

1 **A parameterization of respiration in frozen soils based on substrate availability**

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7 **Abstract**

8 Respiration in frozen soils is limited to thawed substrate within the thin water films
9 surrounding soil particles. As temperatures decrease and the films become thinner, the
10 available substrate also decreases, with respiration effectively ceasing at -8 °C. Traditional
11 exponential scaling factors to model this effect do not account for substrate availability and
12 do not work at the century to millennial time scales required to model the fate of the nearly
13 1700 Gt of carbon in permafrost regions. The exponential scaling factor produces a false,
14 continuous loss of simulated permafrost carbon in the 20th century and biases in estimates of
15 potential emissions as permafrost thaws in the future. Here we describe a new frozen
16 biogeochemistry parameterization that separates the simulated carbon into frozen and thawed
17 pools to represent the effects of substrate availability. We parameterized the liquid water
18 fraction as a function of temperature based on observations and use this to transfer carbon
19 between frozen pools and thawed carbon in the thin water films. The simulated volumetric
20 water content (VWC) as a function of temperature is consistent with observed values and the
21 simulated respiration fluxes as a function of temperature are consistent with results from
22 incubation experiments. The amount of organic matter was the single largest influence on
23 simulated VWC and respiration fluxes. Future versions of the parameterization should
24 account for additional, non-linear effects of substrate diffusion in thin water films on
25 simulated respiration. Controlling respiration in frozen soils based on substrate availability
26 allows us to maintain a realistic permafrost carbon pool by eliminating the continuous loss
27 caused by the original exponential scaling factors. The frozen biogeochemistry
28 parameterization is a useful way to represent the effects of substrate availability on soil
29 respiration in model applications that focus on century to millennial time scales in permafrost
30 regions.

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31 1. Introduction

32 Incubated frozen soil samples show a strong decrease in respiration with temperature below
33 freezing associated with decreased substrate availability [Mikan *et al.*, 2002]. Here we define
34 substrate availability as the portion of soil organic matter accessible as a medium for
35 microbial activity. The sharp decline in respiration results from the fact that soils maintain
36 some liquid water at temperatures below freezing [Romanovsky and Osterkamp, 2000; Davis,
37 2001; Kurylyk and Watanabe, 2013]. The mechanism is well understood: freezing point
38 depression driven by the curvature of water around small, hydrophilic soil particles,
39 analogous to freezing point depression caused by solutes in water [Davis, 2001]. The result
40 is thin liquid water films surrounding soil particles at temperatures below freezing.

41 Essentially, microbial activity becomes limited to available thawed organic matter or
42 Dissolved Organic Carbon (DOC) within the thin water films. The diffusion of substrates to
43 the microbes becomes limited to narrow water channels in the thin water films [Rivkina *et al.*,
44 2000]. As temperatures drop below freezing, the water films become thinner and the
45 available substrate and associated microbial activity rapidly decreases, with respiration
46 effectively ceasing below temperatures of -7 to -8 °C [Oechel *et al.*, 1997; Mast *et al.*, 1998;
47 Hobbie *et al.*, 2000; Mikan *et al.*, 2002].

48 The most common way to model this sharp decline in respiration below 0 °C is to apply an
49 exponential temperature scaling factor to the simulated microbial decay rates:

$$50 \quad (1) \quad S_f = Q_{10f}^{\frac{(T-T_{ref})}{10}},$$

51 where S_f is a freezing scaling factor, T is soil temperature, T_{ref} is a reference temperature
52 (typically 0 °C), and Q_{10f} is the change in respiration for a 10 K drop in temperature below
53 freezing. Substrate availability in frozen soil is determined by the amount of thawed organic
54 matter and the diffusion of DOC in the thin water films. The Q_{10f} formulation does not
55 account for substrate availability, but rather is based on the Arrhenius equation for kinetic
56 controls on respiration in thawed soils:

$$57 \quad (2) \quad S_T = Q_{10}^{\frac{(T-T_{ref})}{10}},$$

58 where, S_T is a thawed respiration scaling factor, T_{ref} is a reference temperature (typically 5 or
59 10 °C), and Q_{10} is the change in respiration changes for a 10 °C change in temperature [Raich
60 and Schlesinger, 1992; Denning *et al.*, 1996; Potter *et al.*, 1993]. The kinetic Q_{10}
61 formulation is based on the Arrhenius equation for chemical reaction rates: the higher the

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62 temperature, the greater the number of molecules that have energies greater than the
63 minimum activation energy and the faster the rate of microbial decay. Q_{10} varies between 1.5
64 and 3.0 based on incubation studies or analysis of eddy covariance flux data [Oechel *et al.*,
65 1997; Mast *et al.*, 1998; Hobbie *et al.*, 2000; Mikan *et al.*, 2002]. In contrast, Q_{10f} varies
66 between 164 and 237 based on incubation of frozen soil samples [Mikan *et al.*, 2002].

67 Because substrate availability rather than kinetics control respiration below freezing, the Q_{10f}
68 formulation is inappropriate when attempting to model the large amount of frozen organic
69 matter in permafrost regions. Permafrost is soil at or below 0 °C for at least two years and
70 permafrost soils in the high northern latitudes contain ~1100 Gt of carbon, mostly in the form
71 of frozen organic matter [Tarnocai *et al.*, 2009; Hugelius *et al.*, 2013]. This frozen
72 permafrost carbon was buried over millennial time scales by alluvial sedimentation, dust
73 deposition, and peat development, which increase soil depth and freeze organic matter at the
74 bottom of the active layer into the permafrost [Zimov *et al.*, 2006a, 2006b; Schuur *et al.*,
75 2008; Ping *et al.*, 2015]. Permafrost carbon was buried during or since the last ice age with
76 maximum ages between 15,000 and 30,000 years [Schuur *et al.*, 2008; Dutta *et al.*, 2006].
77 Most models do not include these burial mechanisms and simply initialize the frozen carbon
78 based on observed carbon densities in permafrost [Schaefer *et al.*, 2011]. Applying the Q_{10f}
79 formulation results in effective turnover times of 200 to 500 years such that the simulated
80 permafrost carbon does not persist long enough in the model to match observed vertical
81 carbon distributions [Harden *et al.*, 2012; Hugelius *et al.*, 2013]. To counter this slow loss of
82 permafrost carbon, Koven *et al.* [2011] increased Q_{10f} to 1000 and we initially increased Q_{10f}
83 to 10,000, which are well beyond observed values. These large Q_{10f} values increased the
84 effective turnover time in permafrost to 10,000 years or more and allowed the proper buildup
85 of permafrost carbon. However, they also had the undesired effect of effectively shutting
86 down wintertime respiration, which can account for a significant fraction of total annual
87 respiration [Alm *et al.*, 1999; Fang *et al.*, 1999; Zimov *et al.*, 1993a, 1993b, 1996; Schmidt
88 and Lipson, 2004]. The problem is that the Q_{10f} formulation based on the Arrhenius equation
89 does not account for substrate availability, making it inappropriate when representing
90 permafrost carbon dynamics on time scales of 500 to 10,000 years.

91 Here we present a new frozen biogeochemistry parameterization based on substrate
92 availability. We link the physical processes that determine the amount of liquid water in
93 frozen soils to a fully prognostic set of biogeochemical carbon pools. Tucker [2014]

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94 successfully combined liquid water content in frozen soils with an enzyme kinetic model of
95 respiration accounting for DOC diffusion. We integrated the liquid water content of frozen
96 soils into the biogeochemistry parameterization of the Simple Biosphere/Carnegie-Ames-
97 Stanford Approach (SiBCASA) model. The frozen biogeochemistry parameterization
98 separates kinetic controls from substrate availability in frozen soils to simultaneously
99 reproduce observed liquid water fractions and frozen carbon content in permafrost.

100 2. Methods

101 SiBCASA is a full land surface parameterization with fully integrated water, energy, and
102 carbon cycles [Schaefer *et al.*, 2008]. SiBCASA predicts the moisture content and
103 temperature of the canopy, canopy air space, and soil [Sellers *et al.*, 1986; Vidale and Stockli,
104 2005]. Schaefer *et al.* [2009] modified the snow module to better simulate permafrost
105 dynamics and SiBCASA has been used to predict future permafrost degradation and global
106 carbon emissions from thawing permafrost [Schaefer *et al.*, 2011]. The SiBCASA soil model
107 has 25 layers to a depth of 15 m with geometrically increasing layer thickness with depth
108 starting with 2 cm at the surface. SiBCASA simultaneously predicts soil moisture and
109 temperature for each soil layer on a 10-minute time step. The soil moisture model accounts
110 for surface infiltration, surface runoff, and subsurface runoff. The soil model separately
111 tracks liquid and frozen water at each time step as prognostic variables, accounting for the
112 effects of latent heat [Schaefer *et al.*, 2008, 2009]. The soil thermodynamic and hydraulic
113 properties are a volume weighted fraction of the properties of liquid water, ice, mineral soil,
114 and organic matter [Schaefer *et al.*, 2009]. SiBCASA does not include any gas diffusion
115 processes within soil pore spaces and does not include solute diffusion processes in the soil
116 water.

117 SiBCASA predicts soil organic matter, surface litter, and live biomass (leaves, roots, and
118 wood) in a system of 13 prognostic carbon pools [Schaefer *et al.*, 2008]. This includes four
119 live pools (starch, leaves, roots, and wood) and nine soil carbon pools (coarse woody debris,
120 slow, etc.). SiBCASA does not currently include a DOC pool. SiBCASA represents the
121 biogeochemistry as a system of coupled, first order linear differential equations:

$$122 \quad (3) \quad \frac{dC_i}{dt} = -S_T S_f S_w \frac{1}{\tau} C_i + G,$$

123 where C_i is the i^{th} carbon pool, t is time, S_T and S_f are the temperature and freezing scaling
124 factors as described above, S_w is a soil moisture scaling factor, τ is the reference turnover
125 time for the pool, and G represents gains from other carbon pools [Schaefer *et al.*, 2008].

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126 The first term represents the decay of organic material, some fraction of which is released as
127 respiration and the rest transferred to other pools, from the coarse woody debris to the slow
128 pool, for example (see *Schaefer et al.*, [2008] for a complete description). SiBCASA uses a
129 Q_{10} of 1.5, which is held constant for all temperatures. Prior to incorporating the frozen
130 biogeochemistry parameterization, SiBCASA used a Q_{10f} of 200, which was also held
131 constant, but only for temperatures below 0 °C.

132 Each soil layer has a complete set of prognostic soil carbon pools. Once per day for each soil
133 layer SiBCASA recalculates the organic soil fraction (f_{org}) used to determine thermodynamic
134 and hydraulic properties. SiBCASA redistributes carbon in the top soil layers to simulate the
135 surface organic layer [*Jafarov and Schaefer*, 2016]. This allows for the buildup of a surface
136 organic layer crucial to simulating soil thermodynamics in permafrost regions. However,
137 SiBCASA does not represent the cryoturbation and sedimentation processes required to build
138 up a large permafrost carbon pool. Instead, we initialize the permafrost carbon content using
139 the observed distribution from the Northern Circumpolar Soil Carbon Dataset version 2
140 (NCSCDv2) [*Hugeluis et al.*, 2013].

141 Substrate availability is determined by the portion of organic matter that is thawed and by the
142 diffusion of DOC in the thin water films. SiBCASA does not have a DOC pool and does not
143 include DOC diffusion, so the new frozen biogeochemistry parameterization represents only
144 the effects of the amount of thawed organic matter on substrate availability. The frozen
145 biogeochemistry parameterization uses three sets of carbon pools for each soil layer: thawed,
146 frozen film, and bulk frozen pools (Figure 1). The bulk frozen pools represent frozen carbon
147 in soil pore spaces away from the thin liquid water films surrounding mineral soil particles.
148 The frozen film pools represent frozen soil carbon within the maximum extent of the thin
149 water films. The thawed pools represent organic matter in the thin liquid water films. Soil
150 carbon in the bulk and film frozen pools is unavailable for microbial decay and remain static
151 and sequestered until thawed. Simulated microbial decay and associated respiration occurs
152 only in the thawed carbon pools in the thin water films and will continue to decay below 0
153 °C. This complete separation of frozen and thawed soil carbon represents the effect of the
154 amount of thawed organic matter on substrate availability in the thin liquid water films for
155 microbial metabolism and respiration in frozen soils. This new frozen carbon
156 parameterization replaced the original Q_{10f} formulation.

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157 The thawed, film frozen, and bulk frozen carbon pools all have the same 13-pool structure as
158 defined in *Schaefer et al.* [2008]. The frozen biogeochemistry parameterization applies only
159 to the nine soil carbon pools. The live biomass pools (starch, leaves, fine roots, and wood)
160 are always considered ‘thawed’ because the growth and mortality processes that govern them
161 do not depend upon soil texture and associated thin water films. Carbon is transferred
162 between the frozen and corresponding thawed pools as the amount of liquid water changes
163 with simulated soil temperature: thawed ‘slow’ pool to bulk frozen ‘slow’ pool, etc.

164 We assumed that the mineral soil, carbon, liquid water, and ice are uniformly distributed
165 within the soil layer such that the liquid water fraction equals the thawed fraction. We
166 calculate the liquid water fraction for each soil type using a modified power law formulation
167 introduced by *Lovell* [1957] and refined by *Nicolosky et al.* [2009]:

$$(4) \quad \begin{aligned} \phi_i &= 1.0 & T > 0 \\ \phi_i &= \left(\frac{T_{ref}-T}{T^*}\right)^{b_i} & T < 0 \end{aligned}$$

169 where ϕ_i is the fraction of liquid water for the i^{th} soil type, T is the soil layer temperature (°C),
170 T_{ref} is a reference temperature (°C), T^* is a temperature offset (°C), and b_i is an empirical
171 constant that depends on soil texture. *Kurylyk and Watanabe* [2013] compare several
172 mathematical formulations for ϕ_i ranging from simple piecewise continuous linear models to
173 full physics models based on the Clapeyron equation. We desired a formulation that
174 produced realistic results, but was not overly complicated, so we decided upon the power law
175 formulation. We assumed four soil types, pure clay, silt, sand, and organic matter, each with
176 different values of b_i (Table 1). We used b_i values from *Romanovsky and Osterkamp* [2000]
177 and *Kurylyk and Watanabe* [2013]. We calculated the ϕ_{crit} by inserting 0 °C into equation 4
178 above. Clay represents the finest grained soil material with the greatest amount of liquid
179 water below freezing and organic material represents the coarsest soil material with the least
180 amount of liquid water.

181 We made two important changes to the *Nicolosky et al.* [2009] model in order to reproduce the
182 observed ϕ_i discontinuity at 0 °C and differentiate between the bulk frozen and film frozen
183 pools. The original *Nicolosky et al.* [2009] formulation produced a continuous ϕ_i for all values
184 of T , but liquid water observations show a discontinuity at 0 °C where the actual ϕ_i is
185 determined by bulk liquid to ice conversion [*Davis*, 2001]. First, SiBCASA does not include
186 aqueous chemistry to calculate the freezing point depression due to dissolved solutes, so we
187 changed T^* from freezing point depression to a simple offset temperature. Second, we fixed

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188 T_{ref} at 0.1 °C rather than allowing it to change with depth and temperature [Nicolson *et al.*,
189 2009]. Together, these two changes reproduced the observed ϕ_i discontinuity at 0 °C. ϕ_{crit}
190 represents the liquid water content at 0 °C and determines the boundary between bulk
191 freezing and thin film processes. Bulk freezing dominated by latent heat effects occurs for ϕ
192 $> \phi_{crit}$, while thin film effects dominate for $\phi \leq \phi_{crit}$. Essentially, ϕ_{crit} represents the maximum
193 thickness of the thin water films around soil grains and allows us to differentiate between the
194 bulk frozen and film frozen pools.

195 Figure 2 shows the parameterized ϕ_i as a function of temperature for clay, silt, sand, and
196 organic soils. The thin dashed lines represent ϕ_{crit} for each soil type defining the boundary
197 between bulk freezing and thin film effects. The shapes and magnitudes of the individual
198 curves are consistent with observed ϕ values [Davis, 2001]. The liquid water fraction below
199 freezing varies between less than 1% to as high as 50%, depending on soil texture: larger soil
200 particles have more negative values of b_i and less liquid water when frozen. For organic
201 soil, we assumed the individual particles of organic matter were, on average, too large to
202 produce unfrozen water and assigned the largest b_i resulting in the smallest values of ϕ_i . ϕ_i is
203 next lowest in frozen sandy soils because the particles are large and hydrophobic with little
204 unfrozen water. ϕ_i is highest in frozen clay soils because the particles are small and
205 hydrophilic with the largest amount of unfrozen water.

206 We assumed that the overall liquid water fraction at any given temperature is the weighted
207 average of those for pure clay, silt, sand, and organic matter:

$$208 \quad (5) \quad \phi = (1 - f_{org})(f_c\phi_c + f_{si}\phi_{si} + f_{sa}\phi_{sa}) + f_{org}\phi_o,$$

209 where ϕ is the liquid water fraction for each soil layer, f_{org} is the volumetric organic soil
210 fraction, and f_c , f_{si} , and f_{sa} are the volumetric fractions of clay, silt, and sand for the mineral
211 portion of the soil. ϕ_c , ϕ_{si} , ϕ_{sa} , and ϕ_o are the liquid water fractions for pure clay, silt, sand,
212 and organic matter as a function of T based on the power law formulation above. f_{org} is
213 calculated as the ratio of simulated carbon density to the observed density of pure organic
214 matter:

$$215 \quad (6) \quad f_o = \frac{M_o}{\Delta z \rho_o},$$

216 where M_o is the simulated organic matter mass per soil layer, Δz is the thickness of the soil
217 layer, and ρ_o is the observed bulk density of pure organic soil, which we assumed was 140 kg
218 m^{-3} [Schaefer *et al.*, 2009]. M_o is the sum of all prognostic carbon pools in each soil layer,

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219 converted from mass of pure carbon to mass of organic matter assuming organic matter is
220 50% carbon [Schaefer *et al.*, 2009]. The calculation of ϕ_{crit} is also a weighted average of the
221 ϕ_{crit} values for each soil type. The carbon content of each soil layer varies relatively slowly
222 with time depending on the prognostic carbon pools and we assume that the soil matrix and
223 associated physical properties do not change when frozen. Consequently, SiBCASA
224 recalculates f_o and ϕ_{crit} for each soil layer once per day for $T \geq 0$ °C. The clay, silt and sand
225 fractions of the mineral portion of the soil are constant in time, but vary in space based on the
226 Harmonized World Soil Database [Wie *et al.*, 2014].

227 SiBCASA transfers carbon between the thawed, film and bulk frozen pools each time step
228 depending on the change in ϕ :

$$229 \quad (7) \quad \Delta\phi = \phi^t - \phi^{t-1},$$

230 where $\Delta\phi$ is the change in thawed soil fraction for a single time step, the superscript t denotes
231 the value at the current time step and $t-1$ the value at the previous time step (Figure 3). A
232 negative $\Delta\phi$ indicates freezing soil and a positive $\Delta\phi$ indicates thawing soil. ϕ stays constant
233 at 1.0 until the soil layer reaches 0 °C. As freezing begins, T stays constant at 0 °C and ϕ
234 decreases to account for the latent heat of fusion for water. When ϕ reaches ϕ_{crit} , T decreases
235 below 0 °C and ϕ follows the liquid water curve. During thaw, ϕ follows the reverse path,
236 ignoring possible hysteresis effects. $\phi > \phi_{crit}$ represents freezing or thawing of the bulk pore
237 space between soil grains and $\phi \leq \phi_{crit}$ represents freezing and thawing of the thin films
238 around soil grains. During freezing, the bulk carbon away from the soil grains freezes first
239 and the liquid water film freezes last. During thaw, the reverse is true with the frozen film
240 carbon thawing first and the bulk carbon last.

241 Table 2 shows the carbon bookkeeping rules governing the transfer of carbon between
242 thawed, film frozen, and bulk frozen carbon pools each time step. C_{i_thaw} is the i^{th} thawed
243 carbon pool, C_{i_film} is the i^{th} film frozen carbon pool, and C_{i_bulk} is the i^{th} bulk frozen pool,
244 where i represents the nine soil carbon pools described above. δ_{i_2bulk} is the carbon
245 transferred from the i^{th} thawed carbon pool to the i^{th} bulk frozen pool, with similar
246 nomenclature for transfers to and from the film frozen pools. Table 2 is organized by
247 freezing starting with bulk pools first and film frozen pools second, with the reverse for
248 thawing. When ϕ crosses ϕ_{crit} , part of the carbon goes to the bulk pools and part to the film

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249 frozen pools. The same equations are applied in sequence to all nine soil carbon pools each
250 time step.

251 We compared simulated response curves for Volumetric Water Content (VWC) vs.
252 temperature against observed values at Bonanza Creek, Alaska [Jafarov *et al.*, 2013].
253 Simulated VWC is $\phi\theta\eta$, where θ is the soil saturation fraction and η is soil porosity for a
254 given soil layer. θ is the fraction of pore space filled with both liquid water and ice. η varies
255 from 0.85 for pure organic matter to between 0.35 and 0.45 for pure mineral soil, depending
256 on soil texture. We used VWC data collected at the Bonanza Creek Long Term Ecological
257 Research site in central Alaska using a Hydro Probe soil moisture sensor from 2009 to 2014.
258 Bonanza Creek is in the discontinuous permafrost zone and we used VWC data from an
259 unburned and recently burned site. Both sites have sensors installed at 19, 36, and 54 cm
260 depths [Romanovsky and Osterkamp, 2001; Romanovsky *et al.*, 2003]. At the unburned site,
261 all three depths fall in the surface organic layer, while at the burned site, all three depths fall
262 within mineral soil below the organic layer. Because of the huge influence of f_{org} on ϕ and
263 thus VWC, we separately compared simulated to observed values for organic soil and
264 mineral soil. The simulated organic layer thickness was 21 cm, so we extracted the simulated
265 VWC in the organic layer at 19 cm depth and compared them with organic soil observations
266 at 19 cm depth at the unburned site. We extracted simulated VWC for mineral soil at 54 cm
267 depth and compared them with mineral soil observations at 54 cm depth at the burned site.

268 We compared response curves for simulated respiration vs. temperature against observed
269 values from four independent incubations of frozen soil samples: Rivkina *et al.* [2000], Mikan
270 *et al.* [2002], Eberling and Brandt [2003], and Panikov *et al.* [2006]. Each of these studies
271 collected samples from different locations and used different temperature ranges, durations,
272 and protocols for the incubations (Table 3). We converted the observed respiration values to
273 common units of flux per mass of carbon per day ($\mu\text{g C g}^{-1} \text{C d}^{-1}$) using total organic carbon
274 (TOC) values and soil bulk densities as noted in each paper. TOC is the ratio of organic
275 matter mass to total dry soil mass, which we converted to f_{org} to help evaluate model output.
276 Rivkina *et al.* [2000] collected ^{14}C counts per minute, which we could not convert into a
277 respiration flux, so we only did a qualitative comparison. Panikov *et al.* [2006] did not report
278 an observed TOC, so we estimated the TOC from the observed bulk densities. For our
279 various unit conversions, we assumed a mineral soil density of 1400 kg m^{-3} and a ρ_o of 140
280 kg m^{-3} [Schaefer *et al.*, 2009]. We converted the normalized values from Eberling and

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281 *Brandt* [2003] to absolute values using the observed respiration at the reference temperature
282 of 7 °C. We averaged the *Mikan et al.* [2002] results for individual soil samples to get an
283 average respiration at each incubation temperature, consistent with reported values in
284 *Elberling and Brandt* [2003] and *Panikov et al.* [2006].

285 We compared results for the frozen biogeochemistry parameterization using two point
286 simulations: Toolik Lake on the North Slope of Alaska (68.65 °N, 149.65 °W) and Bonanza
287 Creek near Fairbanks, Alaska (64.80°N, 148.00 °W). We compared the Toolik Lake
288 simulation output against the incubation data and the Bonanza Creek output against the VWC
289 data. We ran simulations at Bonanza Creek and all the sites in Table 3, but because we are
290 evaluating the simulated temperature response functions of VWC and respiration, the
291 comparisons at the various sites became extremely repetitive. Here we include only the
292 Toolik Lake and Bonanza Creek results because they cover a significant portion of the
293 temperature ranges in the data. The location of the simulation had almost no effect on our
294 results, as long as the simulated soil temperature ranges overlapped sufficiently with the
295 incubation temperatures. More than any other factor, the simulated f_{org} dominated the
296 simulated VWC and respiration response functions. So rather than a site-by-site comparison,
297 we focused on a comparison of organic and inorganic soils by choosing SiBCASA soil layers
298 either within the simulated surface organic layer or below it. The results for the remaining
299 sites are nearly identical to the Toolik Lake and Bonanza Creek simulations.

300 As input weather, we used the Climatic Research Unit National Center for Environmental
301 Predictions (CRUNCEP) dataset [*Wei et al.*, 2014], extracting the CRUNCEP data for the
302 grid cell containing each point. CRUNCEP is reanalyzed weather data at 0.5x0.5 degree
303 latitude and longitude resolution optimally consistent with a broad array of observations
304 spanning 110 years, from 1901 to 2010. Starting from steady state initial conditions, we ran
305 the point simulations from 1901 to 2010 and extracted model output for the five years closest
306 to the time period covered by the observations. The Bonanza Creek observations cover 2009
307 to 2014, so we extracted model output from 2005-2010. This slight mismatch is reasonable
308 since our objective was to evaluate the simulated temperature response functions rather than
309 compare simulated and observed time series. *Mikan et al.* [2002] collected the soil samples
310 in 1998, so we extracted model output from 1996 to 2000 for the Toolik Lake simulation.

311 We also ran simulations with and without the new frozen biogeochemistry parameterization
312 for the entire permafrost domain in the northern hemisphere [*Brown et al.*, 1997]. We

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313 initialized the permafrost carbon content within the top three meters of permafrost using the
314 observed distribution from the Northern Circumpolar Soil Carbon Dataset version 2
315 (NCSCDv2) [Hugeluis *et al.*, 2013]. The permafrost carbon was split between the bulk
316 frozen and film frozen pools based on the ϕ and ϕ_{crit} values at the start of spinup simulation.
317 We selected the first 30 years from the CRUNCEP dataset (1901 to 1931) and randomly
318 distributed them over 4000 years to spin SiBCASA up to steady state initial conditions. We
319 spun the model up to steady state initial conditions in 1900 with the new frozen
320 biogeochemistry parameterization turned on. We then ran two simulations from 1901 to
321 2010 starting from the same initial conditions, one with the new frozen biogeochemistry
322 parameterization and one without.

323 3. Results

324 Our ϕ parameterization produced a VWC vs. temperature response consistent with observed
325 values (Figure 4). Below freezing, the simulated VWC for organic soil are higher than
326 observed values while the simulated VWC for mineral soil closely matches observed values.
327 Above freezing, both the observed and simulated VWC for organic soil varied widely
328 because of a strong variation in simulated saturation fraction over time. SiBCASA assumes a
329 porosity of 0.85 for organic soil, which results in a VWC at saturation just below the
330 maximum observed values of ~ 0.9 . For mineral soil, the simulated and observed VWC both
331 stay near saturation, but the simulated values are greater than observed above freezing. This
332 difference above freezing probably results from the assumed soil texture in our simulation,
333 but we lacked observations of soil texture at Bonanza Creek to confirm this.

334 The frozen biogeochemistry parameterization reproduced the VWC discontinuity at 0 °C, but
335 the observed VWC shows some noise at 0 °C because we converted to daily averages. A
336 large observed diurnal cycle in soil temperature resulted in conditions where the soil froze at
337 night and thawed during the day. Thus, the daily average temperature may be 2 °C, for
338 example, but the daily average VWC reflects both frozen and unfrozen conditions. This
339 produces a horizontal ‘spread’ in the VWC around 0 °C, and thus noise in the discontinuity.
340 The SiBCASA soil model had less diurnal variability in simulated soil temperature, so the
341 noise was less than the observed values. The spread appears in observed values for both the
342 mineral and organic soils, but is greater for the mineral soil because the observed temperature
343 amplitude is greater.

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344 Although each incubation study sampled from different locations and used different
345 protocols, the overall results show consistent magnitudes and patterns (Figure 5). The
346 observed respiration values for Plotnikovo and Koppara were so close that we plotted them
347 using the same color for clarity. Respiration decreased exponentially with decreasing
348 temperature, with a faster rate of decline below freezing. The observed respiration at 0 °C is
349 $\sim 60 \mu\text{g C g}^{-1} \text{ C d}^{-1}$, with no obvious discontinuity. The respiration decreases to $\sim 2 \mu\text{g C g}^{-1} \text{ C}$
350 d^{-1} at -10 °C, a reduction of 97%. Observed respiration below -10 °C varies between 0.1 and
351 $2 \mu\text{g C g}^{-1} \text{ C d}^{-1}$ representing a 97-99% reduction compared to 0 °C, with the Barrow
352 incubations showing residual respiration at temperatures as low as -39 °C. Except for
353 Plotnikovo and Koppara, all the incubated soil samples had $TOC < 0.07$ ($f_{org} < 0.45$),
354 indicating a mix of mineral and organic soil with corresponding higher values of ϕ and
355 respiration. In contrast, the Plotnikovo and Koppara samples were pure organic matter with
356 $TOC = 1.0$ ($f_{org} = 1.0$) and, because ϕ was much less, showed the lowest observed respiration
357 of all the studies.

358 Above freezing, the simulated respiration as a function of temperature was consistent in
359 magnitude with observed values from incubation experiments, but showed much greater
360 variability (Figure 6). The variability in simulated respiration above freezing results from
361 temporal variability in simulated soil moisture content. Of course, the incubation data shows
362 no such variability because experiment protocols held soil moisture constant. Organic soil
363 has greater hydraulic conductivity and porosity than mineral soil with corresponding greater
364 variability in soil moisture, and thus respiration. On average, the simulated respiration for
365 organic soil above freezing was greater than the incubation data because of higher values of
366 simulated TOC than in the soil samples. For the mineral soil, the average simulated
367 respiration above freezing is consistent with the incubation values.

368 At 0 °C, temporal variations in simulated hydraulic conductivity produced a ‘tail’ of low
369 simulated respiration values in the mineral soil simulation results. The effective pore space
370 and associated hydraulic conductivity decreases as liquid water changes to ice during the
371 freezing process. This produced an increase in VWC and an associated increase in
372 respiration as the simulated soil froze during fall and early winter. The effect occurs for both
373 organic and mineral soil, but is more prominent in mineral soil because it is deeper in the soil
374 column and because thawed mineral soil has lower hydraulic conductivity than thawed

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375 organic soil. Again, the incubation data does not show such an effect because soil moisture is
376 held constant.

377 Below freezing, the simulated organic soil has lower respiration than mineral soil (Figure 6a),
378 consistent with the Plotnikovo and Koppara observations and demonstrating the strong
379 influence of organic matter on frozen soil respiration. The observed *TOC* for nearly all of the
380 incubation samples varied between 0.01 and 0.07, consistent with the simulated *TOC* of 0.04
381 for the mineral soil ($f_{org} = 0.27$). The simulated *TOC* for the organic soil is 0.7 ($f_{org} = 0.95$),
382 much closer to the observed *TOC* of 1.0 for the Plotnikovo and Koppara incubations. The
383 high *TOC* results in lower ϕ and respiration such that the simulated respiration matches the
384 Plotnikovo and Koppara incubation data within 10% at all temperatures. In contrast, the
385 simulated respiration from mineral soil was less than the incubation data between 0 and -5
386 °C, and greater than the incubation data for temperatures less than -8 °C (Figure 6b). The
387 frozen biogeochemistry parameterization produced a sharp discontinuity in simulated
388 respiration at 0 °C that mirrors the VWC discontinuity. The incubation data does not indicate
389 such a sharp discontinuity, resulting in lower respiration than observed for temperatures
390 between 0 and -5 °C.

391 The frozen biogeochemistry parameterization maintains a realistic permafrost carbon pool in
392 the model. Figure 7 shows the total simulated permafrost carbon in the top three meters of
393 soil for the entire northern hemisphere permafrost domain, both with and without the frozen
394 biogeochemistry parameterization. *Hugelius et al.* [2014] indicate a total of 800 Gt of carbon
395 frozen in permafrost, with 619 Gt in the top three meters, or 10% higher than the 560 Gt C
396 we simulate. Using the old kinetic Q_{10f} formulation, the permafrost carbon decreased at a
397 nearly linear rate as it slowly decayed. In contrast, the new frozen biogeochemistry
398 parameterization based on substrate availability allows SiBCASA to maintain a nearly
399 constant permafrost carbon pool throughout most of the 20th century. After 1950, the
400 temperatures slowly rise, resulting in thawing of ~3 Gt of permafrost carbon representing
401 0.6% of the initial pool.

402 4. Discussion

403 We hypothesize that the diffusivity of DOC and microbial waste products, and thus
404 respiration, does not respond linearly to changes in VWC. Because we use the ϕ curve to
405 explicitly define substrate availability, the frozen biogeochemistry parameterization assumes

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406 a linear response to VWC. As a result, the shape of the simulated respiration curve exactly
407 matches the simulated VWC curve, with a discontinuity in simulated respiration at 0 °C not
408 seen in the incubation data. As the bulk of the water in the soil freezes, the DOC
409 concentration in the thin water films increases. This counteracts the decrease in the amount
410 of thawed organic matter and decline in DOC diffusivity as the thickness of the thin films
411 decrease from 15 to 5 nm between -1.5 and -10 °C [Rivkina *et al.*, 2000; Tucker, 2014]. The
412 result is a non-linear response in respiration to changing VWC between 0 and -5 °C. Rivkina
413 *et al.* [2000] found observed ¹⁴C counts in respired CO₂ exactly matched the VWC curve, but
414 they infused their samples with ¹⁴C-labeled glucose, which may not be strongly affected by
415 decreases in diffusivity. In contrast, Panikov *et al.* [2006] achieved an R^2 of 0.99 with an
416 exponential curve fit of respiration to both temperature and VWC. Since VWC is a function
417 of soil temperature, this additional dependency on VWC hints that DOC concentration and
418 diffusion influences respiration in frozen soils. Tucker [2014] explicitly modeled DOC
419 diffusion in the thin water films and consequently better reproduced observed respiration at
420 temperatures just below freezing. Improving the simulated respiration at temperatures
421 between -5 and 0 °C requires both the representation of the thawed organic matter and the
422 effects of DOC diffusion. Incorporating a DOC carbon pool and DOC diffusion into
423 SiBCASA is not within the scope of our current study and left as a future improvement to the
424 frozen soil biogeochemistry parameterization.

425 For temperatures below -5 °C, the simulated respiration for the organic soil agrees with the
426 incubation data, while the simulated respiration for the mineral soil is higher than observed.
427 Our frozen biogeochemistry parameterization may not include some key processes that
428 influence respiration below -5 °C. Eberling and Brandt [2003] found that the frozen samples
429 trapped 10% of the CO₂ produced, but this would apply to all temperatures and would not
430 explain the higher simulated values below -5 °C. Intracellular desiccation or similar internal
431 processes may slow down microbial activity and reduce respiration [Mikan *et al.*, 2002].
432 However, nearly all frozen carbon lies in the top 3 meters of permafrost [Tarnocai *et al.*,
433 2009; Hugelius *et al.*, 2013]. Since permafrost soils at these depths spend only a portion of
434 the year at temperatures below -5 °C, the overall effect of this bias is small.

435 Whether a model needs the frozen biogeochemistry parameterization to represent substrate
436 availability or whether the original Q_{10f} formulation would suffice depends upon the model
437 application. If the model application focuses on short-term carbon fluxes on a seasonal to

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438 decadal time scale, the original Q_{10f} formulation would suffice. In such short-term
439 applications, the Q_{10f} formulation will produce realistic respiration fluxes, especially in
440 winter. However, the Q_{10f} formulation does not work well in model applications focusing on
441 500 to 10,000 year time scales to study the buildup of frozen carbon or potential future
442 emissions from thawing permafrost. For such long time scales, the model will need to
443 account for substrate availability in order to correctly simulate the frozen permafrost carbon
444 pools and correctly estimate future carbon fluxes from thawing permafrost.

445 When accounting for substrate availability, both the bulk and film frozen pools are required
446 to build up or maintain the frozen permafrost carbon. A single set of frozen pools effectively
447 reproduces the temperature effects represented by the original Q_{10f} formulation, but does
448 maintain the permafrost carbon pool. A single set of frozen pools suffers from numerical
449 diffusion, which is an artificial dispersion of carbon in the model resulting from insufficient
450 spatial finite differencing. For a single set of frozen pools, even though the permafrost was
451 always below freezing, the simulated permafrost temperature and thus ϕ varied throughout
452 the year such that carbon was artificially pumped from the frozen pools into the thawed
453 pools. The amount of frozen carbon in the permafrost steadily decreased with effective
454 turnover times of 200 to 500 years, the same result achieved using the original Q_{10f}
455 formulation. Two sets of frozen carbon pools is the minimum number required to represent
456 the physical separation of soil carbon located in the thin water films and minimizes artificial
457 carbon loss due to numerical diffusion. The film frozen pools still have numerical diffusion,
458 which can be decreased further by increasing the number of film frozen pools, but we leave
459 such exploration as potential future work. Separating frozen carbon into film and bulk frozen
460 pools is sufficient to minimize numerical diffusion and limit microbial activity to the
461 substrate physically within thin water films.

462 Improving the frozen biogeochemistry parameterization will require additional measurements
463 focusing on the effects of TOC and soil texture on respiration and VWC. The incubation
464 studies we show here emphasized the lower temperature limits of microbial activity in frozen
465 soil, with incubations at temperatures as low as $-39\text{ }^{\circ}\text{C}$. Since the top three meters of
466 permafrost containing the bulk of the frozen carbon rarely reach such low temperatures, a
467 more useful range for modelers would be $0\text{ to }-5\text{ }^{\circ}\text{C}$, where VWC and respiration show the
468 greatest changes with temperature. Studies that quantify nutrient availability and diffusion in
469 the thin water films would prove especially useful to quantify the non-linear response of

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470 respiration to VWC. For both incubation studies and VWC measurements, including
471 ancillary data is very important in applying the data to models, especially the TOC, soil
472 texture, soil bulk density, and water content. Also, the soil texture and organic content are
473 much more important than where the sample was collected, so we need incubations and
474 measurements that explore how TOC and soil texture influence VWC and respiration in
475 frozen soils. Lastly, modelers need uncertainty estimates for the incubation and VWC
476 measurements. The ideal performance for any model is to match observations within
477 uncertainty, which indicate model output and observations are statistically identical. This
478 makes uncertainty estimates as important as the observations themselves, but none of the
479 incubation and VWC studies shown here included uncertainty.

480 5. Conclusions

481 The frozen biogeochemistry parameterization successfully links soil physics, microbiology,
482 and biogeochemistry to model substrate availability and associated effects on simulated
483 respiration fluxes in frozen soils. The resulting simulated VWC are consistent with observed
484 values and are strongly influenced by soil organic content. The simulated respiration fluxes
485 as a function of temperature are consistent with observed values from incubation experiments
486 and also depend very strongly on soil organic content. Future versions of the frozen
487 biogeochemistry parameterization should account for additional, non-linear effects of
488 substrate diffusion in thin water films on simulated respiration. Controlling respiration in
489 frozen soils based on substrate availability allows us to maintain a realistic permafrost carbon
490 pool by eliminating the continuous carbon loss seen in the original kinetic Q_{10f} formulation.
491 The frozen biogeochemistry parameterization is a useful way to represent the effects of
492 substrate availability on soil respiration in model applications that focus on century to
493 millennial time scales in permafrost regions.

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497 7. References

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626 8. Tables

627 Table 1: Parameters used to calculate liquid water fraction.

Soil Type	T_{ref} (°C)	T^* (°C)	b (-)	ϕ_{crit} (-)
Clay	0.1	0.01	-0.3	0.50
Silt	0.1	0.01	-0.5	0.32
Sand	0.1	0.01	-0.9	0.13
Organic	0.1	0.01	-1.0	0.10

628 Table 2: Transfer rules between thawed, frozen film, and frozen bulk pools

Case	ΔL	L_{t-1}	L_t	Transfer	δ
Freezing	$\Delta\phi < 0$	$\phi^{t-1} > \phi_{crit}$	$\phi^t > \phi_{crit}$	thaw to bulk	$\delta_{i_2bulk} = \frac{\Delta\phi}{\phi^{t-1}} C_{i_thaw}$
Freezing	$\Delta\phi < 0$	$\phi^{t-1} > \phi_{crit}$	$\phi^t < \phi_{crit}$	thaw to bulk and film	$\delta_{i_2bulk} = \frac{\phi^{t-1} - \phi_{crit}}{\phi^{t-1}} C_{i_thaw}$ $\delta_{i_2film} = \frac{\phi_{crit} - \phi^t}{\phi^{t-1}} C_{i_thaw}$
Freezing	$\Delta\phi < 0$	$\phi^{t-1} < \phi_{crit}$	$\phi^t < \phi_{crit}$	thaw to film	$\delta_{i_2film} = \frac{\Delta\phi}{\phi^{t-1}} C_{i_thaw}$
Thawing	$\Delta\phi > 0$	$\phi^{t-1} < \phi_{crit}$	$\phi^t < \phi_{crit}$	film to thaw	$\delta_{i_2thaw} = \frac{\Delta\phi}{\phi_{crit} - \phi^{t-1}} C_{i_film}$
Thawing	$\Delta\phi > 0$	$\phi^{t-1} < \phi_{crit}$	$\phi^t > \phi_{crit}$	film and bulk to thaw	$\delta_{i_2thaw} = \frac{\phi_{crit} - \phi^t}{1 - \phi^{t-1}} C_{i_film}$ $\delta_{i_2thaw} = \frac{\phi_{t-1} - \phi_{crit}}{1 - \phi^{t-1}} C_{i_bulk}$

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$$\text{Thawing} \left| \begin{array}{c} \Delta\phi > 0 \\ \phi^{t-1} > \phi_{crit} \\ \phi^t > \phi_{crit} \end{array} \right| \text{bulk to thaw} \left| \delta_{i_2thaw} = \frac{\Delta\phi}{1 - \phi^{t-1}} C_{i_bulk} \right.$$

629 Table 3: Summary of incubation data used to evaluate the frozen biogeochemistry parameterization

Paper	Site	lat (deg)	lon (deg)	T range (°C)	Duration (day)	ρ_{bulk} (g cm ⁻³)	TOC (-)
<i>Eberling and Brandt</i> [2003]	Nødebo, Denmark	55.979	12.346	-11 to 27	na	1.310^a	0.07
<i>Eberling and Brandt</i> [2003]	Zackenbergl, Greenland	74.467	20.567	-11 to 27	na	1.310	0.07
<i>Mikan et al.</i> [2006]	Toolik Lake, Alaska	68.633	-149.633	-12 to 14	2 to 20	na	na
<i>Panikov et al.</i> [2006]	Barrow, Alaska	71.317	-156.600	-39 to -1	60	1.059	0.27
<i>Panikov et al.</i> [2006]	Koppara, Sweden	57.125	14.500	-39 to -1	60	0.089	1.00
<i>Panikov et al.</i> [2006]	Plotnikovo, West Siberia	57.017	82.583	-39 to -1	60	0.092	1.00
<i>Rivkina et al.</i> [2000]	Kolyma, Siberia	69.483	156.983	-20 to 5	270	1.384	0.01

630 ^a Numbers in bold were calculated from information supplied in the paper.

631 9. Figure Captions

632 Figure 1. A schematic of the new frozen biogeochemistry parameterization around a single, idealized
 633 soil particle. Soil carbon is divided into thawed carbon in the thin water films surrounding soil
 634 particles, film frozen carbon in the maximum extent of the thin liquid water film, and bulk frozen
 635 carbon in the pore spaces between soil particles. The thawed carbon represents available substrate
 636 for metabolism by microbes in the thin water film.

637 Figure 2. The parameterized liquid water fraction, ϕ_l , as a function of temperature for pure sand, silt,
 638 clay, and organic matter. The thin dashed lines show the corresponding values of critical water
 639 fraction, ϕ_{crit} , defining the boundary between bulk freezing and thin film effects for each soil type.

640 Figure 3. A schematic showing the transfers of carbon between the thawed, bulk frozen, and film
 641 frozen as the liquid water fraction (ϕ) changes with time and temperature (T). As the soil freezes, ϕ
 642 follows the red line and carbon is transferred from the thawed pool to the bulk frozen carbon pool until
 643 ϕ reaches ϕ_{crit} , then carbon is transferred from the thawed to the film frozen pool. The reverse
 644 happens during thawing.

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645 Figure 4. Simulated daily average VWC for organic soil at 19 cm depth (a) and mineral soil at 54 cm
646 depth (b) as a function of daily average temperature at Bonanza Creek.

647 Figure 5. Observed respiration as a function of temperature from the incubation studies in Table 3.

648 The Koppara and Plotnikovo incubation results appear as the same color.

649 Figure 6. Observed respiration from the incubation studies in Table 3 and simulated hourly
650 respiration as a function of daily average temperature at Toolik Lake, Alaska for organic soil (a) and
651 mineral soil (b).

652 Figure 7. Simulated permafrost carbon in northern hemisphere permafrost with and without the
653 frozen biogeochemistry parameterization.