APPENDIX A

COMPARISONS OF PROPOSED AND EXISTING MIDP MODELS

3 Table A1. Comparison of Existing MIDP Models and the Presented Next Generation MIDP
4 Model

Modeling Component	O'Donnell et al. (2019)	Pham (2017)	This Model
Baseline Substrate Recipe Estimation for Desaturation		X	X
Baseline Substrate Recipe Estimation for Precipitation			X
Complex Acid-base Equilibria		X	X
Denitrifier Growth and Decay	X	X	X
Other Microbe Growth and Decay			X
Microbial Electron Donor Competition			X
Nitrous Acid Inhibition	X	X	X
Alternative MIDP Inhibition			X
Other Microbial Inhibition			X
pH Calculation	X	X	X
CaCO$_3$ Mineral Formation	X	X	X
Other Mineral Equilibrium			X
Mineral Precipitation and Dissolution Kinetics			X
N$_2$ Phase-transfer Kinetics		X	X
Other Gas Production and Phase-transfer Kinetics			X
Ground Improvement Metric Calculations (i.e., desaturation and % precipitation)			X

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CONSTANTS USED IN BIOGEOCHEMICAL MODEL

7 Table A2. Constants used during modeling; these do not include constants found within the
8 ORCHESTRA database for acid-base speciation (Meeussen, 2003), nor those dependent on
9 electron donor and acceptor (e.g., K_a and K_d).

Parameter	Value	Reference
$\Delta G_c^{0'}$ (kJ e$^-$ eq^{-1}): free energy of the carbon source	Acetate: 27.4 Glucose: 41.0 Molasses: 41.0	(Rittmann & McCarty, 2020)
ΔG_{pc} (kJ e$^-$ eq^{-1}): free energy to convert pyruvate carbon to cellular carbon,	Nitrate: 14.1 Ammonium: 19.5	(Rittmann & McCarty, 2020)

depending on the nitrogen source		
$\Delta G_a^{0'}$ (kJ e⁻ eq⁻¹): free energy required to reduce an electron acceptor	Nitrate: -41.65 Nitrite: -92.56 Sulfate: 20.85 Oxygen: -78.72	(Rittmann & McCarty, 2020)
$\Delta G_d^{0'}$ (kJ e⁻ eq⁻¹): free energy released to oxidize an electron donor	Acetate: 27.4 Glucose: 41.0 Molasses: 41.0	(Rittmann & McCarty, 2020)
$\hat{q}_e$: maximum flow of electrons (e-equivalent g⁻¹ biomass d⁻¹)	1.0	(Rittmann & McCarty, 2020)
RM_A: (g Chemical Oxygen Demand (donor e⁻ equivalent)⁻¹)	8	(Rittmann & McCarty, 2020)
RM_B: (mol donor g⁻¹ Chemical Oxygen Demand)	Acetate: 84 Glucose: 192 Molasses: 192	Calculated from half reactions (Rittmann & McCarty, 2020)
e_d^- (mol electron donor (donor e⁻ equivalent)⁻¹) is the amount of donor per electron equivalent	Acetate: 0.13 Glucose: 0.04 Molasses 0.04	Calculated from RM_A, RM_B, and $\hat{q}_e$
ε: energy transfer efficiency term	0.6	(Rittmann & McCarty, 2020)
n: considers energy efficiency due to thermodynamics, depending on electron donor	Acetate: 1 Glucose: 1 Molasses: 1	(Rittmann & McCarty, 2020)
X_a (mmol biomass L⁻¹): Active biomass concentration	Denitrifiers: 0.5 Sulfate Reducers: 0.25	
k_La (d⁻¹): gas mass transfer constant	0.5	(Yongsiri et al., 2004)
$K_{sp(CaCO_3)}$: speciation constant for calcium carbonate	$10^{-8.3}$	
R (L atm K⁻¹ mol⁻¹): universal gas constant	0.082057	
T (K): temperature	298	
K_H (L_aq atm mol⁻¹): Henry's Law coefficients	N₂: 1600 CO₂: 29 H₂S: 10	
e (L_pore L_soil⁻¹): void ratio	0.64	Within a value of acceptable ranges (Christopher et al., 2006)
ka (L d⁻¹): combined coefficient considering a constant mass transfer and the average crystal surface area	100	Within a value of acceptable ranges (Rittmann et al., 2003)

ρ_{soil} (g soil L_{soil}^{-1}): soil density	1950	Within a value of acceptable ranges (Christopher et al., 2006)

10

DERIVATIONS OF IMPORTANT PARAMETERS

11

12   The value of $\hat{q}$ (mol electron donor mol^{-1} biomass d^{-1}) was estimated using Eq. A1

13   (Rittmann & McCarty, 2020).

$$\hat{q} = \frac{\hat{q}_e e_d^-}{f_e^0} \qquad \text{Eq. A1}$$

14   where $\hat{q}_e$ is the maximum electron flow from the donor to the acceptor for energy production

15   (acceptor e$^-$ eq mol^{-1} biomass d^{-1}), f_e^0 is the fraction of donor electrons used for energy

16   production (acceptor e$^-$ eq (donor e$^-$ eq)$^{-1}$), and e_d^- is the amount of donor per electron equivalent

17   (mol electron donor (donor e$^-$ equivalent)$^{-1}$).   The molecular formula for biomass was

18    $CH_{1.8}O_{0.5}N_{0.2}$, and the resulting $\hat{q}_e$ is 24.6 e$^-$ eq mol^{-1} biomass d^{-1}. For acetate, e_d^- is 0.13 electron

19   donor e$^-$ equivalent^{-1}. f_e^0 was determined using Eq. A2 (Rittmann & McCarty, 2020).

$$f_e^0 = 1 - \frac{1}{-\left(\frac{\frac{30.09 - \Delta G_c^{0\prime}}{\varepsilon^n} + \frac{\Delta G_{pc}}{\varepsilon}}{\varepsilon(\Delta G_a^{0\prime} - \Delta G_d^{0\prime})}\right) + 1} \qquad \text{Eq. A2}$$

20   where 30.09 is the amount of energy required to form the representative intermediate during

21   synthesis, acetate (acetyl-CoA) (kJ e$^-$ eq), $\Delta G_c^{0\prime}$ is the energy required to convert the carbon

22   source to forms useful in synthesis (in this case, the carbon source is also the electron donor) (kJ

23   e$^-$ eq^{-1}), ε is the energy transfer efficiency term ($\varepsilon = 0.6$), n is used to consider energy efficiency

24   when the reaction is thermodynamically positive ($n = -1$) or negative ($n = -1$), ΔG_{pc} is the energy

25   required to convert the carbon source (acetate in this case) to carbon used for biomass synthesis,

26   depending on the nitrogen source (kJ e$^-$ eq^{-1}), and ΔG_r is the energy released during each redox

27   reaction (kJ e$^-$ eq^{-1}). ΔG_{pc} was calculated to consider either nitrate or ammonium as the nitrogen

28   source (Rittmann & McCarty, 2020). All free-energy parameters, listed in Table A3, were found

29   in Rittmann and McCarty (2020).

30   Table A3. Bacterial Energetic Parameters for all Compounds Considered in the Model at pH = 7.

Parameter	Value (kJ e$^-$ eq^{-1})
$\Delta G_c^{0'}$: free energy of the carbon source	Acetate: 27.4 Glucose: 41.0 Molasses: 41.0
ΔG_{pc}: free energy to convert pyruvate carbon to cellular carbon, depending on the nitrogen source	Nitrate: 14.1 Ammonium: 19.5
$\Delta G_a^{0'}$: free energy required to reduce an electron acceptor	Nitrate: -41.65 Nitrite: -92.56 Sulfate: 20.85 Oxygen: -78.72
$\Delta G_d^{0'}$: free energy released to oxidize an electron donor	Acetate: 27.4 Glucose: 41.0 Molasses: 41.0

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32   The model considers biogeochemical reactions that involve alternative electron acceptors and the

33   presence of alternative minerals and metals (i.e., iron, sulfate). Table 2 in the main manuscript

34   details the microbial energetic values used to calculate the expected substrate utilization and

35   maximum specific growth rates (μ_{max}). Within the model, two different nitrogen sources are

36   considered: nitrate and ammonium. Ammonium as a nitrogen source is more

37   thermodynamically favorable, as shown in Table A3. Therefore, more electron equivalents of

38   nitrate are needed to form biomass than ammonium. The thermodynamic favorability of

39   ammonium over nitrate is reflected in the fraction of electrons going to energy generation (f_e^0)

40   and fraction of electrons going to biomass synthesis (f_s^0) values (Table A4).

41 Table A4. Microbial Energetics Expected During MIDP, Considering Acetate as the Electron
42 Donor and Natural Electron Acceptors

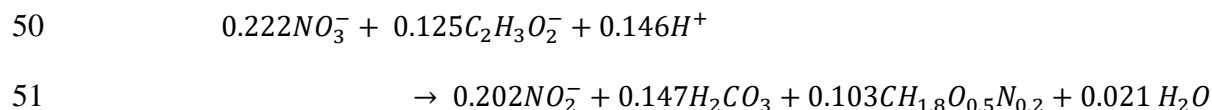| Electron Acceptor	Nitrogen Source	G_r (kJ e⁻ eq⁻¹)	f_e^0	f_s^0	$\hat{q}$ (mol e⁻ donor mol⁻¹ biomass d⁻¹)
Nitrate	Nitrate	-69.05	0.40	0.60	8.12
Nitrite	Nitrate	-119.96	0.28	0.72	11.69
Sulfate	Nitrate	-6.55	0.88	0.12	3.74
Nitrate	Ammonium	-69.05	0.47	0.53	6.95
Nitrite	Ammonium	-119.96	0.34	0.66	9.65
Sulfate	Ammonium	-6.55	0.90	0.10	3.63

43

44 **pH Determination**

45 The steps for how pH was determined within the model is as follows (Meeussen, 2003; van

46 Turnhout et al., 2016), using H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- to illustrate the process.

47   1. At t = 0, the program loads the input concentrations file, which includes the concentration

48   of all total species (e.g., H_2CO_3 representing DIC, H^+) and the stoichiometry for

49   metabolic and kinetic reactions: e.g.,

50       $0.222NO_3^- + 0.125C_2H_3O_2^- + 0.146H^+$

51             $\rightarrow 0.202NO_2^- + 0.147H_2CO_3 + 0.103CH_{1.8}O_{0.5}N_{0.2} + 0.021\ H_2O$

52   2. Ordinary differential equations are used to determine compound consumption and

53   production based on the reaction stoichiometry and kinetic equations (i.e., precipitation

54   and mass transfer) at each time step. The graphic below illustrates that, as $C_2H_3O_2^-$ is

55   consumed from microbial consumption, H_2CO_3 is produced.

Time   Time
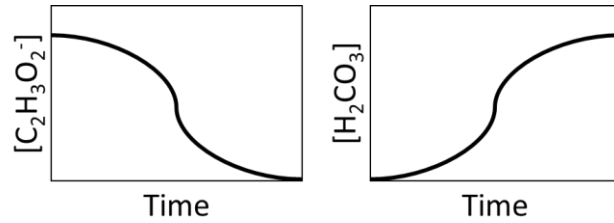
56

57   3. At each time step, the following set of linear equations are solved to determine the

58   relative derived concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, and OH^- from H_2CO_3

59   produced in the previous steps. This is done in the ORCHESTRA biochemical module.

60   a. Mass balance equations – the left side of the equation is the total dissolved

61   inorganic carbon, H_2CO_3, from the stoichiometry described in steps 1 and 2. The

62   right side are the derived concentrations of species as a result of speciation and

63   indicated with italics.

64    $$\mathrm{H_2CO_3} \;=\; H_2CO_3 + HCO_3^- + CO_3^{2-}$$
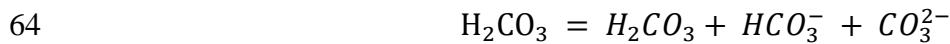
65   b. Electroneutrality – all potentially produced charged species related to this balance

66   are considered.

67    $$H^+ \;=\; OH^- + HCO_3^- + CO_3^{2--}$$

68   c. Acid equilibrium for H_2CO_3

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

70   d. Acid equilibrium for HCO_3^-

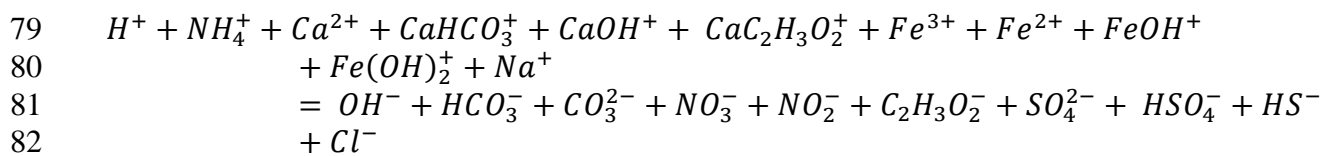71 $$K_a = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

72   e. Water equilibrium

73
$$K_w = [OH^-][H^+] = 1.0 \cdot 10^{-14}$$

74   4. pH is calculated based on the derived H^+ concentration.

75 While the carbonate system is used here as an example, this stepwise process is used for all acid-

76 base species and considers the total system set of reactions and species to achieve equilibrium.

77 The total system electroneutrality considered in the model for all considered species is as

78 follows:

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

83 These compounds are user defined in the input spreadsheet, but are used within the model by

84 Orchestra using the Minteq4 chemical database to determine species complexation.

85