Iron cycle interactions with hydrological dynamics reduce methane production in a simulated Arctic soil

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November 30, 2022

Abstract

The fate of organic carbon (C) in permafrost soils is important to the climate system due to the large global stocks of permafrost C. Thawing permafrost can be subject to dynamic hydrology, making redox processes an important factor controlling soil organic matter (SOM) decomposition rates and greenhouse gas production. In iron (Fe)-rich permafrost soils, Fe(III) can serve as a terminal electron acceptor, suppressing methane (CH4) production and increasing carbon dioxide (CO2) production. Current large-scale models of Arctic C cycling do not include Fe cycling or pH interactions. Here, we coupled Fe redox reactions and C cycling in a geochemical reaction model to simulate the interactions of SOM decomposition, Fe(III) reduction, pH dynamics, and greenhouse gas production in permafrost soils subject to dynamic hydrology. We evaluated the model using measured CO2 and CH4 fluxes as well as changes in pH, Fe(II), and dissolved organic C concentrations from oxic and anoxic incubations of permafrost soils from polygonal permafrost sites in northern Alaska, United States. In simulations of higher frequency oxicanoxic cycles, rapid oxidation of Fe(II) to Fe(III) during oxic periods and gradual Fe(III) reduction during anoxic periods reduced cumulative CH4 fluxes and increased cumulative CO2 fluxes. Lower pH suppressed CH4 fluxes through its direct impact on methanogenesis and by increasing Fe(III) bioavailability. Our results suggest that models that do not include Fe-redox reactions and its pH dependence could overestimate CH4 production and underestimate CO2 emissions and SOM decomposition rates in Fe-rich, frequently waterlogged Arctic soils.

1	Simulated hydrological dynamics and coupled iron					
2	redox cycling impact methane production in an Arctic					
3	soil					
4 5 6	Benjamin N. Sulman ¹ , Fengming Yuan ¹ , Teri O'Meara ¹ , Baohua Gu ¹ , Elizabeth Herndon ¹ , Jianqiu Zheng ³ , Peter Thornton ¹ , and David E. Graham ²					
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 11 12 13 14 15 16 17 18 	Notice: This manuscript has been authored by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE). The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).					
19	Key Points:					
20 21	• Ferric iron reduction can fuel decomposition in iron-rich Arctic soils. Higher rates of iron reduction reduce methane production					
22	• We coupled iron and carbon cycling in a geochemical reaction model under simulated					
23 24	• Ovic-anovic cycling in simulations reduced methane emissions and increased carbon					
2 4 25	dioxide production by regenerating oxidized iron					
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47

48 Plain language summary

49 Soils in cold regions store large amounts of carbon that may be converted to climate-warming 50 greenhouse gases as frozen soils thaw. Methane, a powerful greenhouse gas, is primarily 51 produced when soils are flooded and lack oxygen. However, Arctic soils are also rich in iron, 52 which some soil microorganisms can use instead of oxygen through a decomposition pathway 53 that also produces carbon dioxide rather than methane. The computer models that are currently 54 used to predict greenhouse gas emissions from thawing Arctic soils do not include iron 55 interactions. We built a new model to simulate how iron, oxygen, and carbon interact in soils that 56 are repeatedly flooded and drained. We tested the model using laboratory measurements of 57 greenhouse gas production and iron cycling in Arctic soils. Our model simulations showed that 58 when soils cycle more often between being flooded and exposed to air, iron is recycled to forms 59 that can fuel carbon dioxide production while reducing methane gas production. Our results

suggest that including iron cycling in soil carbon models could improve predictions of theclimate warming potential of greenhouse gas emissions from thawing Arctic soils.

62 1. Introduction

63 Permafrost regions contain enormous soil organic carbon (C) stocks (Hugelius et al., 2014). 64 The fate of this vast C pool is critical to the global climate system because of the potential for 65 decomposition of permafrost organic matter (OM) and C release into the atmosphere as 66 greenhouse gases (Schuur et al., 2015; Turetsky et al., 2020). Because thawing permafrost often 67 drives physical collapse and flooding, anoxic processes are an important component of 68 permafrost OM decomposition. Major uncertainties in current understanding of permafrost thaw 69 include the amount of C that will be mineralized and the relative amounts of CO₂ and CH₄ that 70 will be produced by decomposition of OM in thawing permafrost soils.

71 Decomposition processes in saturated Arctic soils are tightly coupled to cycling of other 72 elements including oxygen (O), nitrogen (N), and iron (Fe), which can serve as terminal electron 73 acceptors (Dettling et al., 2006; Lipson et al., 2010). The presence of electron acceptors such as 74 Fe(III) has been shown to suppress the production of CH₄, which provides a lower energy benefit 75 to microbial metabolism, when Fe reducers are able to outcompete methanogens for substrates 76 (Lipson et al., 2012; Miller et al., 2015). Simultaneous methanogenesis and ferric Fe (Fe(III)) 77 reduction have been observed in Arctic soils, however, indicating that microbial processes do not 78 necessarily strictly follow the redox ladder (Roy Chowdhury et al., 2015; Herndon et al., 2015; 79 Yang et al., 2016; Reiche et al., 2008; Zheng et al., 2018). Many Arctic soils are rich in Fe(III)-80 bearing minerals and OM-bound Fe(III), and as a result, redox cycling of Fe can be an important 81 control on OM degradation and C mineralization in permafrost soils (Herndon et al., 2017). 82 Terminal electron acceptor availability and CH₄ production are also strongly dependent on soil 83 pH (Zheng et al., 2019). 84 Despite the importance of such redox cycling processes for determining organic matter 85 decomposition and greenhouse gas production in Arctic soils, the models applied at ecosystem to 86 global scales to predict C cycling and related climate change feedbacks do not explicitly 87 represent redox processes or pH dynamics (Wang et al., 2019; Wania et al., 2013; Xu et al., 88 2016). This omission opens the possibility that model projections could overestimate CH₄

89 emission and underestimate organic C mineralization and CO₂ production rates in soils where

alternate terminal electron acceptors are abundant. Such bias could be amplified in soils with
 dynamic hydrology that drives oscillations in redox conditions and consequent fluctuations in
 terminal electron acceptor variability.

93 Here, we simulated coupled OM decomposition and Fe redox cycling in the reactive 94 transport model PFLOTRAN (Hammond et al., 2014). PFLOTRAN has been applied in 95 biogeochemical contexts such as hyporheic zones (Dwivedi et al., 2018), and has previously 96 been directly coupled to a land surface model and used to simulate soil organic matter cycling 97 (Tang, Yuan, et al., 2016). We parameterized a biogeochemical reaction network using 98 laboratory incubations of permafrost soils collected from different layers and microtopographic 99 settings in a polygonal permafrost landscape, and then used the model to investigate how 100 interactions between C and Fe cycling affect CH₄ and CO₂ production over oxic-anoxic cycles 101 across a range of soil pH.

102

103 2. Methods

104 2.1. Model simulations

105 Simulations were conducted using a reaction network defined in PFLOTRAN (Figure 1, Table 1) 106 building on reaction network developments from previous modeling studies using a different 107 chemical reaction model, PHREEQC (Tang, Zheng, et al., 2016; Zheng et al., 2019) and 108 previous implementation of soil organic matter decomposition reactions in PFLOTRAN (Tang, 109 Yuan, et al., 2016). Organic matter pools in the reaction network included solid soil organic 110 matter (SOM) and dissolved organic matter (DOM). Solid organic matter was first hydrolyzed to 111 DOM, which could then be completely oxidized to CO_2 through aerobic decomposition 112 (consuming O₂) or decomposed to produce organic acids (represented in the model by acetate) and CO₂ through fermentation (in anoxic conditions). Under anoxic conditions, acetate could be 113 114 mineralized either by microbial reduction of Fe(III) or by acetoclastic methanogenesis. Aqueous 115 Fe(III) ions were equilibrated with amorphous Fe(OH)₃ minerals through kinetic precipitation 116 and dissolution reactions, which were calculated using Transition State Theory type rate laws 117 (Dwivedi et al., 2018). These precipitation-dissolution relationships were highly pH dependent, 118 with extremely low concentrations of uncomplexed aqueous Fe(III) ions under typical pH 119 conditions. The model included equilibrium aqueous complexes of Fe(III) with DOM and

120 acetate, which greatly increased the concentration of total aqueous Fe(III). However, note that in 121 PFLOTRAN, aqueous chemical reaction rates, including Fe(III) reduction rates, are calculated 122 based on free ion concentrations rather than total aqueous concentrations. Fe(III) reduction 123 converted Fe(III) to more soluble ferrous Fe (Fe(II)) ions. Under oxic conditions, Fe(II) was 124 rapidly oxidized back to Fe(III), with the oxidation rate estimated using data from oxic 125 incubations (see Section 2.2). Fe(III) reduction and Fe(II) oxidation effectively functioned as 126 reductive dissolution and oxidative precipitation of Fe(OH)₃ due to the tight coupling between 127 the aqueous and mineral phases.

Methanogenesis was simulated as a combination of acetoclastic and hydrogenotrophic pathways. pH dependence of the two methane pathways were determined based on an optimization to measurements of Kotsyurbenko et al. (2007) (Figure S1). The optimized pH dependence had the form:

132
$$F(pH) = \frac{10^{-pH}}{10^{-pH} + 10^{-k_1}} \frac{10^{-k_2}}{10^{-pH} + 10^{-k_2}}$$
(1)

133

Where F(pH) is relative reaction rate as a function of pH for either methanogenesis pathway, and k_1 and k_2 are parameters determining limitation by low and high pH, respectively. For acetoclastic methanogenesis, the optimization found k_1 and k_2 both equal to 5.5. For hydrogenotrophic methanogenesis, the optimization found $k_1 = 6.75$ and $k_2 < 0$, indicating no limitation at low pH.

139 We conducted two sets of simulations representing alternative approaches to the 140 interaction between methanogenesis and Fe(III) reduction. In one set of simulations, 141 methanogenesis was directly inhibited by the presence of Fe(III) and O₂, which represented more 142 energetically favorable terminal electron acceptors. This approach assumes that simultaneous 143 Fe(III) reduction and methanogenesis is limited, which is consistent with the traditional redox 144 ladder conceptual model but may not be accurate for systems where simultaneous 145 methanogenesis and Fe(III) reduction are common as noted above. In the second approach, the 146 direct inhibition of methanogenesis by Fe(III) was removed, and methanogenesis was inhibited 147 only by O₂. SOM aerobic decomposition and anaerobic hydrolysis followed CLM-CN decomposition kinetics (Tang, Yuan, et al., 2016) modified to allow Monod and inverse Monod 148 149 (inhibition) responses to aqueous chemical species and assuming no nitrogen limitation of

decomposition. Microbial aqueous reactions were assumed to follow multi-Monod kinetics of theform:

152
$$R = V_{max} \prod_{N} \frac{c_{S_N}}{\kappa_{S_N} + c_{S_N}} \prod_{M} \frac{\kappa_{I_M}}{\kappa_{I_M} + c_{I_M}}$$
(2)

where *R* is reaction rate (mol (L H₂O)⁻¹ s⁻¹), V_{max} is maximum reaction rate (mol L⁻¹ s⁻¹), *N* is the set of reactant species (including substrates and terminal electron acceptors), *M* is the set of inhibiting species, C_{S_N} is the concentration of the *N*th substrate, K_{S_N} is the half-saturation constant of the Nth substrate, C_{I_M} is the concentration of the *M*th inhibiting species, and K_{I_M} is the inhibition constant of the *M*th inhibiting species.

In addition to the kinetic reactions described above, the reaction network included the pH buffering effect of soil organic matter. The soil matrix was assumed to contain surface complexation sites that could exchange H⁺ ions under changing pH conditions. The volumetric density of these proton exchange sites was proportional to organic matter concentration in the soil layer being simulated (following Zheng et al., 2019) and the fraction of sorbed H⁺ followed equilibrium sorption kinetics as defined in PFLOTRAN

164 (https://www.pflotran.org/documentation/theory_guide/mode_reactive_transport.html).

Aerated and saturated conditions were simulated by varying the diffusion rate of O₂ between the simulated soil layer and a boundary condition representing aqueous O₂ concentration at equilibrium with the atmosphere. Flux was calculated based on the difference

between O₂ concentration in the soil layer and in the boundary condition:

$$F_{O_2} = \left(\frac{[O_2]_{sat} - [O_2]_S}{\Delta z}\right) k_d$$

(3)

where F_{O_2} is flux rate of O₂ between the soil porewater and boundary condition (mol cm⁻² s⁻¹), 170 $[O_2]_{sat}$ is the aqueous O₂ concentration at saturation with respect to the atmosphere (mol cm⁻³), 171 $[O_2]_S$ is the soil aqueous O₂ content, Δz is the soil layer thickness (cm), and k_d is the diffusion 172 coefficient (cm² s⁻¹). Under aerated conditions, k_d was set to 0.1 cm² s⁻¹, and under saturated 173 174 conditions, k_d was set to zero, preventing O₂ from being replenished. For purposes of gas 175 diffusion, Δz was assumed to be 10 cm. For simplicity, soil water content was assumed to be 176 constant and equal to porosity across aerated and saturated conditions. This assumption 177 prevented the model from simulating changes in aqueous concentrations driven only by 178 differences in water content associated with drying. 179

- 181 Table 1: Porewater reactions included in the model. Monod and inhibition species are followed
- 182 by the half-saturation concentration (M, mol L⁻¹) in parentheses. DOM is expressed per mol C
- 183 and is assumed to have a stoichiometry 6 C:12 H:6 O.

Reaction	Stoichiometry	Reaction	Reaction	Monod	Inhibition
		type	rate	species (half-	species
			parameter	saturation	(inhibition
			(s ⁻¹ for	concentration	constant
			SOM and	[M])	[M])
			M s ⁻¹ for		
			Monod)		
SOM hydrolysis	$SOM-C + H_2O$	SOM	1.0x10 ⁻⁸		DOM
	\rightarrow DOM-C				(0.5)
Fermentation	DOM-C +0.33	Monod	4.0x10 ⁻⁷	DOM-C	Acetate
	${ m H_2O} ightarrow 0.33$			(0.5)	(0.04)
	CH ₃ COO ⁻ +				O ₂ (10 ⁻⁵)
	$0.33 \text{ CO}_2^- +$				
	$0.33 \ {\rm H^{+}} + 0.67$				
	H ₂				
DOM aerobic	$DOM-C + O_2$	Monod	5.0x10 ⁻⁷	O ₂ (10 ⁻⁴)	
respiration	$\rightarrow \mathrm{CO}_2 + \mathrm{H}_2\mathrm{O}$			DOM-C	
				(0.5)	
Acetate aerobic	$CH_3COO^- + 2$	Monod	5.0x10 ⁻⁷	O ₂ (10 ⁻⁴)	
respiration	$\mathrm{O}_2 + \mathrm{H}^{\scriptscriptstyle +} \to 2$			Acetate	
	$CO_2 + 2 H_2O$			(0.04)	
Fe(III) reduction	$CH_3COO^- + 8$	Monod	3.0x10 ⁻⁸	Acetate	O ₂ (10 ⁻⁵)
	$Fe^{3+} + 2 H_2O \rightarrow$			(0.04)	
	$2 \text{ CO}_2 + 8 \text{ Fe}^{2+}$			Fe(III) (10 ⁻¹⁰)	
	$+ 7 H^{+}$				

Fe(II) oxidation	$Fe^{2+} + 0.25 O_2$	Monod	1.0x10 ⁻⁶	O ₂ (10 ⁻⁴)	
	$+ H^+ \rightarrow Fe^{3+} +$			Fe(II) (0.1)	
	0.5 H ₂ O				
Acetoclastic	$CH_3COO^- + H^+$	Monod	2.0x10 ⁻⁸	Acetate	O ₂ (10 ⁻⁵)
methanogenesis	$\rightarrow CH_4 + CO_2$			(0.04)	Fe(III)
				$H^{+}(10^{-5.5})$	(10-10)**
					H ⁺ (10 ^{-5.5})
Hydrogenotrophic	$4 \text{ H}_2 + \text{CO}_2 \rightarrow$	Monod	9.6x10 ⁻⁹	H ₂ (0.1)	O ₂ (10 ⁻⁵)
methanogenesis	$\mathrm{CH}_4 + 2~\mathrm{H}_2\mathrm{O}$			$HCO_{3}^{-}(0.1)$	Fe(III)
					(10-10)**
					H ⁺ (10 ^{-6.75})
H ₂ oxidation	$2 \text{ H}_2 + \text{O}_2 \rightarrow 2$	Monod	1.0x10 ⁻⁶	H ₂ (0.1)	
	H ₂ O			O ₂ (10 ⁻⁴)	
Fe(OH) ₃	$Fe(OH)_3 + 3 H^+$	Precipitation-	1.0x10 ⁻⁶		
	$\leftrightarrow \mathrm{F}\mathrm{e}^{3+} + 3~\mathrm{H_2O}$	dissolution	mol m ⁻²		
			surface		
			area s ⁻¹		
*Fe(OH) ₃	Fe(OH) ₃ +				
reductive	0.125 CH ₃ COO ⁻				
dissolution	$+ 2.125 \text{ H}^+ \rightarrow$				
	2.75 H ₂ O +				
	$0.25 \text{ CO}_2 + \text{Fe}^{2+}$				
*Fe(OH) ₃	$Fe^{2+} + 0.25 O_2$				
oxidative	$+ 2.5 \text{ H}_2\text{O} \rightarrow$				
precipitation	$Fe(OH)_3 + 2 H^+$				

184 *The Fe(OH)₃ reductive dissolution and oxidative precipitation equations are represented in the 185 model through separate precipitation-dissolution and oxidation/reduction steps but the combined 186 stoichiometries are shown here to ease interpretation of their effects on pH.

187 ******Fe(III) inhibition terms for methanogenesis were included in one set of simulations and

188 omitted in the other to test the impact of this assumption on simulation results.



191 Figure 1: Network diagram of reactions included in the PFLOTRAN reaction network. Circles 192 show chemical pools, and stars show reactions. Some chemical species, including H⁺, are 193 omitted for clarity.

194

195 2.2. Comparison with incubation measurements

196 Model simulations were parameterized using previously published measurements from

197 laboratory microcosm incubations of seasonally thawed soil from the active layer of permafrost-

198 underlain polygons (Figure 2; S5), as synthesized by Zheng et al. (2018, 2019) and porewater

- 199 chemistry measurements from Herndon et al. (2016). Briefly, intact frozen soil cores were
- 200 collected from Utqiagvik, Alaska and include trough, ridge, and center locations in ice-wedge
- 201 polygons. Frozen soils were processed under anoxic conditions, and 15 g of soil from organic or
- 202 mineral layers was used to establish triplicate microcosm incubations under anoxic conditions
- 203 (N₂ headspace) or oxic conditions (air) (Zheng et al., 2018; Roy Chowdhury et al., 2015). Layers
- 204 were distinguished by color and abundance of soil organic carbon. Incubations included an oxic

205 incubation of a high-centered polygon center organic horizon and anoxic incubations of organic 206 and mineral horizons from a trough and a rim location. Head space CH₄ and CO₂ concentrations 207 were measured using gas chromatography throughout the incubation period, and subsamples 208 from separate microcosm incubations were used to determine changes in pH and exchangeable 209 Fe(II) concentrations (Roy Chowdhury et al., 2015). Water extractable organic carbon was 210 extracted from ground, freeze-dried soil, and low molecular weight organic acids were analyzed 211 using ion chromatography (Herndon et al., 2015). Averages and standard errors over replicate 212 incubation CO₂ and CH₄ flux measurements were used for comparison with modeled values at 213 the appropriate time point. Reported standard errors of observed Fe(II) concentrations from Roy 214 Chowdhury et al. (2015) and reported standard errors of water extractable organic carbon and 215 total organic acids from Herndon et al. (2015) were used for comparisons with those quantities. 216 Measurement uncertainties were not available for pH.

217 Model rate constants and key parameters were adjusted to maximize agreement (based on 218 root mean square error (RMSE) and correlation coefficient (R)) between modeled and measured 219 time series of CO₂ flux, CH₄ flux, pH, and concentrations of Fe(II), DOM, and organic acids 220 (compared with acetate in the model) across four incubations with the multiple time points of the 221 relevant measurements. Fermentation rate constant and half-saturation (K_S) for acetate were 222 identified as particularly sensitive parameters, and simulations were conducted across a range of 223 these parameters to identify the optimal values (Figs. S2 and S3). The same rate constants and 224 half-saturation constants were applied to all horizons. Simulated incubations were initialized 225 using available measurements from each incubation. SOC and bulk density were determined 226 using measured SOC, assuming bulk density followed the relation of (Bockheim et al., 2003): 227

228
$$BD = e^{\frac{8.2432 - SOC(\%)}{9.7872}}$$
 (4)

229

where SOC (%) is SOC in mass percentage and BD is bulk density in units of g cm⁻³. Note that
since measurements were expressed per unit dry soil mass, the lack of reported bulk density
measurements means that any mismatch between actual and measured bulk density would
introduce error to model-measurement comparisons.

234 Soil pH at the beginning of the simulated incubation was set as the measured pH at time zero 235 of the incubation. Initial aqueous Fe(II) concentration was set as the measured aqueous Fe(II) 236 concentration at time zero, and initial Fe oxide mineral mass was set to 1.5 times the increase in 237 measured Fe(II) concentration (per unit soil mass) over the course of the incubation, thereby 238 assuming that two thirds of initial Fe oxides were reduced to Fe(II) over the course of each 239 incubation. This correction was based on the assumption that some fraction of the Fe oxides were 240 not reduced over the course of the incubations, likely representing crystalline oxides that are 241 more resistant to microbial reduction, and aligned $Fe(OH)_3$ concentrations in the model with 242 measurements of total extractable Fe relative to Fe(II) concentrations from similar soils 243 (Herndon et al., 2017). Initial DOM and acetate concentrations were set using measured DOM 244 and organic acid concentrations, respectively. Cation exchange capacity (CEC) was set using SOC content, assuming that CEC of organic matter was 200 meg (100 g)⁻¹ and CEC of mineral 245 246 material was 25 meg (100 g)⁻¹ (Ping et al., 1998). Initial hydrolysable SOC was set using 247 measured SOC, assuming that hydrolysable SOC represented 5% of total SOC (consistent with a small labile fraction; Schädel et al., 2013). Initial concentrations of Mg²⁺, Ca²⁺, Na⁺, and K⁺ were 248 249 set using mean porewater chemistry measurements from (Herndon et al., 2015, 2016).

250 2.3. Simulated oxic-anoxic cycling

251 Oxic-anoxic cycles were simulated by varying the k_d over time to represent transitions 252 between aerated and saturated states. k_d was changed instantaneously at the time of transition 253 between aerated and saturated conditions. Simulations were conducted over a 150-day period, 254 beginning with a 15-day anoxic spinup period. 10% of the remaining simulation time was spent 255 under aerated conditions to represent a wetland system that was periodically aerated but 256 primarily under flooded conditions. Simulations with only one cycle were aerated for 15 days at 257 the end of the 15-day spinup period and then remained under anoxic conditions for the remainder 258 of the simulation. Simulations with multiple cycles shortened the length of each aerated period 259 so that the total time under aerated and saturated conditions was the same (15 days under aerated 260 conditions) in all simulations. The effect of pH was tested by repeating simulations with initial 261 pH conditions ranging in increments of 0.5 from 4.5 to 6.0, a range typical of Arctic tundra soils. 262 These simulations were set up for mineral and organic horizons from the permafrost polygon 263 trough location using the same data sources and initialization approach described above.

264 3. Results

265

266 3.1. Comparison of model simulations and incubations

Model simulations correlated well with observations for Fe(II) concentrations, pH, and DOM 267 268 concentration (Figure 2). Simulated acetate concentrations were not as well correlated with total 269 organic acid measurements, particularly later in the incubations. Simulated CO₂ production was 270 overestimated by the model for the polygon rim organic horizon (squares on Fig. 2e), while other 271 incubations were more accurately simulated. This overestimation may have been due to the high 272 organic content (39%) and consequently low calculated bulk density (0.28 g cm⁻³) of polygon 273 rim organic horizon, which meant that fluxes expressed on a per-weight basis were divided by a 274 small mass. Note that the model simulated cumulative production of CO_2 and CH_4 in porewater 275 and did not explicitly simulate transport of dissolved gases across the soil surface to the head 276 space. CH₄ production was also overestimated for organic horizons but was well correlated 277 between model and observations for mineral horizons (Fig. 2c,d). Including direct inhibition of 278 CH₄ production by Fe(III) lowered organic horizon CH₄ fluxes early in the incubations, which 279 increased overall correlation between model and observations (Fig. 2d). In the oxic incubation of 280 the center organic horizon, the model simulated a very rapid decline in Fe(II) concentrations as 281 Fe(II) was rapidly oxidized to Fe(III) (Fig. 2a). The model did not reproduce the higher Fe(II) 282 concentration observed later in the oxic incubation. The model reproduced measured increases in 283 pH during the Fe(III) reduction phase in the trough cores but not in the rim cores.



285 Figure 2: Comparisons between incubation measurements and model simulations. Measurements 286 (Zheng et al., 2018, 2019) are shown on the horizontal axis and corresponding simulated values 287 are shown on the vertical axis. The dotted line shows a 1-1 relationship. Symbol colors indicate 288 day of the incubation, with lighter colors occurring later in the incubation. Symbols show 289 permafrost polygon setting of the incubation source material (trough, rim, or oxic center) and soil 290 horizon (organic or mineral). Coefficient of determination (R²) between modeled and measured 291 points is show on each panel. Panel (c) shows CH₄ flux from simulations without direct 292 inhibition of methanogenesis by Fe(III), and panel (d) shows CH₄ flux from simulations

293 including direct inhibition. Only CH₄ flux is shown for both configurations because the other

294 quantities were not visually different between configurations.

296 3.2. Simulations of oxic-anoxic cycles

297 Simulations of repeated oxic-anoxic cycles highlighted the succession of decomposition phases 298 as the system depleted different terminal electron acceptors, as well as the interaction of these 299 phases with pH (Fig. 3, S4). During oxic periods, CO₂ fluxes were high, supported by abundant 300 oxygen (Fig. 3b). During anoxic periods, O₂ was rapidly depleted, causing a sharp decline in 301 CO₂ production rate. Early in each anoxic period, Fe(III) reduction increased quickly, as shown 302 by the production rate of Fe(II) ions (Fig. 3c). Fe(III) reduction depleted Fe oxide minerals (Fig. 303 3d) and increased pH (Fig. 3e) due to the net proton consumption effect of Fe(OH)₃ reductive 304 dissolution (Table 1). CH₄ fluxes (Fig 3a) were inhibited by Fe(III), delaying the increase in CH₄ 305 production rates under anoxic conditions. Fe(III) reduction produced twice as much CO₂ per unit 306 acetate consumed as methanogenesis and had a faster reaction rate, causing CO₂ production to be 307 higher during the Fe(III) reduction phase than during the methanogenesis phase. The temporal 308 pattern of Fe(III) reduction and its effect on methanogenesis were controlled by a combination of 309 Fe(III) accessibility and pH. Under lower pH conditions (dotted lines), Fe oxide mineral 310 solubility was higher, leading to higher Fe(III) availability and consequently more rapid Fe(III) 311 reduction rates and stronger inhibition of methanogenesis. Rapid Fe(III) reduction at pH of 5.0 312 was consistent with high observed accumulation rates of Fe(II) in incubations starting at pH of 313 around 5 (Fig. S5). Under higher pH conditions (solid and dashed lines), the lowered Fe oxide 314 solubility, combined with the rise in pH driven by Fe oxide dissolution, inhibited further Fe(III) 315 reduction. Rising pH allowed methanogenesis rates to increase over time in simulated mineral 316 horizons (Fig. 3) while methanogenesis rates increased after depletion of soluble Fe oxides in 317 simulated organic horizons (Fig. S4). The effect of including direct inhibition of methanogenesis 318 by Fe(III) was most apparent in CH₄ fluxes, which were lower overall and increased more slowly 319 when direct inhibition was included (Fig. 3a). In simulations with the lowest initial pH and direct 320 inhibition, CH₄ production did not begin until iron oxides had been depleted. However, the 321 general pattern of increasing CH₄ production over time during anoxic periods was evident in 322 simulations with or without direct inhibition.



324

Figure 3: Simulated oxic-anoxic cycles for a mineral horizon. Blue backgrounds indicate anoxic
conditions and white backgrounds indicate oxic conditions. Black lines show simulations with
direct inhibition of methanogenesis by Fe(III) and blue lines show simulations without direct
inhibition (a): CH₄ flux rate. (b): CO₂ flux rate. (c): Fe(II) production rate via Fe(III) reduction.
(d): Fe oxide mineral concentration. (e): pH. (f): Acetate concentration.

331 Integrating CO₂ and CH₄ fluxes across multiple oxic-anoxic cycles showed the cumulative

- impact of the Fe-C-pH interactions on CO₂ and CH₄ fluxes (Fig. 4). Integrated CO₂ fluxes
- increased with more oxic-anoxic cycles, with a stronger increase in the simulated organic than in

- the simulated mineral horizon (Fig. 4a). Cumulative CO₂ fluxes were minimally affected by pH
- and were not sensitive to whether the simulation included direct inhibition of CH₄ production by
- 336 Fe(III). The total increase in cumulative CO₂ production from one to five cycles was
- 337 approximately 1.9 mmol g dwt⁻¹ (a 120% increase relative to one cycle) in the organic horizon
- and 0.52 mmol g dwt⁻¹ (a 100% increase) in the mineral horizon.
- 339 Cumulative CH₄ production declined with increasing numbers of oxic-anoxic cycles. At
- 340 pH of 6, CH₄ fluxes from the organic horizon declined from 0.12 to 0.09 mmol g dwt⁻¹ (25%)
- between one and five cycles, and at pH of 4.5 integrated CH₄ fluxes declined from 0.047 to
- 342 0.035 mmol g dwt⁻¹ (26%). In the mineral horizon, CH₄ flux declined from 0.08 to 0.03 mmol g
- dwt^{-1} (62%) at pH of 6.0 and from 0.03 to < 0.01 mmol g dwt⁻¹ at pH of 4.5. Note that while the
- 344 fractional changes in CH₄ fluxes were comparable with the fractional changes in CO₂ fluxes, the
- 345 magnitude of C flux change was an order of magnitude higher for CO₂ than for CH₄.



Figure 4: Integrated CO_2 and CH_4 fluxes over a 150-day period with varying pH and number of oxic-anoxic cycles. Each simulation had a total of 15 days of oxic conditions, divided evenly across the oxic-anoxic cycles. pH is indicated by symbol colors. Solid lines and circles show a simulated organic horizon; dashed lines and pluses show a simulated mineral horizon. (a): CO_2 flux. (b): CH_4 flux.

352 4. Discussion

- 353 4.1. Implications for model projections of Arctic carbon cycling
- 354 Current Earth system models omit redox interactions such as Fe-C coupling in simulations of
- 355 SOM degradation, CO₂ emissions, and CH₄ production (Wania et al., 2013). Most models

356 simulate CH₄ production as a function of soil respiration, water content, and temperature. Our 357 results suggest that models omitting redox processes such as Fe-C interactions could 358 substantially overestimate CH₄ production and underestimate both CO₂ production and SOM 359 decomposition in soils subject to water table fluctuations, particularly under acidic pH 360 conditions. Our simulations confirm previous findings that Fe cycling under oxic and anoxic 361 conditions driven by water table variation is an important driver of permafrost C cycling (Lipson 362 et al., 2012) as well as C cycling in other wetland systems such as rice paddies (Kögel-Knabner 363 et al., 2010; Yao et al., 1999). One model, CLM4Me (Riley et al., 2011), does include a 364 parameterization of depletion of alternative terminal electron acceptors, which is simulated as a 365 delayed increase in CH₄ production rate with a characteristic time scale of 30 days. While 366 incorporating a temporal delay between the onset of anoxic conditions and maximum CH₄ 367 production can partially mitigate overestimates of CH₄ production, such models depend on 368 simplified parameterizations of the delay length and cannot easily accommodate the effects of 369 variations in pH and Fe availability in different soils. Our results suggest that both the length and 370 the strength of CH₄ emission suppression depend strongly on pH and the availability and 371 solubility of Fe(III) oxide minerals (Fig. 3).

372 Thermodynamic calculations support the potential for increased Fe(III) reduction at low 373 pH (Flynn et al., 2014; Bethke et al., 2011), although the available energy of the electron 374 donating half-reaction (e.g., acetate oxidation) decreases as pH declines. The overall metabolic 375 rate of Fe(III) reduction depends on both factors, making the rate's pH response sensitive to the 376 soil chemical context and likely variable across soil types. Significant rates of Fe(III) reduction 377 under low pH conditions are consistent with previous observations such as significant Fe(II) 378 accumulation at pH < 4.5 in a northern peatland (Ye et al., 2012) and increased conversion of 379 reducible iron to soluble forms at lower pH in paddy soils (Gotoh and Patrick, 1974). There is 380 also evidence that Fe(III) reduction in normally alkaline paddy soils can be suppressed under low 381 pH conditions; however, iron reduction proceeded rapidly in acidic paddy soils incubated under 382 similar pH conditions (Jia et al., 2015). A biological dependence on pH was not included in our 383 model structure, as we did not find sufficient quantitative evidence to support adding an 384 additional pH dependence term of microbial Fe(III) reduction to the model at this time. Our 385 results are consistent with previous model simulations of permafrost biogeochemical dynamics, 386 which have highlighted the importance of pH buffering capacity (Tang, Zheng, et al., 2016;

387 Zheng et al., 2019). Our simulations extend previous model applications by simulating

388 fluctuations in oxygen availability which serve as proxies for hydrological transitions.

389 Furthermore, our simulations use a model with an existing interface to a full-featured land

390 surface model (Tang, Yuan, et al., 2016), providing a pathway toward integrating detailed

391 biogeochemical dynamics into large-scale model simulations.

392 Thawing permafrost undergoes substantial changes in hydrology that can drive varying 393 biogeochemical processes, including flooding of collapsed permafrost (Turetsky et al., 2020) and 394 drying of deeper thawed soil layers under warming (Pegoraro et al., 2020). While projections of 395 how hydrology of permafrost itself will change are a grand challenge for predicting the future of 396 Arctic systems (Walvoord & Kurylyk, 2016), the impacts of hydrological changes on 397 biogeochemical cycles represent their own set of challenges for predictive modeling. 398 Hydrological changes driven by permafrost thaw can drive rapid organic matter losses 399 (O'Donnell et al., 2012) and increases in CO₂ and CH₄ emissions (Natali et al., 2015). The 400 complex and rapidly-changing hydrological patterns in thawing permafrost systems can drive 401 dynamic water tables that make predictions of biogeochemical cycling particularly challenging, 402 but emerging hydrological model frameworks are allowing more accurate simulations of 403 permafrost hydrology (Jan et al., 2018; Painter et al., 2013). Our biogeochemical model 404 framework builds the groundwork for coupling next-generation hydrological simulations to 405 biogeochemical dynamics for improved simulation of biogeochemical cycling in thawing 406 permafrost.

407

408 4.2. Factors not considered

409 Our simulations did not explicitly include the role of organic matter sorption onto reactive Fe 410 oxide surfaces as a stabilization process for soil carbon. Both stabilization of OM through 411 sorption and destabilization of sorbed OM by dissolution of iron oxides under anoxic conditions 412 have been recently highlighted as important components of permafrost soil C cycling (Opfergelt, 413 2020; Patzner et al., 2020). While the focus of the present study was on short-term CH_4 and CO_2 414 production rather than SOC stabilization processes, the explicit representation of Fe oxide 415 mineral precipitation and dissolution processes and their dependence on pH and redox conditions 416 makes this model framework well suited to incorporating SOC stabilization effects of Fe oxides 417 in the future. The assumption that Fe(III) reduction occurs in the aqueous phase may also ignore

418 the role of direct microbial interactions with Fe oxide mineral surfaces and formation of biofilms 419 (Roden and Zachara, 1996), does not allow explicit treatment of Fe(III) reduction from 420 organically complexed Fe(III) species, and omits the diverse set of strategies that microbial 421 Fe(III) reducers can use to access solid iron oxides as electron acceptors (Kappler et al., 2021). 422 These omissions could bias the model with respect to Fe(III) reduction under circumneutral pH 423 since direct reduction of solid-phase Fe-oxide can occur, allowing Fe(III) reduction to continue 424 but with different forms of Fe(III) being reduced. Including additional Fe oxide phases beyond 425 Fe(OH)₃ could also allow more exploration of how variations in mineral properties such as 426 specific surface area and solubility affect coupled Fe-C cycling. Soil humic acids, such as 427 quinones, are not considered as terminal electron acceptors here. Similarly, the present model 428 does not include nutrient cycling, but would be well suited to represent N cycle processes such as 429 nitrification and denitrification as well as the role of Fe oxides in sequestering phosphorus in 430 Arctic soils (Herndon et al., 2019; Herndon et al., 2020). This model also does not account for 431 microbial biomass production and maintenance, which assimilates a portion of reduced substrate 432 and nutrients, releasing oxidized products.

433 Our model simulations tested alternative assumptions with respect to the inhibition of 434 methanogenesis by Fe(III) availability. In one approach, methanogenesis was directly inhibited 435 by Fe(III). This is consistent with the redox ladder conceptual model, and with studies finding 436 suppression of methanogenesis following Fe(III) additions (Reiche et al., 2008; Miller et al., 437 2015), but may not adequately reproduce previous observations of positive correlations between 438 Fe(III) reduction and methanogenesis (Herndon et al., 2015; Yang et al., 2016). The alternative 439 approach relaxed this assumption, allowing simultaneous Fe(III) reduction and methanogenesis. 440 The direct inhibition approach did reduce simulated CH₄ production, especially in the early 441 stages following a transition from oxic to anoxic conditions (Fig. 3a) as well as lowering 442 cumulative CH₄ production over multiple cycles for both organic and mineral soils (Fig. 4b,c). 443 However, the qualitative dependence on pH and oxic/anoxic cycling was similar for both 444 approaches, and fit between model and observations was only slightly different between the two 445 approaches (Fig. 1). The similar outcomes are likely due to the role of pH, which has a strong 446 impact on methanogenesis and responded to Fe(III) reduction similarly in both approaches (Fig. 447 3e), as well as the depletion of substrates by more rapid Fe(III) reduction (Fig. 3f) which in turn 448 reduced methanogenesis even without direct inhibition (Lovely, 1991). Overall, we conclude that

direct inhibition of methanogenesis by Fe(III) availability was not necessary for the model torepresent key Fe-C interactions.

451 Our simulations focused on a single soil layer and did not include vertical variations in 452 soil properties or vertical transport of gases such as O₂, CO₂, or CH₄. Thus, they omitted 453 potentially important effects such as water table fluctuations and methanotrophy. Aerobic 454 methanotrophy reduces net methane fluxes in oxic and suboxic layers, while anaerobic methane 455 oxidiation can slowly remove methane in anoxic layers. The oxic-anoxic cycles in the current 456 model could be viewed as a time-for-space substitution approach for characterizing soil 457 transition zones close to a dynamic water table. A vertically resolved model would allow more 458 realistic simulations of how the key Fe-C interactions we identified act across vertical oxic-459 anoxic transitions in soils. More explicit vertically resolved simulations are planned as a next 460 step with this model framework. Future applications of the model that include transport and 461 vertical interactions, will make direct comparisons with field measurements more 462 straightforward.

463 5. Conclusions

464 We developed a biogeochemical model framework to represent interactions among carbon, Fe, 465 and pH dynamics in Arctic soils. The model reproduced CO₂ and CH₄ emission patterns along 466 with pH and Fe redox dynamics from oxic and anoxic soil microcosm incubations. Simulations 467 of repeated oxic-anoxic cycles showed that Fe(III) reduction could suppress CH₄ but enhance 468 CO₂ production when oxic-anoxic cycles were more frequent, as the reduced Fe(II) was oxidized 469 during oxic periods and served as a preferential electron acceptor at the beginning of each anoxic 470 period. The effects of Fe on CO₂ and CH₄ emissions were stronger under lower pH conditions. 471 Our results suggest that models that omit Fe and other terminal electron acceptors as well as pH 472 dynamics could overestimate CH₄ production and underestimate CO₂ production in systems with 473 dynamic water tables, and that site-specific chemical factors including pH, bulk density, and Fe 474 availability may be necessary for improved simulations of C cycle dynamics and greenhouse gas 475 emissions from hydrologically dynamic Arctic soils.

- 476
- 477

478 Acknowledgements:

- 479 The NGEE Arctic project is supported by the Office of Biological and Environmental Research
- 480 in the US Department of Energy's Office of Science. This research used resources of the
- 481 Compute and Data Environment for Science (CADES) at the Oak Ridge National Laboratory,
- 482 which is supported by the Office of Science of the U.S. Department of Energy under Contract
- 483 No. DE-AC05-00OR22725. JZ is supported by COMPASS-FME, a multi-institutional project
- 484 supported by the U.S. Department of Energy, Office of Science, Biological and Environmental
- 485 Research as part of the Environmental System Science Program. The Pacific Northwest National
- 486 Laboratory is operated for DOE by Battelle Memorial Institute under contract DE-AC05-
- 487 76RL01830. Thanks to Erin Berns for helpful comments on the manuscript.
- 488

489 **Data availability:**

- 490 Model code, output data, and analysis scripts are archived in the NGEE Arctic Data Repository
- 491 [doi:<u>10.5440/1814844;</u> Sulman et al., 2021].
- 492

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Journal of Geophysical Research - Biogeosciences

Supporting Information for

Iron cycle interactions with hydrological dynamics reduce methane production in a simulated Arctic soil

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Introduction

This supporting information includes four supplemental figures. Figure S1 shows the pH response function used for methanogenesis along with the data points used to parameterize it. Figures S2 and S3 show the results of simulations using a range of fermentation rate constant and acetate half saturation constants. Figure S4 shows time series of various quantities from a simulation of repeated oxic-anoxic cycling in an organic horizon. Figures S5 and S6 show time series comparisons between measured and modeled quantities for simulations with an without direct inhibition of methanogenesis by Fe(III), respectively.



Figure S1: pH dependence of acetoclastic and hydrogenotrophic methanogenesis. Measurements show reported mean and uncertainty values from Kotsyurbenko et al. (2007). Lines show a least squares optimization of Eq. (1). (a): Optimization (lines) and measurements (circles) of acetoclastic and hydrogenotrophic methanogenesis rates as a function of pH, normalized to the maximum acetoclastic rate. (b) Acetoclastic methanogenesis rate as a fraction of total methanogenesis rate.



Fig. S2: RMSE between measured and modeled quantities for different values of fermentation reaction rate constant ("Fermentation rate") and K_S parameter associated with acetate ("Acetate scale"). Each column shows a different quantity (from left to right: pH, Fe(II), CO2 flux, CH4 flux, log DOM concentration, and log acetate concentration). Each row shows a different incubated soil core (from top to bottom: Trough organic horizon, rim organic horizon, trough mineral horizon, rim mineral horizon). Lower RMSE (bluer colors) indicate better fit between model and measurements.



Fig. S3: Correlation coefficient (R) between measured and modeled quantities for different values of fermentation reaction rate constant ("Fermentation rate") and K_S parameter associated with acetate ("Acetate scale"). Each column shows a different quantity (from left to right: pH, Fe(II), CO2 flux, CH4 flux, log DOM concentration, and log acetate concentration). Each row shows a different incubated soil core (from top to bottom: Trough organic horizon, rim organic horizon, trough mineral horizon, rim mineral horizon). R closer to 1 (yellow colors) indicate better fit between model and measurements.



Figure S4: Simulated oxic-anoxic cycles for an organic horizon. Blue backgrounds indicate anoxic conditions and white backgrounds indicate oxic conditions. Black lines show simulations with direct inhibition of methanogenesis by Fe(III) and blue lines show simulations without direct inhibition (a): CH_4 flux rate. (b): CO_2 flux rate. (c): Fe(II) production rate via Fe(III) reduction. (d): Fe oxide mineral concentration. (e): pH. (f): Acetate concentration.



Figure S5: Time series comparison between incubation measurements and model simulations for the model version including direct inhibition of methanogenesis by Fe(III). Each column shows results from an individual incubation. Each row shows a different measured quantity. Lines show model simulation results and circles show measurements. Oxic conditions are shown with a white background and anoxic conditions are shown with a blue background.



Figure S6: Time series comparison between incubation measurements and model simulations for the model version without direct inhibition of methanogenesis by Fe(III). Each column shows results from an individual incubation. Each row shows a different measured quantity. Lines show model simulation results and circles show measurements. Oxic conditions are shown with a white background and anoxic conditions are shown with a blue background.