RC #1

We thank the reviewer for their comments, as they have substantially improved the draft. Below we present the original question, followed by our response.

1. Line 54. I like Table A.1 that summarizes the capabilities of different models. There is a paper that just was published in Water Resources Research by some of these same authors (https://doi.org/10.1029/2022WR032907) - should this be included?
    a. **Thank you for bringing this to our attention, we now include this paper in Table A.1 of our revision.**
2. Consider adding a schematic 'cartoon' showing a porous medium representative elementary volume with liquid, gas, biomass phases, relevant biogeochemical processes, etc.
    a. **We will add such a diagram to illustrate the process.**
3. 50, Sec. 2, Model Foundation. I am not familiar with the van Turnhout Toolbox. This is used to solve the coupled system on nonlinear ordinary equations, coupled with the nonlinear algebraic equations for aqueous speciation. Can you add a few sentences to explain more about the numerical techniques used?

a. **We added the following text to describe the Toolbox in Section 2 of the manuscript:**

The modeling equations (e.g., microbial growth, $CaCO_3$ precipitation, and biogenic gas evolution) were programmed within the original, publicly available van Turnhout Toolbox, a general-form mechanistic batch model for environmental systems that considers species in the gas, liquid, and solid phase (van Turnhout et al., 2016). The van Turnhout Toolbox is a system of ordinary differential equations coupled with ORCHESTRA to simulated chemical speciation (Meeussen, 2003), an extensive database of established geochemical equilibria. The MIDP-specific biogeochemical model components (i.e., stoichiometry, type of inhibition and kinetics, potential chemical species) were specified in an input spreadsheet that the program accesses. The degree of saturation and percent (by weight) of mineral precipitation were calculated outside of the van Turnhout Toolbox using model results, as discussed in Section 3.2 of this paper.

The Toolbox's logic flow and calculation sequence are as follows (Meeussen, 2003; van Turnhout et al., 2016), using H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- to illustrate the process for the carbonate system.

1.   At t = 0, the program loads the input concentrations file, which includes the concentration of all total species (e.g., H_2CO_3 representing DIC, H^+) and the stoichiometry for metabolic and kinetic reactions: e.g.,

2.   Ordinary differential equations are used to determine compound consumption and production based on the reaction stoichiometry and kinetic equations (e.g.,

precipitation, biotransformation, and mass transfer) at each time step. For example, the graphic in Figure illustrates that, as $C_2H_3O_2^-$ is consumed from microbial consumption, H_2CO_3 is produced.
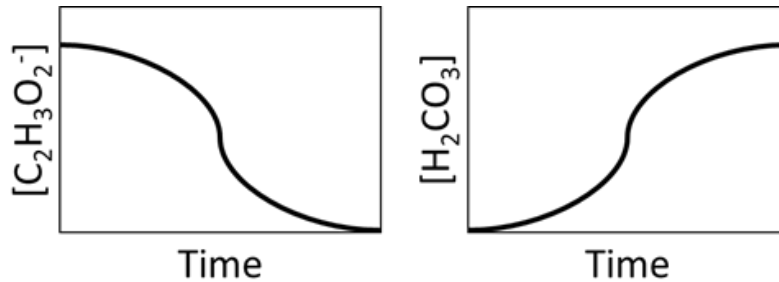

Figure 1. Illustration of consumption of the consumption of C2H3O2- and production of H2CO3 during MIDP.

3. At each time step, the following set of linear equations are solved to determine the relative derived concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- from H_2CO_3 produced in the previous steps and already present. This is carried out in the ORCHESTRA biochemical module.

a. Mass balance equations – the left side of the equation is the total dissolved inorganic carbon, H_2CO_3, from the stoichiometry described in steps 1 and 2. The right side are the derived concentrations of species as a result of speciation and indicated with italics.

$$H_2CO_3 = H_2CO_3 + HCO_3^- + CO_3^{2-}$$
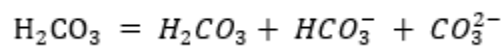
b. Electroneutrality – all potentially produced charged species related to this balance is considered.

$$H^+ = OH^- + HCO_3^- + CO_3^{2-}$$
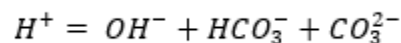
c. Acid-base equilibrium for H_2CO_3

$$K_a = \frac{[CO_3^{2-}][2H^+]}{[H_2CO_3]}$$

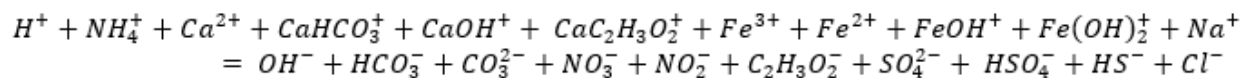d. Acid-base equilibrium for HCO_3^-

$$K_a = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

e. Water equilibrium

$$K_w = [OH^-][H^+] = 1.0 \cdot 10^{-14}$$

4. pH is then calculated based on the derived H^+ concentration based on 3(a-e).

While the carbonate system is used here as an example, this stepwise process is used for all acid-base species and considers the total system set of reactions and species to achieve equilibrium. The total system electroneutrality considered in the model for all considered species is as follows:

$$H^+ + NH_4^+ + Ca^{2+} + CaHCO_3^+ + CaOH^+ + CaC_2H_3O_2^+ + Fe^{3+} + Fe^{2+} + FeOH^+ + Fe(OH)_2^+ + Na^+$$
$$= OH^- + HCO_3^- + CO_3^{2-} + NO_3^- + NO_2^- + C_2H_3O_2^- + SO_4^{2-} + HSO_4^- + HS^- + Cl^-$$

These compounds are user defined in the input spreadsheet, but are used within the model by ORCHETRA using the Minteq4 chemical database to determine species complexation.

4. 81, eqn (1). I believe there are other mathematical forms to account for the impact of an inhibitory compound (e.g., Haldane Kinetics). Why is this form selected? Does this form only account for the 'inhibition' due to presence of a competing electron acceptor?
   a. **We included this type of inhibition because the inhibition is non-competitive inhibition. We did not include Haldane kinetics because the compounds are not self-inhibitive, as might be valid for aromatic hydrocarbons and chlorinated solvents. We added the following text to reflect this comment (state where):**
   b. **"The van Turnhout Toolbox has the capability to model different inhibition mechanisms, but we only used non-competitive inhibition during denitrification because the enzymes that perform nitrate, nitrite, and sulfate reduction are different and not self-inhibitory (Glass and Silverstein, 1998)."**
5. 84. Can you comment on the assumed initial conditions for biomass of denitrifying and sulfate-reducing microbes? Are these 'typical'? I would expect that the simulation results might be highly sensitive to these values.

    a. **These values can vary greatly depending on the environment, and the time to achieve the target treatment woulddepend on the initial active biomass concentration (i.e., more biomass leads to faster treatment). We added additional results showcasing the sensitivity of the model results to initial biomass concentration.   This is in Figure Z, which is shown here, along with accompanying text.**

6. 111, Table 3. The half maximum-rate constants are in units of mole/liter. Converting to mmole/L and looking at the conditions for the example simulation (Table 6) it appears that the K_d, K_a values may be much smaller than the aqueous concentrations so that the Monod terms reduce to zero-order rate expressions (max possible rate). This is just an observation and may warrant some sensitivity study since the half-max rate constants are highly variable in the literature.

    a. **Wee believe that the largest impact on the process would be the initial biomass concentration, not the K values. Thus, we performed a sensitivity analysis looking at varying concentrations of initial biomass (see the preceding response).**

7. 119-120. Does the model formulation automatically switch between electron acceptors that are more thermodynamically favorable? How does the model switch to using ammonium as the electron acceptor?

    a. **We added additional text to address this question [where?]:**

    b. **"Since NH_4^+ is thermodynamically favorable over NO_3^- as a nitrogen source, it is used before NO_3^- during denitrification; this is implemented using a user-defined switch functiondescribed in Section 3.2; it stops biomass from using NO_3^- as the nitrogen source in the presence of NH_4^+."**

8. 135. The text states that Ki value is the same for inhibition of nitrate and nitrite reduction by nitric acid, however Table 4 has different values. Please explain.

    a. **Thank you for catching this. It was a mistake that we corrected in Table 4.**

9. 3.3. I like the explanation in this section about computing the gas volume required to achieve target desaturation.

    a. **Thank you!**

10. 172. Sec. 3.3. As noted, the mass transfer coefficients are lumped values that are a function of the liquid-gas interfacial area. Therefore, I would expect there to be a dependence on the gas saturation. The sentence "We did not include pore-scale kinetics" is not clear. Does this sentence mean that you did not account for changing interfacial area?   Given the complexity and uncertainty in modeling kinetic mass transfer, why not just use equilibrium partitioning? Is there field or laboratory evidence that kinetics are needed? I would expect the mass transfer coefficient would also be a highly sensitive parameter. The default value assumed (5 per day) is from a paper on sewer networks. I recommend checking the groundwater remediation literature (e.g., air sparging) for more representative values.

a. **First, we added a sentence in our manuscript with the following to justify our inclusion of kinetics:**

b. **"We considered gas-phase-transfer kinetics because assuming instantaneous gas phase transfer clearly would be an oversimplification, based on the review on mass transfer of biologically driven gas production completed by Kraakman et al. (2011)."**

c. **Second, following the recommendations of the reviewer, we adjusted our k_La value to be 1 d^{-1} based on bioremediation literature in soils.**

11. 185. Should the symbol [NO3]_d be added to Table 1?

a. **Thank you for catching this omission; it was added to Table 1.**

12. 204, Eqn (8). I do not understand the statement that this rate expression is first-order with- respect-to calcium concentration, since the product [Ca] [CO3] is in the denominator. Calcite precipitation and dissolution has been studied extensively in the geology/geochemistry literature and I suggest adding a few key citations (e.g., Chou, L., R. M. Garrels, and R. Wollast (1989), Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals, Chem. Geol., 78, 269–282.). As noted, calcite precipitation is a complex process and there are several calcium carbonate polymorphs of different stability.

a. **We adjusted the text to address that precipitation is driven by CO_3^{2-} concentrations, and we added the recommended citation in Section 3.4: The model considers first-order precipitation and dissolution kinetics with respect to the Ca^{2+} and CO_3^{2-} concentrations (Rittmann et al., 2002; Chou et al., 1989)...**

13. 217, Sec. 3.5. Does the modeling framework allow for the presence of other mineral phases at equilibrium with the aqueous solution?

a. **Yes! We added the following text to explain the models ability,**

b. **"While we only considered calcium carbonate precipitation, the model has the flexibility to model other mineral precipitation. The user would need to add in separate equations to model precipitation kinetics based on the reactants, desired products, and the *ka* and *K_{sp}* values appropriate for the desired precipitation reaction and product."**

14. 255-260, Table 6. I am a little confused by the treatment recipes. I was expecting to see numbers in Table 6 that were 25% greater and lesser than the matched case. L. 258 implies that the matched nitrate equals 22.4 mmol/L, but the table shows 19.0 mmol/L.

a. **The 25% excess and reduced acetate are based on our original estimation, following Eq. 6 in the text. We added a column in Table 6 to reflect this to reduce confusion.**

Table 6. MIDP treatment recipes for each modeled condition.

	Original Estimation	Matched	Excess Acetate	Reduced Acetate
Nitrate (mmol L^{-1})	22.4 (1.84 g calcium nitrate L^{-1})	19.0 (1.56 g calcium nitrate L^{-1})	22.4 (1.84 g calcium nitrate L^{-1})	22.4 (1.84 g calcium nitrate L^{-1})
Acetate (mmol L^{-1})	32.1 (1.84 g calcium nitrate L^{-1})	22.4 (1.77 g calcium acetate L^{-1})	40.1 (3.17 g calcium acetate L^{-1})	24.0 (1.90 g calcium acetate L^{-1})

15. 225, Sec. 4, Case Study. Table 5. Are there any solid mineral phases present at the start of the simulation? Should the initial fluid composition be in equilibrium with solid phases? This equilibrium is then perturbed by the input of the treatment fluid? Is there any possibility of iron minerals precipitating?
    a. **Please see the response in RC1, Comment 3. We also added the following to the precipitation section:**
    b. **"At the beginning of each run, the concentration of species available for precipitation are calculated as their dissolved form as discussed in Section 2, then solids precipitation is determined."**
    c. **Second, since this is a batch model, how the treatment solution is added is not considered.   This is an important topic, but beyond the scope of this manuscript.**
    d. **Finally, iron precipitation is possible within the model but was not discussed due to the low concentration of iron in the background environment (0.60 nmol L^{-1}).**
16. Figs 1 & 2 simulation results. Please refer to my general comments regarding sensitivity analysis.
    a. **Thank you for your comments on sensitivity; please refer to RC1, comment 6.**