

Is adding charcoal to soil a good method for CO₂ sequestration? : modeling a spatially homogeneous soil

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Modeling a spatially homogeneous soil

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Is adding charcoal to soil a good method for CO₂ sequestration? – Modeling a spatially homogeneous soil

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Abstract

We propose a simple mathematical model (a coupled system of nonlinear ODEs) able to capture dynamical effects produced by adding charcoal to fertile soils. Our main aim is to understand to which extent charcoal (in its biochar form) is able to lock up carbon in soils. Our results are preliminary in the sense that we do not actually solve the CO₂ sequestration problem, but we do set up a modeling framework in which this can be tackled by means of mathematical tools.

We show that our model is well-posed and has interesting steady states. Depending on the reference parameter range and chosen time scale, numerical simulations suggest that adding charcoal postpones the release of CO₂ for a large variety of soils.

Keywords: Modeling chemical kinetics in fertile soils, Solvability of a nonlinear ODE system, Equilibria and steady states, Simulation, Biochar, CO₂ sequestration

1. Introduction

Global warming is an increasingly important issue for mankind. It seems that it is no longer enough to reduce CO₂ emissions; one also needs to remove CO₂ from the atmosphere (carbon sequestration). In his Nature paper [1], J. Lehmann argues that locking carbon up in soil makes more sense than storing it in plants and trees that eventually decompose, but can this idea work on a large timescale? A large community of scientists (mostly biologists, chemists,

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soil engineers) started to support such ideas and tried, with their experimental means, to explore the sustainability of adding charcoal (biochar) to soils; compare for instance [2, 3, 4] and see also the review paper [5]. For more information on this research trend, often called the *Biochar project*, we refer the reader also to the sites www.biochar-international.org and <http://en.wikipedia.org/wiki/Biochar>. The Biochar project¹ brings clear advantages² (e.g. reduces soil greenhouse gas emissions, improves both water holding and nutrient holding capacities, improves environment for soil life, doesn't alter the carbon/nitrogen ratio, reduces soil acidity, remove pollutants), *but* is it a secure solution? Is it a permanent one? What about the possible negative effects like charcoal increases soil fertility and so increases the microbe population, which finally can lead to an increase in the rate at which the natural soil carbon is broken down and then released as CO_2 ? In spite of the intense current experimental research, there is no conclusive evidence yet about whether putting charcoal in soil is a good idea, therefore our interest.

In our opinion, Lehmann's question (see *loc. cit.* in [1]) can be translated into mathematical terms as follows: What is the large time behavior of the complex dynamical system (including transport, soil geometry and chemistry) provoked by adding charcoal? The major issue is the complexity of the situation – it is *a priori* not clear what a good model is to capture the effect of charcoal on CO_2 emissions. This is the place where we wish to contribute.

In particular, note that charcoal (or biochar) is characterized by a very special porous structure (see Figure 1), which is responsible for the high retention of water, dissolved organic nutrients, and even of pollutants such as hydrocarbons and pesticides³. On top of this, the chemistry of fertile soils is rather complex and precise characterizations of the microbial evolution are not available. Furthermore, describing the transport of water together with nutrients, phenolics, pollutants (etc.) requires a good understanding of the heterogeneities of the soils.

¹*Biochar* := The idea of trapping carbon in soil for longer by storing it in the form of charcoal.

²Note also the additional advantage of producing energy by burning organic matter to make charcoal.

³As a direct consequence of this fact, there are several situations when the soil fertility has increased after charcoal addition.

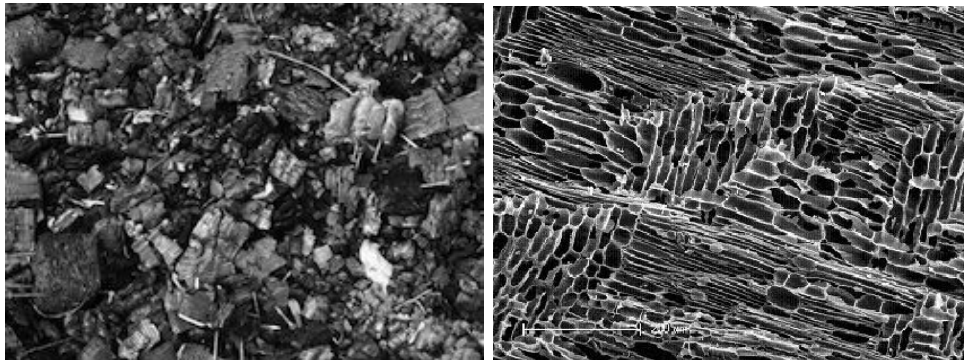


Figure 1: Multiscale geometry of biochar (left: macro, right: micro). This is the place where nutrients, phenolics etc. undergo adsorption and desorption.

Within this framework we treat a spatially homogeneous soil. Hence we avoid the aforementioned complications and propose the simplest mathematical model that is able to capture dynamical effects produced by adding charcoal to fertile soils. This turns to be a nonlinearly coupled system of deterministic ODEs which behaves well mathematically. The main task is to understand to which extent charcoal (in its biochar form) is able to lock up carbon in soils. Our results are only preliminary in the sense that we are not solving here the CO_2 sequestration problem. Rather we are setting up a modeling framework where this can be tackled by means of mathematical tools.

The paper is organized as follows: In section 2 we describe mathematically chemical reactions in homogeneous media (here: fertile soils) and propose a first model based on differential equations. We prove in section 3 that our model is well-posed in the sense of Hadamard and perform a stability analysis of the interesting steady states. We illustrate the behavior of the profiles of the active concentrations and parameter effects in section 5. The effects observed regarding the addition of charcoal to soils are summarized in section 5.2. Appendix A contains a discussion of the equilibria and stability of a reaction sub-block.

We hope that our paper will bring the attention of the mathematical modeling community on the biochar issue – note that, cf. section 5.2, there are many open modeling aspects that would deserve a careful multi-disciplinary attention.

2. Modeling chemical reactions in homogeneous fertile soils

2.1. What happens if charcoal is added to soil?

In this section we provide a simple model for the chemical reactions taking place in charcoal-enriched soil. We model only those processes that are relevant to carbon dioxide emission: the break down of soil organic matter and charcoal by microbes and the subsequent release of carbon dioxide, the reproduction and death of the microbes, and the effect of charcoal on soil fertility.

We denote the species appearing in the chemical reactions by

$$\begin{aligned} CO_2 & \text{ carbon dioxide,} \\ Ch & \text{ charcoal (artificially added to the soil),} \\ Om & \text{ soil organic matter (natural soil carbon),} \\ M & \text{ microbes.} \end{aligned} \tag{2.1}$$

Note that we do not distinguish between different types of soil organic matter (litter, recalcitrant organic matter, humus, etc.). Also we only consider heterotrophic microbes, i.e., those that use organic carbon for growth.

Microbes in the soil break down the organic matter and charcoal (this is called mineralization), releasing the carbon, which then combines with oxygen to form carbon dioxide. Experimental evidence indicates that generally there is no shortage of oxygen in the soil. Having this mind we assume that oxygen is present everywhere in equal amounts and thus it enters our model as a parameter. We model the complex system of mineralization processes by means of the following chemical reactions mechanism:



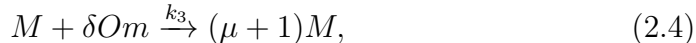
where $n > 0$ is taken as a constant. The reaction “constants” k_1 and k_2 depend generally on the concentration of microbes, i.e.,

$$k_i = k_i(M).$$

Here we assume that, as functions, these reaction constants increase if the concentration of microbes increases. Note that, in general, the reaction constants can also depend on other effects (like the concentration of phenolics

in the soil), but for the sake of keeping things simple we do not include these in our model.

The microbes need organic matter and oxygen to reproduce. Since we assumed that there is an abundance of oxygen, we can model the reproduction of microbes by means of



where $\delta, \mu > 0$ are constants. In general the reaction constant k_3 might depend on the fertility of the soil, which in turn depends on the amount of charcoal in the soil. For our theoretical investigations, we neglect the intermediate step and assume directly that k_3 depends on the amount of charcoal, $k_3 = k_3(Ch)$, and that k_3 increases with charcoal concentration. However, note that the fertility of the soil contains so much *in situ* information that it cannot be neglected in the practical design of a CO_2 sequestration scenario or if one wants to understand why *terra preta* (or ‘black earth’) is so fertile. Furthermore, in practice k_3 depends on many other factors, e.g., temperature, moisture, soil type, but we assume that these are all constant and so they do not appear explicitly in our model.

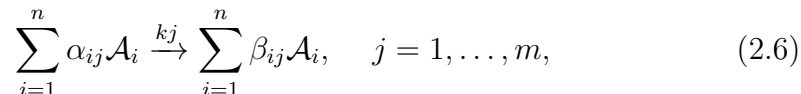
We model the death of microbes by the chemical reaction



where $\eta > 0$ is a constant.

2.2. Basics of chemical kinetics

We denote the concentration of species \mathcal{A} at time t by $[\mathcal{A}](t)$, e.g., $[CO_2](t)$ is the concentration of CO_2 in the soil at time t . In order to derive evolution equations for the species concentrations we use the *simple reaction ansatz*, see, e.g., [6]. This assumption essentially states that if our set of reactions is given by the mechanism



where $n \in \mathbb{N}$ denotes the number of species \mathcal{A}_i , $m \in \mathbb{N}$ denotes the number of chemical reactions, and $\alpha_{ij}, \beta_{ij} \in \mathbb{R}_+$ are stoichiometric coefficients, k_j

reaction constants, then the *elementary reaction rates* are given by

$$r_j(\mathcal{A}_1, \mathcal{A}_2, \dots, \mathcal{A}_n) := k_j \prod_{i=1}^n [\mathcal{A}_i]^{\alpha_{ij}}. \quad (2.7)$$

Balancing the mass of the active species \mathcal{A}_i , we easily derive the evolution equations for the concentrations $[\mathcal{A}_i]$, viz.

$$\frac{d}{dt}[\mathcal{A}_i] = \sum_{j=1}^m (\beta_{ij} - \alpha_{ij}) r_j(\mathcal{A}_1, \mathcal{A}_2, \dots, \mathcal{A}_n), \quad i = 1, \dots, n. \quad (2.8)$$

Before applying this methodology to (2.2)–(2.5), we introduce a new notation, see Table 2.1, which is more convenient for the analysis. For the sake of readability and clarity, we use both notations throughout this paper.

u_1	$[Om]$
u_2	$[M]$
u_3	$[Ch]$
u_4	$[CO_2]$

Table 2.1: Alternative notation for the concentrations.

Remark 2.9. (*Restriction to spatially homogeneous soils*) *Within the framework of this paper, we consider a “continuously stirred tank reactor” case, a scenario intensively used in chemical engineering. See, e.g., [6]. In terms of soils, this means that we focus our modeling on a single space location, where the measurements are made, and we follow how the information “flows” over physically-important timescales. To this end, we assume the soil to be homogeneous in the sense that no spatial substructures (typically called microstructures) appear, i.e., all soil components (gravel, sand, solid nutrients, water, etc) are well-mixed. We postpone for later the study of the more realistic case when the soil heterogeneities will be explicitly taken into account in terms of porosities, tortuosities, permeabilities very much in the spirit of [7] (general theory of flows in porous media), [8, 9, 10] (multiscale approaches to the chemical corrosion of concrete, smoldering combustion and plant growth, respectively), [11] (accumulation of cadmium in plants). Also, at a later stage it would be interesting to study the effect of the charcoal’s platelet-like microstructure (see Figure 1) on the efficiency of adsorption and desorption*

of the nutrients. Most likely this would lead to a two-scale ODE system intimately coupled with evolution equations for the transport and storage of nutrients.

Applying the *simple reaction ansatz* to (2.2)–(2.5), and assuming additionally that the system has a constant source $s \geq 0$ of organic matter, yields the nonlinear coupled system of ODEs

$$\frac{d}{dt}u_1 = -k_1(u_2)u_1 - \delta k_3(u_3)u_2u_1^\delta + \eta k_4u_2 + s, \quad (2.10)$$

$$\frac{d}{dt}u_2 = \mu k_3(u_3)u_2u_1^\delta - k_4u_2, \quad (2.11)$$

$$\frac{d}{dt}u_3 = -k_2(u_2)u_3, \quad (2.12)$$

$$\frac{d}{dt}u_4 = nk_1(u_2)u_1 + k_2(u_2)u_3. \quad (2.13)$$

The source s can be thought of as organic matter entering the soil from the surface in the form of dead leaves, plants, etc. This system also requires initial conditions. Their role is to incorporate the type of soil. Throughout the rest of this paper we study the system (2.10)–(2.13).

3. Mathematical analysis of the system (2.10)–(2.13)

We start by making some assumptions on the model parameters entering (2.10)–(2.13). These assumptions will be of a technical nature and will be used to prove global existence of positive and bounded concentrations u_i and to study the steady states of this nonlinear ODE system.

3.1. Restrictions on the model parameters

We assume that

$$\delta \geq 1. \quad (3.1)$$

Assumption (3.1), together with the assumptions given below on the constitutive functions k_i , ensure that the right-hand side of the system (2.10)–(2.13) is Lipschitz continuous, which guarantees that our ODE system admits a unique local classical solution.

In addition to assuming that $\delta, \eta, \mu, n > 0$, we assume that

$$\delta \geq \eta\mu. \quad (3.2)$$

This condition is used in Section 3.3 to show that the solution to (2.10)–(2.13) does not blow-up in finite time.

Since the k_i are reaction constants, we assume that they satisfy $k_i > 0$ for $i \in \{1, 2, 3, 4\}$. Note however that k_i are nearly never true constants; they often incorporate a certain dependence on important physical/environmental quantities (here: spatial location, temperature, soil fertility, oxygen content, water content, etc). Here we take k_4 to be constant and assume that the functions $k_i : \mathbb{R} \rightarrow (0, \infty)$, $i \in \{1, 2, 3\}$, are Lipschitz continuous and strictly increasing. For example, k_1 being strictly increasing means that an increase of microbes in the soil leads to an increase in the rate of break down of organic matter.

Finally, we assume that the initial concentrations are positive and bounded, i.e. $u_i(0) = u_i^0 \in [0, \infty)$, $i \in \{1, 2, 3, 4\}$.

3.2. Positivity of concentrations

In this section we show that the concentrations u_1, u_2, u_3, u_4 are nonnegative for all times if their initial values are nonnegative. It suffices to show for each $i \in \{1, 2, 3, 4\}$ that if $u_i = 0$ and $u_j \geq 0$ for all $j \neq i$, then $\dot{u}_i \geq 0$. This turns to be a trivial exercise:

$$\begin{aligned}\dot{u}_1(0, u_2, u_3, u_4) &= \eta k_4 u_2 + s \geq 0, \\ \dot{u}_2(u_1, 0, u_3, u_4) &= 0, \\ \dot{u}_3(u_1, u_2, 0, u_4) &= 0, \\ \dot{u}_4(u_1, u_2, u_3, 0) &= n k_1(u_2) u_1 + k_2(u_2) u_3 \geq 0.\end{aligned}$$

3.3. L^∞ bounds on concentrations

We prove that the concentrations u_i do not blow-up in finite time. Fix arbitrary initial conditions u_i^0 . Then, based on the result of Section 3.2, we can assume that $u_i \geq 0$ for all $i = 1, 2, 3, 4$.

From the positivity of u_i and k_i , it follows immediately from (2.12) that

$$\|u_3\|_\infty \leq u_3^0. \quad (3.3)$$

Adding equation (2.10) to η times equation (2.11) gives

$$\frac{d}{dt}(u_1 + \eta u_2) = -k_1(u_2)u_1 - (\delta - \eta\mu)k_3(u_3)u_2u_1^\delta + s \leq s. \quad (3.4)$$

The inequality (3.4) follows from (3.2) and the positivity of the k_i and u_i . From (3.4) we conclude that u_1 and u_2 satisfy L^∞ bounds on any finite time interval. The numerics suggest that this bound is independent of the length of this time interval, but we do not need this here; see section 5.

Relying on the L^∞ bounds on u_i for $i \in \{1, 2, 3\}$ on any finite time interval $[0, \tau]$, we can bound the right-hand side of (2.13) by a constant $C(\tau)$. Integration yields the bound

$$u_4(t) \leq C(\tau)t + u_4^0 \quad (3.5)$$

for all $t \in [0, \tau]$, which immediately gives a bound on u_4 on any time interval $[0, \tau]$.

3.4. Well-posedness

Based on the positivity and the L^∞ bounds on concentrations, together with the Lipschitz continuity of the right-hand side of (2.10)–(2.13), we recall classical ODE theory (see [12, 13], e.g.) to prove the following result:

Theorem 3.6. (*Global solvability*). *Assume that the assumptions stated in section 3.1 hold. Then for any set of initial conditions $u_i(0) = u_i^0 \geq 0$, the system (2.10)–(2.13) has a unique classical solution $u_i : [0, \infty) \rightarrow \mathbb{R}$, $i \in \{1, 2, 3, 4\}$.*

Furthermore, a Gronwall-like argument can be employed to show that this classical solution depends continuously on the initial data and *all* model parameters. Since this argument is rather standard, we omit to show it here.

3.5. Equilibria and stability of the system (2.10)–(2.12)

First note that u_4 does not appear in the right hand side of (2.10)–(2.13). Hence equation (2.13) decouples from the system, in the sense that we do not need (2.13) to solve the subsystem (2.10)–(2.12). Having this in mind, it is sufficient to study the equilibria of the reduced system (2.10)–(2.12). The reader is referred to Appendix A for a discussion of the equilibria and stability of the reaction block given by (2.4) and (2.5). For basic notions of dynamical systems⁴, see [16], e.g.

⁴Dynamical systems theory proved to be very successful in a series of cases arising in biology and ecology; compare for instance [14, 15] and references cited therein. We expect therefore that dynamical systems delivers results in the case of biochar research as well.

We first search for the equilibria of the decoupled system given by (2.10), (2.11) and (2.12). By equating the right-hand side of (2.12) to zero, it follows that $u_3 = 0$. By substituting this into equations (2.10) and (2.11) we obtain

$$0 = -k_1(u_2)u_1 - \delta k_3(0)u_2 u_1^\delta + \eta k_4 u_2 + s, \quad (3.7)$$

$$0 = (\mu k_3(0)u_1^\delta - k_4)u_2. \quad (3.8)$$

For convenience we write k_3 instead of $k_3(0)$ in the remainder of this section. Equation (3.8) is satisfied if and only if either

$$u_2 = 0, \text{ or} \quad (3.9)$$

$$u_1 = \left(\frac{k_4}{\mu k_3} \right)^{\frac{1}{\delta}} =: C_2. \quad (3.10)$$

Let us treat the two cases separately:

Case (3.9): It immediately follows from (3.7) that $u_1 = s/k_1(0)$.

Case (3.10): By inserting (3.10) in (3.7) we get

$$0 = -k_1(u_2)C_2 - \frac{k_4}{\mu}(\delta - \eta\mu)u_2 + s. \quad (3.11)$$

The right-hand side of (3.11) is strictly decreasing as a function of u_2 . Hence it has at most one solution u_2 . A necessary condition for the existence of such a solution is that the right-hand side is nonnegative for $u_2 = 0$. This is the case when

$$s \geq k_1(0)C_2. \quad (3.12)$$

From now on we assume that the k_i and the parameters δ, η, μ are chosen such that (3.11) has a solution whenever (3.12) holds. We will call this solution u_2^* . For example, a solution exists if (3.12) holds and $\delta - \eta\mu > 0$.

Therefore, depending on the parameter s , we have one or two equilibrium points: If $s \leq k_1(0)C_2$, then we have only one equilibrium point u_e^1 given by

$$u_e^1 := (u_1, u_2, u_3) = \left(\frac{s}{k_1(0)}, 0, 0 \right). \quad (3.13)$$

If $s > k_1(0)C_2$, we have the additional equilibrium point u_e^2 given by

$$u_e^2 := (u_1, u_2, u_3) = \left(C_2, u_2^*, 0 \right), \quad (3.14)$$

where u_2^* satisfies (3.11). Therefore $s = k_1(0)C_2$ is a bifurcation point.

To test the stability of the equilibrium points u_e^1 and u_e^2 , we linearize the system (2.10), (2.11), (2.12). Let J denote the Jacobian matrix of this system. A brief calculation shows that

$$J(u_e^1) = \begin{bmatrix} -k_1(0) & -\frac{k_1'(0)}{k_1(0)}s - \delta k_3 \left(\frac{s}{k_1(0)} \right)^\delta + \eta k_4 & 0 \\ 0 & \mu k_3 \left(\frac{s}{k_1(0)} \right)^\delta - k_4 & 0 \\ 0 & 0 & -k_2(0) \end{bmatrix}. \quad (3.15)$$

The eigenvalues of $J(u_e^1)$ are given by the entries on the diagonal. The eigenvalues $-k_1(0)$ and $-k_2(0)$ are negative, whereas the sign of the third eigenvalue changes from negative to positive as s passes the bifurcation point. So u_e^1 is asymptotically stable if $s < -k_1(0)C_2$ and is unstable if $s > -k_1(0)C_2$.

We follow the same procedure for u_e^2 . First we obtain

$$J(u_e^2) = \begin{bmatrix} -k_1(u_2^*) - \delta^2 k_3 u_2^* C_2^{\delta-1} & -k_1'(u_2^*)C_2 - \frac{k_4}{\mu}(\delta - \eta\mu) & -\frac{\delta}{\mu} \frac{k_3'(0)}{k_3(0)} k_4 u_2^* \\ \delta \mu k_3 u_2^* C_2^{\delta-1} & 0 & \frac{k_3'(0)}{k_3(0)} k_4 u_2^* \\ 0 & 0 & -k_2(u_2^*) \end{bmatrix}. \quad (3.16)$$

Let us denote the 2×2 upper-left block of $J(u_e^2)$ by

$$\begin{bmatrix} A_1 & A_2 \\ A_3 & 0 \end{bmatrix}.$$

Note that $A_1, A_2 < 0$ and $A_3 > 0$. Therefore the eigenvalues of $J(u_e^2)$ are

$$-k_2(u_2^*), \quad \frac{A_1}{2} + \sqrt{\frac{A_1^2}{4} + A_2 A_3}, \quad \text{and} \quad \frac{A_1}{2} - \sqrt{\frac{A_1^2}{4} + A_2 A_3}.$$

Since $A_1 < 0$ and $A_2 A_3 < 0$, the real parts of all the three eigenvalues are negative, which proves that u_e^2 is asymptotically stable.

In summary, for each $s > 0$ there is one stable equilibrium of the decoupled system (2.10), (2.11), (2.12). Depending on the size of the source s , this

equilibrium is either given by (3.13) or by (3.14). Note that the full system (2.10)–(2.13) does not have any equilibrium points since $\dot{u}_4 > 0$ (unless $s = 0$, in which case $u_i = 0$ for all $i = 1, 2, 3, 4$ is an equilibrium).

4. Nondimensionalisation

Before solving the system numerically, we rescale it (very much in the spirit of [17]). We consider the following scalings for the time, concentrations, and reaction rates: $t = \tau \tilde{t}$, where τ is the reference time, $u_i = U_i \tilde{u}_i$, where U_i is the reference concentration of species i , and $k_i = K_i \tilde{k}_i$, where K_i is the reference reaction constant. Substituting these into equations (2.10)–(2.13) gives

$$\begin{aligned}
\frac{d}{d\tilde{t}} \tilde{u}_1 &= -\tau_1 \tilde{k}_1 \tilde{u}_1 - \tau_2 \tilde{k}_3 \tilde{u}_1^\delta \tilde{u}_2 + \tau_3 \tilde{k}_4 \tilde{u}_2 + \tau_4 s, \\
\frac{d}{d\tilde{t}} \tilde{u}_2 &= \tau_5 \tilde{k}_3 \tilde{u}_1^\delta \tilde{u}_2 - \tau_6 \tilde{k}_4 \tilde{u}_2, \\
\frac{d}{d\tilde{t}} \tilde{u}_3 &= -\tau_7 \tilde{k}_2 \tilde{u}_3, \\
\frac{d}{d\tilde{t}} \tilde{u}_4 &= \tau_8 \tilde{k}_1 \tilde{u}_1 + \tau_9 \tilde{k}_2 \tilde{u}_3,
\end{aligned} \tag{4.1}$$

where $\tau_\alpha, \alpha \in \{1, 2, \dots, 9\}$, denote the characteristic time scales. Table 4.1 lists their dependence on the reference constants.

Characteristic time scale	Typical size
τ_1	τK_1
τ_2	$\tau \delta K_3 U_1^{\delta-1} U_2$
τ_3	$\tau \eta K_4 U_2 U_1^{-1}$
τ_4	τU_1^{-1}
τ_5	$\tau \mu K_3 U_1^\delta$
τ_6	τK_4
τ_7	τK_2
τ_8	$\tau n K_1 U_1 U_4^{-1}$
τ_9	$\tau K_2 U_3 U_4^{-1}$

Table 4.1: List of characteristic time scales and their expected size.

parameter	value	ref. constant	value	unit
a_1	1	C_2	1	mol m^{-3}
a_2	1	K_1	0.01	s^{-1}
a_3	1.9	K_2	10^{-3}	s^{-1}
b_1	1	K_3	1	$\text{m}^{3\delta} \text{mol}^{-\delta} \text{s}^{-1}$
b_2	1	K_4	0.1	s^{-1}
b_3	0.1	U_1	1	mol m^{-3}
b_4	1	U_2	1	mol m^{-3}
η	10	U_3	1	mol m^{-3}
μ	1	U_4	10^3	mol m^{-3}
δ	10	s	0.02	$\text{mol m}^{-3} \text{s}^{-1}$
n	10	τ	1	s

Table 5.1: Parameter values (first two columns) and reference constant values (last three columns) used for the simulations.

5. Numerical simulation of the system (2.10)–(2.13)

Here we illustrate numerically the behavior of the solution to our ODE system and test the effects of the various parameters. The main interest lies in predicting how the emission of CO_2 into the atmosphere changes if we put charcoal in the soil [1]. We make such predictions for different parameter values.

We start by choosing the following linear constitutive functions for the reaction rates:

$$\begin{aligned} \tilde{k}_1(\tilde{u}_2) &= a_1\tilde{u}_2 + b_1, & \tilde{k}_2(\tilde{u}_2) &= a_2\tilde{u}_2 + b_2, \\ \tilde{k}_3(\tilde{u}_3) &= a_3\tilde{u}_3 + b_3, & \tilde{k}_4 &= b_4. \end{aligned} \tag{5.1}$$

The coefficient values are given in Table 5.1, along with the reference values C_2 , K_i , U_i , s and τ , and the parameters η , μ , δ , n . Note that we have chosen the parameters so that $\delta = \eta\mu$. From (3.10) it follows that

$$C_2 = \left(\frac{K_4 b_4}{\mu K_3 b_3} \right)^{\frac{1}{\delta}}.$$

We take $s = 2K_1 a_1 C_2$ so that u_e^2 (see (3.14)) is a stable equilibrium point of the reduced system (2.10)–(2.12).

5.1. Searching for the effects of adding charcoal to soil

First we simulate what happens to the equilibrium state u_e^2 when charcoal is added to the soil. This corresponds to the following initial condition:

$$(\tilde{u}_1, \tilde{u}_2, \tilde{u}_3, \tilde{u}_4)|_{t=0} = \left(\frac{C_2}{U_1}, \frac{s - K_1 C_2 b_1}{K_1 a_1 C_2 U_2}, 1, 0 \right). \quad (5.2)$$

We have exploited the special form of \tilde{k}_1 to calculate u_e^* explicitly.

Although the simulation is carried out for the dimensionless \tilde{u}_i , we will refer to them by $[Om]$, $[M]$, $[Ch]$ and $[CO_2]$ for clarity. Figure 2 shows the simulation results. We see here various interesting phenomena:

- The concentrations $[Om]$ and $[M]$ change on a short time scale ($\mathcal{O}(\tilde{t}) = 0.1$). Essentially this is because their time derivatives depend on $[Ch]$ through k_3 .
- On a long time scale ($\mathcal{O}(\tilde{t}) = 100$), $[Ch]$ decreases exponentially fast to 0. Therefore $[Om]$ and $[M]$ converge back to their initial, equilibrium values.
- On the same long time scale, $[CO_2]$ increases linearly.

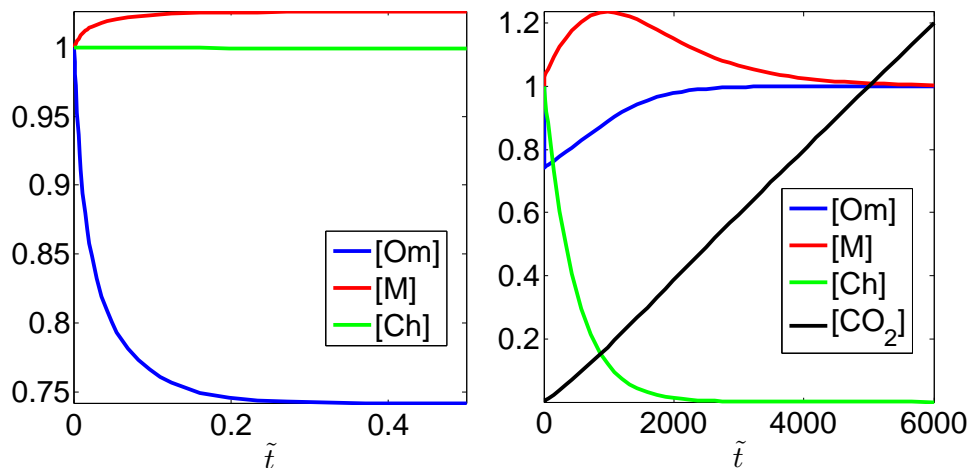


Figure 2: These figures show short-time (left) and long-time (right) behavior of the system initially at equilibrium. Charcoal is added at time $\tilde{t} = 0$. The graph of $[CO_2]$ is omitted in the left picture, because it would be too close to the \tilde{t} -axis to see anything interesting.

Now we turn our attention to CO_2 emission. In Figure 3 we compare the case in which we put charcoal in the soil at time $\tilde{t} = 0$, which corresponds to initial condition (5.2), with the case in which the soil contains no charcoal, which corresponds to initial condition

$$(\tilde{u}_1, \tilde{u}_2, \tilde{u}_3, \tilde{u}_4)|_{t=0} = \left(\frac{C_2}{U_1}, \frac{s - K_1 C_2 b_1}{K_1 a_1 C_2 U_2}, 0, 0 \right). \quad (5.3)$$

Initial condition (5.3) implies that $[Om]$, $[M]$ and $[Ch]$ are constant in time and that $[CO_2]$ is linear.

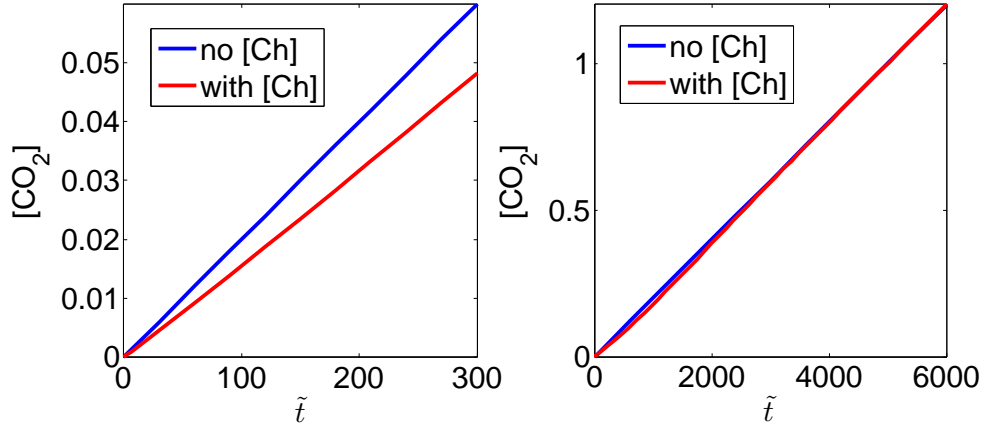


Figure 3: These figures show short-time (left) and long-time (right) emission of CO_2 . We compare the case in which charcoal is added to the soil (in red) with the case when the soil does not contain charcoal (in blue).

From Figure 3 we see that, on the short time scale $\mathcal{O}(\tilde{t}) = 100$, putting charcoal in the soil reduces the CO_2 emission. On the other hand, on a longer time scale ($\mathcal{O}(\tilde{t}) = 1000$), we see that putting charcoal in the soil has no effect on the CO_2 emission; the charcoal concentration $[Ch]$ tends to zero, $[Om]$ and $[M]$ return to their equilibrium values, and the $[CO_2]$ concentration tends to the linear profile.

A natural question that arises is whether we see similar effects if we increase the amount of charcoal that we put in the ground initially. We can simulate this by redoing the previous simulation, but now with $U_3 = 10 \text{ mol m}^{-3}$ so that the amount of charcoal is ten times as much. The results are shown in Figure 4. On the long time scale the behaviour is similar to before. This is remarkable, because it means that the total amount of emitted CO_2

hardly changes when ten times as much charcoal is put into the soil. On the short time scale we do see a difference: the rate of CO_2 emission is slightly increased.

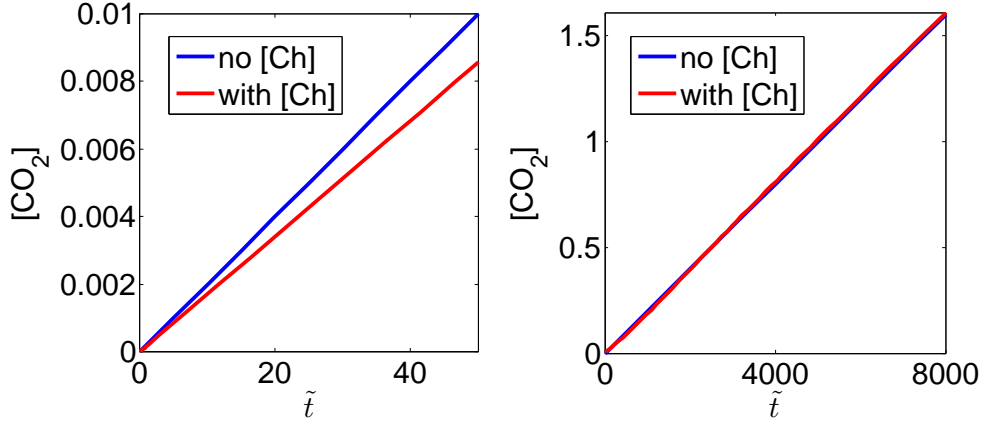


Figure 4: The results of re-running the simulation shown in Figure 3, but now with ten times as much charcoal in the soil.

Now we test the effect of some of the other parameters on the CO_2 emission. Figure 5 shows the results of doing the simulation with the values in Table 5.1, but now with K_2 decreased by a factor of ten, i.e. $K_2 = 10^{-4} \text{ s}^{-1}$. This corresponds to a slower breakdown of the charcoal by the microbes. The qualitative behaviour is the same as Figure 3, but now the corresponding time scales are larger. This is because the charcoal is in the system for longer, and hence it takes longer to reach equilibrium.

Figure 6 is the result of repeating the simulation shown in Figure 3 again, but now with the nonlinear constitutive function $\tilde{k}_1(\tilde{u}_2) = a_1\tilde{u}_2^{100} + b_1$, which corresponds to a very fast breakdown of the organic matter by the microbes. The other parameters are the same as in Table 5.1 and equation (5.1). Note however that changing \tilde{k}_1 changes the equilibrium u_e^2 and so changes the initial condition.

We observe that initially the rate of CO_2 emission is much higher. This is because initially the number of microbes increases due to the presence of the charcoal, which speeds up the mineralization process tremendously because of the exponential constitutive function. On the long time scale, however, adding charcoal to the soil makes little difference.

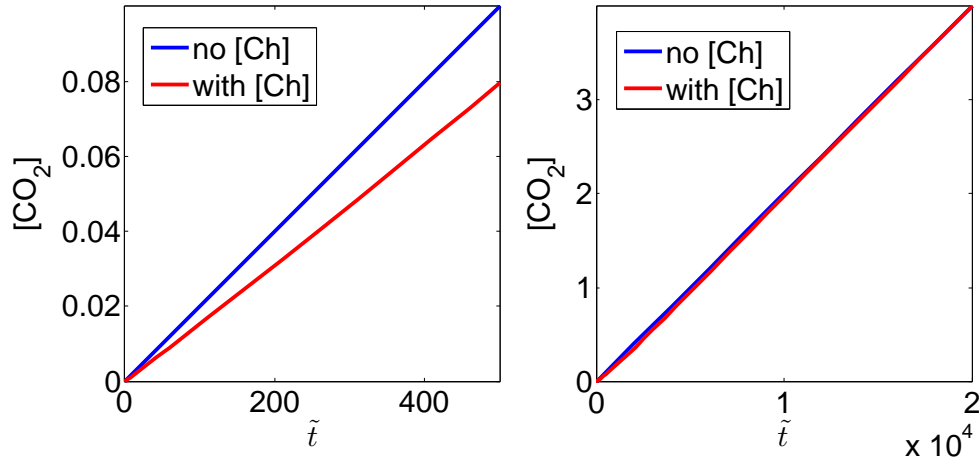


Figure 5: The results of re-running the simulation shown in Figure 3, but with K_2 taken to be ten times as small.

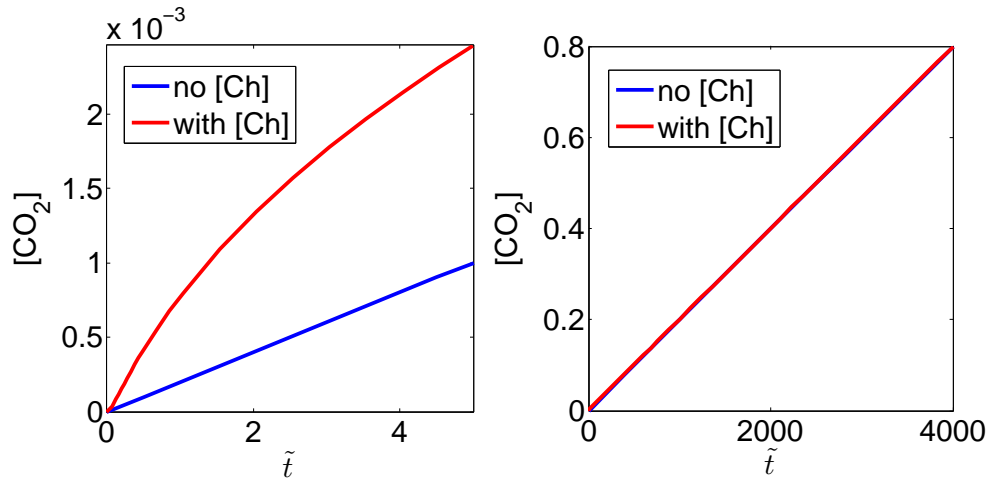


Figure 6: The results of re-running the simulation shown in Figure 3 but with the nonlinear constitutive function $\tilde{k}_1(\tilde{u}_2) = a_1\tilde{u}_2^{100} + b_1$.

5.2. Summary of our results and open problems

For a rather large range of parameter values, our simulations clearly indicate that the short-time behaviour of our system can be significantly different from the long-time behaviour. Therefore, when testing experimentally the effect of adding charcoal to soil on CO₂ emission, it could be important not to make judgements based solely on short-time data.

Our numerical results also suggest that the equilibrium u_e^2 is globally asymptotically stable.

In all of our simulations the long time CO_2 emission seems to be independent of the addition of charcoal to the soil. This curious effect requires further study and possibly a refinement of our model.

We are well-aware that we have a large set of parameters and reference constants that are difficult to relate to available experimental data. Therefore further simulations and comparison with experiments are required. This would naturally lead to a better control of the size of the characteristic time scales and potentially allow for improved predictions on CO_2 sequestration.

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Appendix A. Equilibria and stability of the reaction block given by (2.4) and (2.5)

In this appendix we consider a subsystem of (2.10)–(2.13) that corresponds to reactions (2.4) and (2.5) (without the presence of charcoal, carbon dioxide or a source of organic matter). The reason for studying this subsystem is that it gives us a physical reason for imposing (3.2). Moreover, this subsystem turns out to dominate the short time behaviour of the whole system.

Substituting $s = 0$, $k_1 = 0$ and $[Ch] = 0$ into (2.10) and (2.11) gives

$$\begin{aligned}\frac{d}{dt}[Om] &= -\delta k_3(0)[M][Om]^\delta + \eta k_4[M], \\ \frac{d}{dt}[M] &= \mu k_3(0)[M][Om]^\delta - k_4[M].\end{aligned}\tag{A.1}$$

In the rest of this subsection we write k_3 instead of $k_3(0)$ for brevity.

Figure A.7 shows a sketch of the phase plane corresponding to (A.1). Note that

$$\begin{aligned}\frac{d}{dt}[Om] = 0 &\Leftrightarrow [M] = 0 \text{ or } [Om] = \left(\frac{\eta k_4}{\delta k_3}\right)^{\frac{1}{\delta}} =: C_1, \\ \frac{d}{dt}[M] = 0 &\Leftrightarrow [M] = 0 \text{ or } [Om] = \left(\frac{k_4}{\mu k_3}\right)^{\frac{1}{\delta}} =: C_2.\end{aligned}\tag{A.2}$$

From (A.2) we see that $([Om], [M]) = (c, 0)$ is an equilibrium solution of (A.1) for all $c \in \mathbb{R}$. If $C_1 = C_2$, then so is $([Om], [M]) = (C_1, c)$ for all $c \in \mathbb{R}$.

To determine the stability of the first equilibria, $([Om], [M]) = (c, 0)$, we compute the Jacobian matrix corresponding to the system (A.1):

$$k_3 \begin{bmatrix} -\delta^2 [M][Om]^{\delta-1} & \delta \left(\frac{\eta k_4}{\delta k_3} - [Om]^\delta \right) \\ \delta \mu [M][Om]^{\delta-1} & \mu \left([Om]^\delta - \frac{k_4}{\mu k_3} \right) \end{bmatrix}.\tag{A.3}$$

From (A.3) it easily follows that the equilibria $([Om], [M]) = (c, 0)$ are stable if $c < C_2$.

Now we consider the boundedness of the trajectories. We consider three cases: $C_1 < C_2$, $C_1 = C_2$ and $C_1 > C_2$ (sketches of the corresponding phase planes are given in Fig. A.7). These cases correspond to:

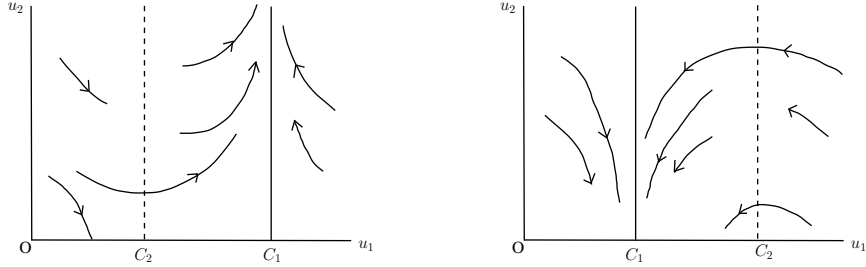


Figure A.7: Sketches of the phase plane corresponding to (A.1), depending on whether C_1 is bigger or smaller than C_2 (see (A.3) for their definitions). Recall that $u_1 = [Om]$ and $u_2 = [M]$.

($\delta > \eta\mu$) : From the phase field analysis, we expect the solution of (A.1) to be bounded for all initial conditions.

($\delta = \eta\mu$) : From (A.2), we see that we have more equilibrium points, which are given by $[Om] = C_1 = C_2$ and $[M] \in \mathbb{R}$ arbitrary. These equilibrium points are stably if and only if $[M] > 0$.

($\delta < \eta\mu$) : From the phase field analysis, we expect the solution to blow up for most initial conditions.

Therefore a sufficient condition for a solution of the reduced system (A.1) to be finite in time is

$$\delta \geq \eta\mu. \quad (\text{A.4})$$

This is the same as our assumption (3.2) for the whole system. Equality in (A.4) would mean that the amount of organic matter that is converted into microbes by reaction (2.4) is equal to one over the amount of microbes that is converted into organic matter by reaction (2.5). This means that $[Om] + \eta[M]$ is conserved. Indeed, one sees immediately from (A.1) that

$$\frac{d}{dt}([Om] + \eta[M]) = 0.$$

This quantity $[Om] + \eta[M]$ was also useful for proving L^∞ bounds for the whole system. See equation (3.4).

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