{k_1}{k_2}\right)^{1/P} A_2^{-R_q}$$

Denote

$$\begin{aligned}\mathsf{SUM}^0 &:= A_1^0 + A_3^0 + A_4^0 + A_5^0; \text{ and}\\ \mathsf{SUM}^* &:= A_1^* + A_3^* + A_4^* + A_5^*.\end{aligned}$$

A set of initial conditions $\mathcal{A}^0$ determines a unique stoichiometric class $\mathcal{S}^0$. Suppose there is another point in $\mathcal{S}^0$ with $A_2 = \lambda A_2^0$, where $0 < \lambda < 1$. Moreover, suppose there is a positive or negative DAC system with an equilibrium in $\mathcal{S}^0$ whose A_2-value is λA_2^0. For all positive equilibria in $\mathcal{S}^0$, we have

$$\mathsf{SUM}^0 + A_2^0 = \mathsf{SUM}^* + A_2^*.$$

From the set of positive equilibria of positive and negative CDAC in Proposition 11, we have

$$\mathsf{SUM}^0 + A_2^0 = \left(\frac{k_1}{k_2}\right)^{1/P} \left(\lambda A_2^0\right)^{-R_q} + \left(\frac{1}{\beta} + \frac{k_5}{k_4} + \frac{k_5}{k_6} + 1\right) \lambda A_2^0 \tag{7}$$

From the last equation, we state the following necessary condition for the reduction of A_2 from its initial value to its steady-state value:

Proposition 12. *All the values of P, R_q, β, and the rate constants satisfying Equation (7) enable atmospheric carbon reduction from the initial A_2^0 to the steady-state value λA_2^0.*

4.3.2 Sufficient conditions for atmosphere carbon reduction

Since the DAC system is conservative, each stoichiometric class is compact (s. Appendix 1 of Horn & Jackson [14]). Hence, the continuous maps $\mathsf{pr}_i : \mathbb{R}^{\mathscr{S}}_{>0} \to \mathbb{R}_{>}$ and their sums attain maxima and minima on any stoichiometric class.

Proposition 13. *Consider the P-null DAC system with set of initial conditions $\mathcal{A}^0$ and positive steady state $\mathcal{A}^*$ in the corresponding $\mathcal{S}^0$ (viewed as a compact subset of $\mathbb{R}^{\mathscr{S}}_{>0}$). Then if*

$$\left(\frac{k_1}{k_2}\right)^{\frac{1}{q_2-q_1}} < T - M'',$$

where T is the conserved quantity and M'' is the maximum of $\mathsf{pr}_1 + \mathsf{pr}_3 + \mathsf{pr}_4 + \mathsf{pr}_5$ on $\mathcal{S}^0$, then $A_2^* < A_2^0$.

Proof. From the first equation of the ODE system in (2), we observe that for a P-null DAC system (i.e., $p_1 = p_2$), $A_2^* = \left(\frac{k_1}{k_2}\right)^{\frac{1}{q_2-q_1}}$. Moreover,

$$T - M'' \leq T - \left(A_1^0 + A_3^0 + A_4^0 + A_5^0\right) = A_2^0.$$

■

Proposition 14. *Consider the positive or negative DAC system with set of initial conditions $\mathcal{A}^0$ and positive steady state $\mathcal{A}^*$ in the corresponding $\mathcal{S}^0$. Let m' be the minimum of the continuous map pr_2 on $\mathcal{S}^0$. Then if*

$$1 + \frac{M''}{m'} < \left(\frac{k_2}{k_1}\right)^{\frac{1}{p_1-p_2}} (m')^{\frac{q_2-q_1}{p_1-p_2}} + \frac{1}{\beta} + \frac{k_5}{k_4} + \frac{k_5}{k_6},$$

where M'' is the maximum of $\mathsf{pr}_1 + \mathsf{pr}_3 + \mathsf{pr}_4 + \mathsf{pr}_5$ on $\mathcal{S}^0$, then $A_2^* < A_2^0$.

Proof. Denote $A_1^* + A_2^* + A_3^* + A_4^* + A_5^*$ by $= A_2^* \left(\mathsf{SUM}^+\right)$, where in SUM^+, the summands are given in the parametrization of the equilibria set of positive/negative DAC system (Prop. 11). Now,

$$\begin{aligned} 1 < \frac{A_2^0}{A_2^*} \Longleftrightarrow 1 &+ \frac{(\mathsf{pr}_1 + \mathsf{pr}_3 + \mathsf{pr}_4 + \mathsf{pr}_5)(\mathcal{A}^0)}{A_2^*} \\ &< \frac{A_2^0}{A_2^*} + \frac{(\mathsf{pr}_1 + \mathsf{pr}_3 + \mathsf{pr}_4 + \mathsf{pr}_5)(\mathcal{A}^0)}{A_2^*} = \mathsf{SUM}^+. \end{aligned}$$

We have

$$1 + \frac{(\mathsf{pr}_1 + \mathsf{pr}_3 + \mathsf{pr}_4 + \mathsf{pr}_5)(\mathcal{A}^0)}{A_2^*} \leq 1 + \frac{M''}{m'}$$

by the definition of numerator and denominator. Furthermore,

$$\left(\frac{k_2}{k_1}\right)^{\frac{1}{p_1-p_2}} (m')^{\frac{q_2-q_1}{p_1-p_2}} + \frac{1}{\beta} + \frac{k_5}{k_4} + \frac{k_5}{k_6} < \mathsf{SUM}^+.$$

Hence, the RHS of the first equivalence above is fulfilled and $A_2^* < A_2^0$. ■

5 Conclusion, summary, and outlook

We analyzed a global carbon cycle system that incorporates direct air capture technology by utilizing the tools and insights in Chemical Reaction Network Theory. We aim to demonstrate the distinct advantages of applying Chemical Reaction Network Theory (CRNT), which provides a fundamentally different class of insights. By examining a dynamically equivalent reaction network of a global carbon cycle system with DAC technology, this study efficiently identified crucial dynamic features: the existence of positive steady states, the possibility of multiple steady states, the absolutely robust concentration levels of carbon pools, and conditions for atmospheric carbon reduction

While numerical computations can indicate properties such as multistationarity for particular parameter sets, CRNT verifies these properties conclusively by analyzing the network's topology and kinetics, with minimal reliance on specific parameter values. Furthermore, by treating kinetic orders symbolically, the resulting conclusions are not limited to specific numerical values and are therefore more general than those obtained solely from simulation.

Irrespective of kinetic orders and rate constants, the DAC system is expected to exhibit a positive steady state. Additionally, assessments concerning the system's multistationarity and ACR traits are based on the sign of ratios R_p and R_q. Table 2 outlines the results discussed earlier, connecting the signs of R_p and R_q to the dynamic characteristics of the associated DAC system.

It can be seen from Table 2, that the desirable outcome of a unique and stable concentration of carbon dioxide in the atmosphere may be realized if $R_p = 0$. No tipping points from the existence of multistationarity would

Property	**DAC system**
Existence of at least one steady state	True for all systems
Capacity for multiple steady states	$R_p = 0$: only one steady state
	$R_q = 0$: only one steady state
	R_p or $R_q > 0$: all parameter combinations result in more than one steady state
	R_p or $R_q < 0$: some parameter combinations may result in more than one steady state
ACR	$R_p = 0$: ACR in A_2, A_3, A_4, A_5
	$R_q = 0$: ACR in A_1
	R_p or $R_q > 0$: no ACR in any species
	R_p or $R_q < 0$: no ACR in any species

Table 2. Summary of the dynamic properties of the DAC system.

be expected.

Indeed, the use of CRNT provides a more structural understanding than numerical methods. While simulations offer results for specific parameters, they can obscure the underlying system design. CRNT, in contrast, analyzes the network's topology to reveal the fundamental motifs, such as weak reversibility and deficiency zero architecture, that govern the system's dynamics. This moves beyond mere computation to explain why a system behaves as it does, based on its inherent design.

The approach utilized in this research could prove valuable for rapidly evaluating other negative emission technologies (NETs). It can efficiently determine if the system fails to meet specified crucial criteria (such as the absence of a positive steady state in the long run or bistability), prompting a reassessment of the technology's deployment.

The framework presented here, while demonstrated on a limited system, shows significant potential for refinement and application to more complex carbon cycle models. Its foundation in the kinetic representations of canonical power law models (e.g., Generalized Mass Action systems) demonstrates the potential for transferability and scalability. This study thus provides the essential preliminary results needed to justify and inform subsequent research targeting intricate carbon cycle models with CDR techniques, where numerical methods can be computationally expensive or fail to generate broader insights. When dealing with a broader or

CRN representation of a carbon cycle, incorporating network decomposition theory in CRNT to dissect the system into smaller elements could be a promising approach.

The idea of "planetary boundaries," highlighted by Anderies et al. [1], has had a profound influence on the global sustainability community, as demonstrated in the research conducted by Steffen et al. [29]. Our ongoing research efforts focus on developing kinetic representations for various CDR methods such as bioenergy with carbon capture and storage and ocean fertilization. Tan et al. [31] have stressed the significance of optimizing combinations or "portfolios" of NETs. To address this challenge, we aim to investigate other combinations of NETs to determine if these may exhibit steady-state multiplicity.

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