Responses to the Associate Editor

Dear Dr. Keenan,

Thank you very much for handling the review of our manuscript. We appreciate your extra effort in reaching out to three referees and securing quality review comments. We are very pleased by the overall positive, encouraging and constructive comments. We thank the three referees for their time and help. As shown in the point-to-point responses to the three referees, we have made extensive revisions to address every of the comments, with the major ones summarized as below:

Referee #1 expressed discomfort with the introduction, justification, and implication, and suggested better connection between the introductory paragraphs, and alternative framing of the results and discussion. We rewrote the introduction section and added discussion in the final section to clarify the scope of this work, and put it in the comprehensive context of earth system model concisely.

Referee #2 was concerned about the impact of head space trace gas accumulation on carbon mineralization, and potential limitation of the data from microcosms without flushing in reflecting field conditions. We conducted additional numerical experiments using biogeochemical model to evaluate the impact. We demonstrated that the impact is complicate (highly nonlinear as the controlling coupled processes are highly nonlinear), and increasingly mechanistic model are useful in help us understand the processes, with the hope to improve our predictability.

Referee #3 recommended that we provide stronger justification for determining that the most limiting factor for SOM turnover is hydrolysis of macromolecules. We agree that hydrolysis is a limiting factor. We also agree with referee #1 that it is controversial to state that hydrolysis is the most limiting factor. As a result, we try to be balanced and discuss about possible new data needs to better understand and quantify hydrolysis.

With those revisions, the manuscript has been substantially improved. We hope the revised manuscript is acceptable for publication Biogeosciences and will be helpful for both modeling and experimental research. We appreciate you and the three referees for help. Should you have any question, please feel free to contact us.

Response to Referee #1

Comment 1: Soil carbon models are a critical source of uncertainty in Earth system models both due to limitation in model-data and process representation. This manuscript addresses modeling hurdles in a key process (anaerobic decomposition) missing in most soil car- bon models. This work is a timely, novel, and carefully conducted. However I am uncomfortable with the current introduction, justification, and implication presented in the manuscript. The actual results section is very strong but would suggest extensive revisions to the introduction and conclusion.

Response 1: We appreciate that the referee spent valuable time in reviewing this manuscript, and provided very constructive comments from a different perspective. As detailed below and highlighted in the revised version, we made extensive revisions to improve the introduction, justification, and implication components as the referee suggested, with a focus on clarifying the scope of this work, and putting it in the comprehensive context of earth system model concisely. We hope the manuscript is substantially improved.

Comment 2: In general, I would suggest better connections between and within the introductory paragraphs. The main paragraphs jump around and paragraphs themselves lack coherent structure.

Response 2: This is because that we tried to avoid lengthy discussion about the context of carbon mineralization and methane production, consumption, and transport. We add the following paragraph in the end of the introduction section to concisely describe the context and limit our scope of this study, which reads:

"The carbon cycle involves coupled hydrological, geochemical, and biological processes interacting from molecular to global scales. The implicit empirical first order approach used in existing LSMs limits our understanding of the land atmosphere interaction and is a source of prediction uncertainty. To improve our understanding and reduce prediction uncertainty, we attempt to use relatively more explicit mechanistic representations developed in the reactive transport model literature (Tang et al., 2016). Even though explicit representation does not necessarily improve the match between the predictions and observations over well-tuned existing models immediately (e.g., Wieder et al. 2015; Steven et al. 2006), our approach provides a systematic means to incorporate on-going process-rich investigations to improve mechanistic representations in LSMs across scales. As a preliminary study, we constrain our scope to extending CLM-CN with minimum revision to describe anaerobic CO_2 and CH_4 production from several recent microcosm studies in this work. We discuss next steps briefly results and discussion section."

We also add two paragraphs in the end of the results and discussion section to describe the implications as:

"Another following up task is to assess the model in field studies using CLM-PFLOTRAN. This can be done incrementally, i.e., add/remove reactions one at a time without source code modifications. CLM-PFLOTRAN currently uses CLM4.5 vertical resolved grid, The resolution can be adjusted, possibly in three dimension, to reflect the heterogeneity of any structural soil column to account for the limitation of electron donors and electron acceptors at individual locations. As we gradually implement more and more processes, such as gas and aqueous transport, through soils and aerenchyma, explicitly representing microbial processes for carbon decomposition, we hope the new framework will be useful for future investigation and model developments."

Note that the first paragraph is in response to the comments about headspace flushing raised by the second referee.

Comment 3: I would also like to see a discussion/acknowledgement of other mechanisms that could influence anaerobic decomposition which were not captured by the proposed model. While not ALL processes can be included in a model, some acknowledgement of those missing processes and either how then can be incorporated into future work or how they influence current simulations are appropriate and highlight the limitations of the proposed model.

Response 3: as in response 2, we mention the hydrological and biological processes across scales in general; for specific processes, we discuss about mimic impact of flushing/boundary condition/pressure, as well as increase the grid resolution to simulate the heterogeneous structured soil columns. And we talk about potential next steps.

Comment 4: Relatedly the authors need to address how these detailed pool based kinetic models scale to well-structured heterogeneous soils. Great detail is gone into on the chemical processes governing methanogensis in the introduction but there is no discussion of how the physical structure of the soil plays into substrate and oxygen availability and the inherent limitations to applying mechanistic pool models to highly structured soil columns. While this is a common shortcoming of soil carbon models I feel that, given the level of processes detailed covered in the model, this is critical to address and justify utilization of a pool model with such explicit process representation. Minimum the authors need to acknowledge that the scaling of known kinetics from well-mixed experiments to highly structure soil cores is a relevant open question in the field.

Response 4: As in response 2, we add discussion about using high resolution to deal with heterogeneity; in Tang et al. 2016, we actually discussed potential ways to account for oxygen limitation and even oxygen transportation and consumption; While scaling is a grand challenge, there are evidences that the parameters determined in the lab are applicable for field studies in our previous studies (e.g., Tang et al. 2013b). As a preliminary study, we feel it is better to focus on the current scope.

Comment 5: The great strength of this manuscript is the highly detailed and careful analysis of the proposed model, grounded against a data set. This was very well done and I feel should provide the backbone of a new discussion section which could be extended to suggest potential follow up experiments based on the model results. However there is no formal model-data integration nor a comparison with an adequate number of data sets to justify this as a mature component of a new CLM module, as is implied by the current introduction and discussion. If this is the manuscript that the authors want to write then I would suggest more data sets, a formal data-model integration, and demonstration of improvement to previous ratio-based models. But the current analysis would be completely appropriate in a different context which focused more on implications to future experimental designs and long term model projections. I strongly encourage the authors to carefully consider an alternative framing of this very interesting study.

Response 5: We appreciate the referee's positive comments, and very constructive advices. As discussed in response 2, this is a preliminary study with focus on mechanistic representation. We are interested in incorporating more existing data, but are limited by lack of detailed data such as pH, Fe, organic acids, etc., in the existing studies. In the revision, we mention potential next steps and further model data iteration exercises.

--Line by line response--

Comment 6: P2L2 Actually many of the IPCC models suggest that SOC will increase in the northern latitudes due to increases in inputs (Todd-Brown et al 2014), I would suggest softening this statement to reflect the huge uncertainty in the current state of the science. Less controversial would be a statement referring to a general ramping up of the entire car- bon cycle in response to climate change, increases are expected in both primary pro- duction and decomposition. Whether the net effect will be to convert SOC to CO2/CH4 is highly debated.

Response 6: revise "… are widely expected to accelerate …" to "… may …" to soften the statement.

Comment 7: P2L2-14 I like the content of this paragraph but it needs to be re-organized. There are three distinct topics in this paragraph which would be better served breaking them up/integrating with later parts of the manuscript: a review of expected high latitude SOC vulnerability to climate change, summary of CLM-CN representation of anaerobic conditions (coupling this with a general review of aerobic decomposition would not go amiss here but that is a soft suggestion), and the comparison to lab incubations.

Response 7: we separate the paragraphs into two, and put our study in the context concisely (see marked revised manuscript).

Comment 8: P2L15 CH4 is critical not just because of it's high global warming potential but also because of it's emissions rate and residence time in the atmosphere. Please add some citations to reflect this.

Response 8: add residence time and production rate (*italic*) as

"Because CH_4 has a 100-year global warming potential that is about 26 times greater than CO_2 (Forster et al., 2007;IPCC, 2013), *and an atmospheric residence time of approximately 10 years (IPCC, 2013), and methanogenesis rate can be high under favorable conditions,* …"

Comment 9: P2L19 Why is this lag critical?

Response 9: add

"The implication is that a first order rate (including constant CO_2 CH_4 ratio parameterization) overpredicts CH_4 production rate before methanogenosis initiation and underpredicts CH_4 production rate afterwards, and the uncertain lag time introduces large uncertainty in CH_4 production prediction."

Comment 10: P2L25 Why is the CH4:CO2 ratio important? Maybe lead with this being a critical parameter for current models and then show how this is a dynamic response to the competing Redox ladder. I think this is where the authors are trying to go with this but it is lost in the paragraph. Could the proposed model be compared with the standard ratio model?

Response 10: As in response 9, the manuscript shows that a constant CH4:CO2 ratio approach introduces prediction uncertainty, and our mechanistic model has the potential to reduce the prediction uncertainty. We feel it to be premature to conclude whether the mechanistic model perform better than a standard ratio model. The mechanistic model is expected to work better than the empirical for these specific data sets. It is challenging to extend the comparison to other available datasets because the lack of measurements (e.g., pH, Fe, etc.) to support the mechanistic model. Our long term goal is to evaluate if a mechanistic model performs better than a standard ratio model. This is only the first step toward the long term goal.

Comment 11: P2L33 Why is an aqueous phase essential for these calculations? Soil decomposition models are implicit descriptions of carbon dynamics anyway, why do we need an explicit representation of this process? Can a micro scale process like an explicit terminal electron acceptor model be simulated on the macro scale? I would suggest placing this study in the context of the increasing number of ?explicit? soil carbon dynamics models (ex: Wieder et al 2015). These models may or may not increase the overall accuracy of predictive dynamics over a well-tuned traditional model but they can provide critical scientific insights into the process of soil decomposition. This introduction lacks this critical nuance and oversells the capabilities of the proposed model.

Response 11: The aqueous phase is essential in that pH, Eh, thermodynamics, etc., are defined in the aqueous phase. As in detailed in Response 2, we put this study in the general context in the revision and acknowledge that explicit representation may not necessarily improve the match with the observation immediately over existing well-tuned models.

Comment 12: Sect2.2.1(and elsewhere) Please refer to model pools and other variables by name (variable) consistently throughout the manuscript, ex: organic acid pool (Ac). This reduces the need to refer back to tables/sections. Manuscripts are rarely read linearly and having to search for abbreviation definitions slows down reading.

Response 12: spell out.

Comment 13: P8L20 I applaud the authors for making their scripts available in the supplemental. Thank you.

Response 13: Thanks.

Comment 14: P12 Nice job walking through potential drivers of model-data mismatch. These provide a rich pool of candidates for future investigations. I feel that this should be the main focus of the conclusions. Given that a single data set was used and no formal model-data integration done this model is not quite ready for a full land carbon model integration as is implied by the authors in the introduction and conclusions. What IS done quite elegantly is an analysis of several representations of potential mechanisms and how they influence overall carbon mineralization in the context of a common model structure.

Response 14: Thanks for this nice evaluation. We revise the discussion and conclusion section to further strengthen these points.

Comment 15: P12 WEOC, TOTC are an unusual acronym in the field. Consider writing out the full name instead, I found myself forgetting what it stood for around here and having to go look it up. See previous comment about variable/pool references.

Response 15: spell out.

Comment 16: P13L19 This is a highly controversial statement that does not belong in the results section. While it is appropriate to highlight the relatively low amount of mineralized carbon there are several possible mechanisms for this that are unrelated to the chemical structure as suggested by this statement. Just because that is the explanation that fits into the model that is presented, it is not the only explanation (I'm thinking of various physical mechanisms like co-location and aggregate formation, as well as the substrate rarity argument ala Allson 2006). Please move to the conclusion and soften this statement considerably.

Response 16: revise "… is the rate limiting step …" to "… could be a rate limiting step…" to soften the statement.

Comment 17: P14L17 Cite the equation reference for f(pH)

Response 17: add (Eq. 3).

Comment 18: P14L26 Given the noise generally inherent in these measurements I would hesitate to call this a substantial difference. Could you can provide error bars for the data or some kind of significance testing.

Response 18: The sentence reads "These differences translate to substantial differences in model predictions". It is model predictions not observations. We add "(Fig. S7)" to avoid confusion. Instead of showing the average with error bars, the duplicate/triplicate observations were shown for headspace CO2 and CH4 to demonstrate the variation. For organic acids, Fe(II), and pH, the standard deviations are too small to shown as error bars.

Comment 19: Figures: In general, would it be possible to add error/uncertainty bars to the data points in the figures? This would place the modeled sensitivity in the context of the measurement error.

Response 19: see second half of response 18.

Comment 20: P16L5-7 WHAM is an aqueous pool model, claiming that there is no needed modifications when applying it to a well structured soil column seems a bit of a stretch.

Response 20: Windermere Humic Aqueous Model (WHAM) appears to be an aqueous model from its name. In fact, it treats the binding sites in soil organic matter as surface sites, and include other minerals such as Fe(OH)3, Al(OH)3, etc. In our implementation, we use surface sites to simulate organic matter. Namely, it does include solid phase, which is critical for soils.

Comment 21: Table 2 Formatting needs to be fixed for the table entries and I would suggest replacing TOTC with Total Organic Carbon and WEOC with Water Extractable Organic Carbon. OC is a common enough abbr. that it could be used here without explanation but TOTC and WEOC are not.

Response 21: Spell out TOTC and WEOC.

Comment 22: Figure and Table captions: Figure and table captions need to be able to stand alone in the manuscript, people will often scan the figures to get a sense of the results of the manuscript. Please expand the figure captions to more fully reflect the conclusions being illustrated here, this is particularly needed for the supplemental figures.

Response 22: This is improved as shown in the marked revised version of the manuscript and supplement. Please see the enclosed documents for details.

====================

Todd-Brown, K. E. O., Randerson, J. T., Hopkins, F., Arora, V., Hajima, T., Jones, C., Shevliakova, E., Tjiputra, J., Volodin, E., Wu, T., Zhang, Q. and Allison, S. D.: Changes in soil organic carbon storage predicted by Earth system models during the 21st century, Biogeosciences, 11(8), 2341-2356, 10.5194/bg-11-2341-2014, 2014.

Wieder, W. R., Allison, S. D., Davidson, E. A., Georgiou, K., Hararuk, O., He, Y., Hop-kins, F., Luo, Y., Smith, M. J., Sulman, B., Todd-Brown, K., Wang, Y.-P., Xia, J. and Xu, X.: Explicitly representing soil microbial processes in Earth system models, Global Biogeochem. Cycles, 29(10), 1782-1800, 10.1002/2015GB005188, 2015.

Steven D. Allison and Allison, S. D.: Brown Ground: A soil carbon analogue for the green world hypothesis?, Am. Nat., 167(5), 619-627, 10.1086/503443, 2006.

Response to Referee #2

Comment 1: The manuscript proposes a new module to the CLM-CN. It attempts to address a key limitation of existing land surface models in that the anaerobic decomposition is poorly represented. This work is novel and quite thorough. Most of my comments are technical except that I am not 100% comfortable with the testing dataset. It appears that the incubation experiment did not flush the headspace of microcosms. (This manuscript and the original publication both neglected to discuss flushing). It is well known that the accumulation of CO_2 and other trace gases in headspace distorts gas diffusion and greatly impacts decomposition. The suitability of the testing dataset is worth a thorough discussion.

Response 1: We appreciate the positive comments and the reasonable concerns this referee provided. Thanks for your time and consideration.

The major concern is the impact of head space trace gas accumulation on carbon mineralization, and potential limitation of the data from microcosms without flushing in reflecting field conditions. As traditional models (e.g., Knoblauch et al. 2013) do not explicitly account for the tracer gas accumulation impact on mineralization and methanogenesis, it is necessary to mimic the field conditions in the experiments. However, it is not clear that what level of flushing reflect the field conditions. Biogeochemical models like ours explicitly account for the impact of tracer gas accumulation in the headspace. They can describe the observations under various conditions, ranging from open to close system including various levels of flushing. The experimental data in this work were collected in well-defined conditions, and are valuable in quantifying these underlying processes, which is the focus of this work.

To address this concern and acknowledge the limitation, we add numerical experiments with 10 and 100 times headspace volumes. In the results and discussion section, we add the following:

"3.2.9 Predicted impact of headspace gas accumulation

Knoblauch et al. (2013) and Yang et al. (2016) flushed the headspace of the microcosms while Roy Chowdhury et al. (2015) and Herndon et al. (2015) did not. The field conditions are likely somewhere between an open system and a closed system because neither the atmospheric pressure nor the hydrostatic pressure is constant, and the produced CO2 and CH4 are not always free to release to the atmosphere. To assess the impact of CO2 accumulation in the headspace on the soil carbon mineralization and methanogenesis, we conduct numerical experiments with 10 and 100 times the headspace volume of the experimental values. With increased headspace volume, the headspace and aqueous CO2 concentrations are predicted to decrease (Fig. S11 f1-6, g1-6), and the pH increase is predicted to slow down. As a result, the biogeochemical reaction rates are generally slower (Fig. S11e1-6). Eventually, the predicted total CO2 and CH4 production generally decrease with lower headspace CO2 concentration (Fig. S11a1-6,b1-6). However, the impact on CO2 production is very small for the organic soils in the trough and ridge location, and the CO2 production is predicted to increase with decrease in headspace CO2 concentration for the organic center soils. Because of the complicated nonlinear relationships in the biogeochemical processes, the impact of headspace gas accumulation on carbon mineralization and methanogenesis is not linear. While it is debatable that which experimental conditions (flush the headspace or not) reflect the field conditions, biogeochemical models like ours provide a mechanistic method to account for this impact by using boundary conditions that reflect the reality. Additional targeted experiments and mechanistic models are necessary to better understand the impact under different conditions, and develop representations that reflect field conditions.”

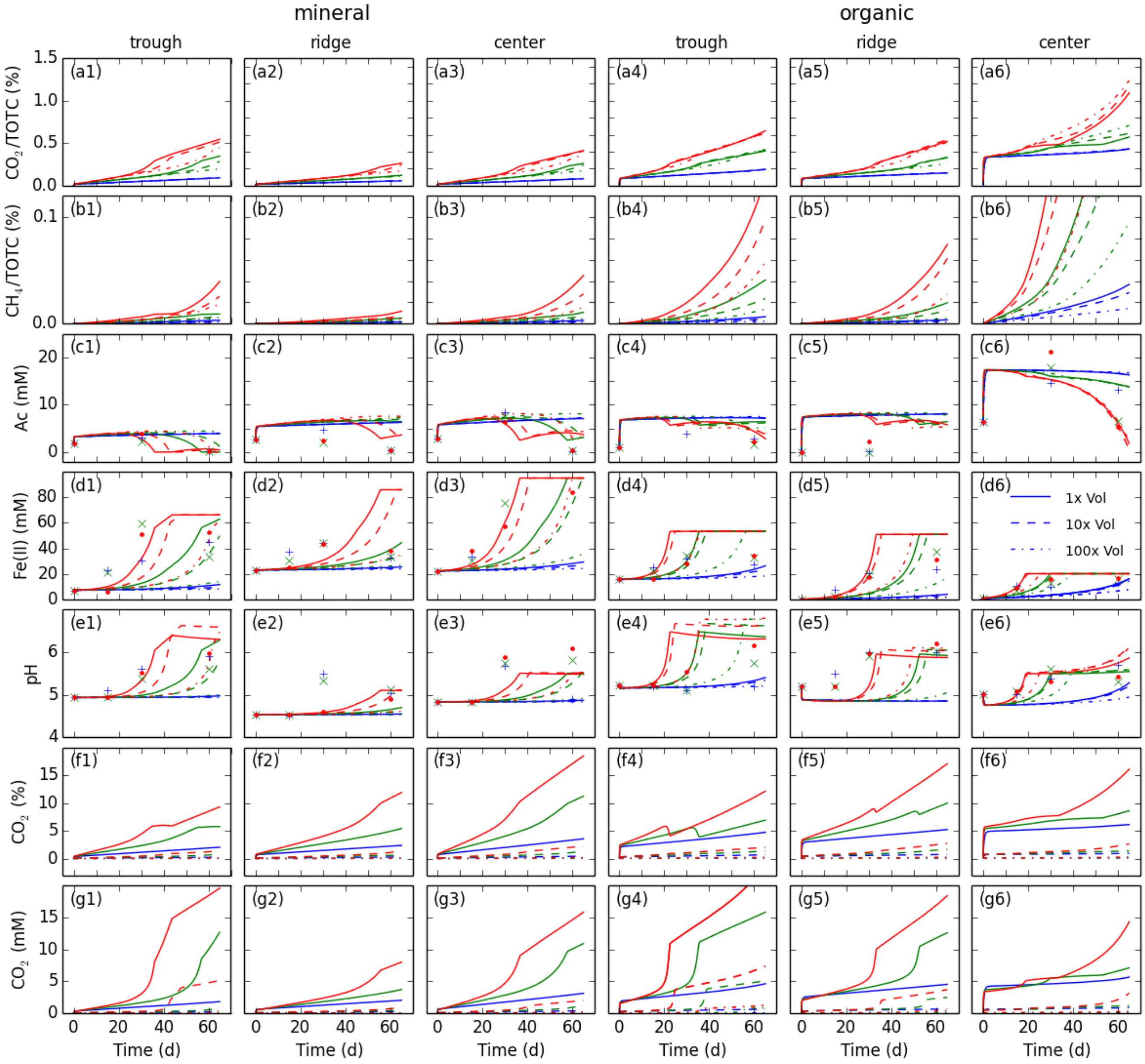


Figure S1: Impact of headspace volume on predictions: increase in headspace volume results in decrease in headspace and aqueous CO_2 concentration, slower pH increase and biogeochemical reaction rates, and generally less CO_2 and CH_4 production prediction. As an exception, predicted CO_2 production is increases with increasing headspace volume for the center oganic soils. The impact is not linear as the underlying biogeochemical processes are nonlinear. See Fig.2 caption for more description about the model and experimental parameters.

Comment 2: I am very intrigued by this model, especially its addition of geochemical components. From an empirical perspective, I agree that redox dynamics and the turnover of pH and single substrates are all key in understanding anoxic decomposition. However, it is still unclear whether adding these processes make sense in modeling decomposition and trace gases production. Personally, I would like to see a comparison between the new model and CLM4ME/CLM-CN and evaluate whether the new model offers meaningful improvement. Other data sources could also be used to calibrate the model. These and other future directions should be discussed in details in the conclusion.

Response 2: We agree that it is debatable that whether adding these processes makes sense, and more work is needed to check if these improvements work. These are in our following work therefore are not included in this study. In our revision, we add in the end of the introduction section to better define our context and scope:

"The carbon cycle involves coupled hydrological, geochemical, and biological processes interacting from molecular to global scales. The implicit empirical first order approach used in existing LSMs limits our understanding of the land atmosphere interaction and is a source of prediction uncertainty. To improve our understanding and reduce prediction uncertainty, we attempt to use relatively more explicit mechanistic representations developed in the reactive transport model literature (Tang et al., 2016). Even though explicit representation does not necessarily improve the match between the predictions and observations over well-tuned existing models immediately (e.g., Wieder et al. 2015; Steven et al. 2006), our approach provides a systematic means to incorporate on-going process-rich investigations to improve mechanistic representations in LSMs across scales. As a preliminary study, we constrain our scope to extending CLM-CN with minimum revision to describe anaerobic CO_2 and CH_4 production from several recent microcosm studies in this work. We discuss next steps briefly results and discussion section."

Comment 3: Title, would it be better to say biogeochemical modeling or A biogeochemical model of CO2 and CH4 production?

Response 3: revise to "biogeochemical modeling of …"

Comment 4: When citing references, please add a space after each semicolon.

Response 4: Done. These were due to the automatic formatting using endnote.

Comment 5: P3L2, there is a disconnect between the topic sentence and the following text. The topic sentence introduces 'simple substrates' and their importance in modeling CH4, while the following sentences switched the focus away from simple substrates. This paragraph can be reorganized to improve the flow of thought.

Response 5: add between the first two sentences “Instead, they are typically lumped together as dissolved organic matter (DOM) or low-molecular-weight organic carbon (LMWOC).” to connect the sentences.

Comment 6: P3L8, lignin should not be classified as polysaccharides.

Response 6: Removed “lignin” from the list.

Comment 7: P3L14, acetate and H2 have been added to models?

Response 7: revise to “representations of acetate and H_2 have been added to models…”

Comment 8: When introducing soil pH and its role in LSMs, it is worth noting that soil pH changes rapidly as a result of redox reactions. For instance, iron(III) reduction consumes protons and usually increases soil pH.

Response 8: the paragraph is revised from

“In addition to electron acceptors and substrates, SOM turnover is also sensitive to soil pH. Most methanogens grow over a relatively narrow pH range (6-8), while some adapt to acidic or basic environments (Garcia et al., 2000; Van Kessel and Russell, 1996; Wang et al., 1993; Sowers et al., 1984; Rivkina et al., 2007; Hao et al., 2012; Kotsyurbenko et al., 2004; Kotsyurbenko et al., 2007). The pH response functions in LSMs are empirical and vary substantially (Xu et al., 2016b). Because of the large buffer capacity, soil pH is often fixed in LSMs (Oleson et al., 2013; Tian et al., 2010). But in reality, pH does change 1-2 logarithmic units in laboratory incubations (Xu et al., 2015; Roy Chowdhury et al., 2015; Peters and Conrad, 1996; Drake et al., 2015) and in the field, where it can vary significantly through the soil profile and along topographic and vegetation gradients (Cao et al., 1995; Van Bodegom et al., 2001; Lipson et al., 2013b). pH is calculated using soil acidity and soil buffer capacity (Van Bodegom et al., 2001) or as a function of acetate concentration (Xu et al., 2015). It is desirable to use a geochemical model to describe pH evolution mechanistically.”

to

“In addition to electron acceptors and substrates, SOM turnover is also sensitive to soil pH. Most methanogens grow over a relatively narrow pH range (6-8), while some adapt to acidic or basic environments (Garcia et al., 2000; Van Kessel and Russell, 1996; Wang et al., 1993; Sowers et al., 1984; Rivkina et al., 2007; Hao et al., 2012; Kotsyurbenko et al., 2004; Kotsyurbenko et al., 2007). Soil pH does change 1-2 logarithmic units in laboratory incubations (Xu et al., 2015; Roy Chowdhury et al., 2015; Peters and Conrad, 1996; Drake et al., 2015). It can vary significantly through the soil profile and along topographic and vegetation gradients in the field (Cao et al., 1995; Van Bodegom et al., 2001; Lipson et al., 2013b). However, soil pH is often fixed in LSMs (Oleson et al., 2013; Tian et al., 2010). pH is calculated using soil acidity and soil buffering capacity (Van Bodegom et al., 2001) or as a function of acetate concentration (Xu et al., 2015). It is desirable to use a geochemical model to describe pH evolution mechanistically. The pH response functions (reaction rate factor as a function of pH) in LSMs are empirical and vary substantially (Xu et al., 2016b). Assessing the efficacy of these functions is needed to better present pH impact on carbon mineralization and methanogenesis."

We do not feel comfortable to say soil pH change rapidly. We delete that sentence "because of the large buffering capacity, " as well.

Comment 9: P3L25, use pH buffering capacity instead of pH buffer capacity. It would also be useful to define 'pH response functions'.

Response 9: revise "buffer" to "buffering", and add "(reaction rate factor as a function of pH)" after pH response function as described above.

Comment 10: P3L26, logarithmic

Response: 10: revise from **"**logarithm" to "logarithmic" as above

Comment 11: P4L4, the last sentence is rather weak and does not connect with the next paragraph. A better transition is needed to highlight why it is necessary to compare temperature response functions.

Response 11: add (italic) to the last sentence as

"*To reduce prediction uncertainty for carbon mineralization and methanogenesis under various temperatures,* the temperature response functions need to be assessed as well."

Comment 12: In 2.2.2, would it be possible to discuss how iron reduction and methanogenesis interact in the model? I can see that both of them reply on mD and kD, but what determines the partitioning of electron donors between these two processes? These details would be valuable to interpret the results later on (P9L28-35).

Response 12: add

"In this model, iron reducers and methanogens interact in different ways under various conditions. When the electron donors (acetate and H_2) are abundant, iron reducers grow faster than methanogens when Fe(III) is not limiting (depending on the $Fe(OH)_{3a}$ surface sites and iron reducers population), i.e., iron reducers have a short doubling time than methanogens. When the electron donors are limiting, iron reducers are expected to outcompete methanogens, depending on the half saturation (substrate affinity) values. The model also accounts for the thermodynamics. However, it does not account for possible different responses to temperatures and pH for iron reducers and methanogens."

Comment 13: P6L26, Riley et al. (2011) in fact cited Meng et al. (2012) Biogeosciences, 9, 2793–2819 for this specific pH function.

Response 13: add the citation/reference.

Comment 14: P7L8, the speciation of what?

Response 14: add "CO_2, CH_4, H_2, Fe, etc."

Comment 15: P8L7, please justify why f(mega) and f(ferb) differ so much during initiation. A coma is missing between 0.5 and f(ferb). Also, I would keep the acronyms consistent, including their letter cases, throughout the manuscript.

Response 15: revise "$f_{mega} = f_{megh} = 0.5 f_{ferb} = 10^{-6}$" to "$f_{bio} = 10^{-6}$, $f_{MeGA} = f_{MeGH} = f_{bio}$, and $f_{FeRB} = 2 f_{bio}$". som1, som2, som3, megh, mega, and ferb in the subscripts are changed to consistent forms as normal text throughout the manuscript. f_{FeRB} is twice f_{MeGA} or f_{MeGH} because FeRB has only one group while methanogens have two groups.

Comment 16: P8L10, 'bioavailable ferric oxides' is a vague and potentially controversial term. Please provide a definition. Also justify why HCl-Fe(III) is used to represent bioavailable ferric oxides. These papers may be useful: Hyacinthe et al. 2006 Geochimica et Cosmochimica Acta 70: 4166-4180, Poulton and Canfield 2005 Chemical Geology 214:

209-221.

Response 16: modify the sentence from "we start with $f_{fe3} = 0.005$" to "While bioavailable Fe(III) in soils is not well defined (e.g., Hyacinthe et al. 2006; Poulton and Canfield 2005), we start with $f_{fe3} = 0.005$ and evaluate the impact with a range of values." and add the references."

Comment 17: P8L26-27, I cannot follow this sentence.

Response 17: the sentence

"The overall observations appear to separate between the soil horizons (organic vs. mineral soils) rather than among the microtopographic locations (center, ridge, and trough) of ice-wedge polygons."

is rewritten as

"The variations in the overall observations appear to be better explained by the differences between the soil horizons (organic vs. mineral soils) than among the microtopographic locations (center, ridge, and trough) of ice-wedge polygons."

Comment 18: P8L28, it appears that soil microcosms were not flushed after gas sampling. Without flushing headspace, CO2 concentration builds up and consequently distorts gas diffusion. Without regular flushing, results from these incubations would misrepresent the decomposition processes in the field. Please comment.

Response 18: as in response 1 in the beginning, our model mechanistically describe the impact of headspace gas composition on mineralization and methanogenesis, therefore, better represent these processes; the field conditions can be simulated by using appropriate boundary conditions.

Comment 19: P9L8, again, the inhibitory effect of high headspace CO_2 on microbial activities likely explained why the CO2 level off in the microcosms. Are these results appropriate for calibrating models? Please comment.

Response 19: as above, our results are generally applicable.

Comment 20: P9L10, except in the center organic soils.

Response 20: add comma.

Comment 21: P9L15, so does microbial activity every year
Response 21: add "so does".

Comment 22: P9L26, pH increased with Fe(III) reduction or the increase in pH
Response 22: revise from "the pH increase" to "the increase in pH".

Comment 23: Qualitatively, there is evidence to support that Fe(III) reduction competes with CH4 production. The center organic soils had the highest CH4 production, while their Fe(III) reduction was the lowest among all treatments. The authors claimed that "the impact appears less significant than expected", but I don't understand what they were expecting. Please elaborate.
Response 23: This is in relative to the belief of strict thermodynamic/redox ladder where methanogenesis does not occur until all alternative electron acceptors that are more favorable than CO_2 are exhausted. We add "(e.g., complete inhibition until bioavailable Fe(III) is exhausted)" to "the impact appears less significant than expected".

Comment 24: P10L24-25, if microcosms in Roy Chowdhury et al. (2015) were not flushed regularly, then their results underestimated CO2 production. Thus, it is not surprising that the models appeared to overestimate CO2 production. Please comment.

Response 24: as addressed in the beginning, our model mechanistically describe the impact of headspace gas composition on mineralization and methanogenesis, therefore, better represent these processes; the field conditions can be simulated by using appropriate boundary conditions.

Comment 25: P10L26, notice that Knoblauch et al. (2013) flushed microcosm headspace whenever CO2 concentration reached 3%.

Response 25: see response 1.

Comment 26: P12L6, Figure 3S, adsorption of CO2 on iron oxides played a bigger role in the mineral soils than in the organic soils. Why?

Response 26: This is because of relatively higher Fe(OH)3a in the mineral soils than in the organic soils.

Comment 27: P12L19, Table 2 should be referenced here instead of Table 1.

Response 27: corrected. Thanks for catching this mistake.

Comment 28: P12L20-23, I agree that higher f(labileDOC) increased model performance. But such improvement occurred mostly in samples kept at 8 degrees. For samples in -2 degrees, models with the lowest f(labileDOC) were actually the best. Please comment on the interactive effects of temperature and f(labileDOC) on CO2 production.

Response 28: as describe in section 3.1, the observed temperature response is diverse and challenging to explain. We do not feel comfortable in assessing the predictions at -2 °C.

Comment 29: P14L10-11, soil redox condition can also explain why mineral soils have lower pH than organic soils. Soils in reducing environments usually have high pH because reduction reactions consume protons. With a much higher water content (Table 2), organic soils are in more reducing conditions and likely have higher pH than mineral soils.

Response 29: add "… and/or more reducing condition in the organic soils as reduction reactions typically consume protons."

Comment 30: Set a hanging indent for references.

Response 30: Done

Comment 31: Tables should be reformatted.

Response 31: done.

Responses to Referee #3

Comment 1: Community land model carbon nitrogen (CLM-CN) predominantly represents aerobic decomposition of SOM. In this manuscript, authors propose to include anaerobic processes in this model by integrating new experimental data for redox potential, pH, and temperature parameters from Arctic soils. This manuscript is very thorough. It's amazing to see parameterization of model with experimental data! While this work has some flaws, it is a huge step forward in closing the gap between modeling and experimental data integration. I'm impressed by the author's knowledge of biogeochemical processes in soil and effort to connect real world mechanisms to the modeling results; this is no small feat. It is clear they gave a great deal of thought to their results.

Response 1: Many thanks for the compliments and very nice constructive comments.

Comment 2: In general, I would recommend the author's provide stronger justification for determining that the most limiting factor for SOM turnover is hydrolysis of macromolecules. This both served as the foundation of this work and is continually provided as an explanation to observations. While it's tough to cover all possible scenarios in soils, authors should address other potential factors that could drive the rate of SOM turnover and justify why they believe hydrolysis of macromolecules is the most limiting factor.

Response 2: We agree that hydrolysis is a limiting factor. We also agree with referee #1 that it is controversial to state that hydrolysis is the most limiting factor. At least, the evidence from the data referred in this work does not unequivocally substantiate the statement. As a result, we try to be balanced and discuss about possible new data needs to better understand and quantify hydrolysis.

All the referees comment on the need to mention other factors. In response, we make revisions to clarify the scope of this work, to put our work in the context of comprehensive hydrologic, geochemical and biologic processes that control soil carbon mineralization, and describe using 3-D high resolution grids to account for heterogeneity, and CLM-PFLOTRAN to use reactive transport models to improve the mechanistic representation in land surface models. Please see response to other referees for more details.

Comment 3. In the conclusion, I think it would be nice for the author's to add some suggestions for parameters/processes that could be incorporated into this model in the future or specific geochemical measurements that experimentalists should consider collecting during their studies.

Response 3: These are nice suggestions. As mentioned in Response 2, we add discussions about next steps.

—Specific comments—

Comment 4: P3L10-11: "… the hydrolysis and fermentation reactions have been poorly quantified." I'm not sure I follow the point being made here. Is this suggesting that hydrolysis/fermentation of SOM is poorly quantified (in general) or specifically in arctic soils?

Response 4: add "represented and quantified in Arctic as well as temperate and tropical soils" to clarify the point.

Comment 5: P4L28-29: What is a "low-center polygon"? It is frequently referred to the in the text of this article, yet it is unclear to me what it is. This seems like site-specific terminology that may be worth describing. I'm not sure how many readers would know what this is. I'm also assuming the "center" sampling location is a slope since the other two are the "ridge" and "trough"?

Response 5: add "(a typical arctic geographic feature in the low lands with soils surround by ice wedges, see cited references for more information)".

Comment 6: P7L28: What do SOM3 and SOM4 represent? LabileDOC, SOM1, SOM2 and the biomass pools were described, but not SOM3 and SOM4. Furthermore, SOM4 isn't included in the fractions listed on P7L29. Is it supposed to be included in this list of fractions? If not, then why is it excluded?

Response 6: SOM3 and SOM4 are like SOM1 and SOM2, two additional soil organic matter pools in CLM-CN (Fig. 1). We add "(the rest is assumed to be SOM4, e.g., $f_{SOM4} = 1 - f_{LabileDOC} - f_{SOM1}$ …)"

Comment 7: P8L1-2: The turnover time of SOM3 and SOM4 are not listed – these fractions need to be better described or explain why they are excluded.

Response 7: add "(as the turnover time for SOM3 and SOM4 are 2 and 27 y, respectively, Fig. 1)".

Comment 8: P8L7-9: Nice explanation for "back of the envelop" biomass estimation

Response 8: Thanks.

Comment 9: P10L26-27: Are there other potential reasons why the rate of CO2 would stabilize? Limitation of some other resource? For instance, N? Does this study have evidence to support that rate of CO_2 respiration stabilized because of hydrolysis of polymers?

Response 9: We appreciated the reviewer for raising these questions. As we mention ahead of section 2.1, "While nitrogen (ammonium and nitrate) concentrations can affect carbon mineralization (Lavoie et al., 2011), we do not account for this effect because of a lack of nitrogen measurements from these experiments." As we mention earlier, we do not have specific direct evidence to support polymer hydrolysis as the limiting factor.

Comment 10: P11L8: parameter Fe3= 0.02 is above the max value in the range of observed values stated on P8L14, can the authors comment on why they might need to increase this value beyond observed values to help the model better match observations for Fe(II)? Do you have any suggestions for some other parameter that should be included or other parameter values that could be altered to help achieve a better model fit, while maintaining values within experimentally observed value range?

Response 10: The observed range is from another site. It is not directly applicable here. In the revision, we revise from "we start with $f_{\mathrm{fe3}} = 0.005$" to "While bioavailable Fe(III) in soils is not well defined (e.g., Hyacinthe et al. 2006; Poulton and Canfield 2005), we start with $f_{\mathrm{Fe3}} = 0.005$ and evaluate the impact with a range of values."

Comment 11: P11L11-14: How do these model observations relate to experimental data? Is there any experimental evidence (either from your original work or other soil Fe literature) to support that as Fe3 increases there is a decrease in CH4 resulting from competition between methanogens and iron reducers? Why wouldn't this also be the case when Fe3 = 0.01?

Response 11: We add "(rather than strict thermodynamic control, e.g., Bethke et al., 2011; direct inhibition, e.g., van Bodegom et al., 2004; or indirect inhibition through substrate competition, e.g., Mill et al., 2015, Reiche et al. 2008)". As discussed in these cited references, Fe reduction is known for inhibition of methanogenesis.

Comment 12: P11L29-31: This statement contradicts L25-26. L25-26 states as pH increases, CO2(aq) increases. L29-31 states as pH increases, CO2 (aq) decreases. Please provide an explanation.

Response 12: This was because CO2 in the aqueous phase here means a specific aqueous species rather than total CO2. To avoid this confusion, we add (aq) after CO2 and the sentence is revised from

"As the pH increases above the carbonic acid pKa (around 6.3 at standard condition), CO_2(g) in the headspace and CO_2 in the aqueous phase decrease as HCO_3^- becomes dominant, and the gas-phase fraction decreases dramatically." to

"As the pH increases above the carbonic acid pKa (around 6.3 at standard condition), CO_2(g) in the headspace and $CO_{2(aq)}$ species decrease as HCO_3^- becomes the dominant species in the aqueous phase, and the gas-phase fraction decreases dramatically."

Comment 13: P12L19: I keep having to look back at what "WEOC" means. I would recommend using some other terminology. Also, this sentence should reference Table 2 not Table 1.

Response 13: As suggested by the other two referees, we spell out WEOC. The table reference is corrected.

Comment 14: P12L20-22: Is this comparable? The values for rapid CO2 release in Figure 4 look nearly double or triple the observed values. It appears that CO2 values for organic center at a LabileDOC = 0.02 fit the experimental data best out of all of these scenarios.

Response 14: revise to "… the underprediction of the early CO_2 increase in the headspace are more or less mitigated."

Comment 15: P12L29: "high center polygon trough"? I thought "center" and "trough" were two different sampling sites? Please clarify and be consistent throughout the paper. Same error P13L6.

Response 15: revise from "…from the high center polygon trough" to "…from a trough location in a high center polygon…"

Comment 16: P13L19-20: I don't follow – how do these studies demonstrate that hydrolysis of macromolecular organics by extracellular enzymes is the rate limiting step? What about bioavailability? Limitation of some other resource?

Response 16: As we discuss earlier, we do not have direct unequivocal evidence for this.

Comment 17: P13L24-26: Please rewrite this sentence for clarity.

Response 17: remove "(or produce substrate for)" and add "in the $s_{\text{labile}} = 0.2$ case". The sentence reads:

"With $s_{\text{labile}} = 0.2$, the model generally predicts less CH_4 and more CO_2 than the case with $s_{\text{labile}} = 0.4$ because less SOM is assumed to respire through the anaerobic pathway in the $s_{\text{labile}} = 0.2$ case (Fig. S5)."

Comment 18: P13L31: "the model substantially underpredicts: : :" Please include a figure number.

Response 18: include figure number: Fig. 4b3.

Comment 19: P14L1: It could also be attributed to populations at that particular site grow more rapidly than the populations at other sites. Hard to say without a T0 measurement: : : I would tread lightly with this, you don't have strong experimental evidence to support this statement.

Response 19: remove ", indicating possible high initial abundance"

Comment 20: P14- first paragraph: The text says the opposite of what is demonstrated in Figure 5.

Response 20: The legend was wrong. It is corrected. The numbering for the subplots was moved to the right corner to avoid overlap with the legend.

Comment 21: Figure 5 shows the lower initial biomass results in more Ch4, FeII, pH increase, etc. Is it possible the figure legend is wrong?

Response 21: See Response 20

Comment 22: P14L10-12: OK, but if the OM soils are better buffered why are there rapid changes in pH for both the observed and experimental data for OM soils? FigureS6. OM soils appear to have rapid pH changes occur sooner than mineral soils, despite buffering? Please explain.

Response 22: The initial drastic drop in pH for OM soils are due to the fermentation of a large amount of initial labile carbon. Because of the abundance of simple substrates, Fe reduction and methanogenesis rates are high later, resulting in fast pH increase. It is really a complex nonlinear relationship.

Comment 23: P16L21: change "enhancing" to "enhances"

Response 23: revised.

Comment 24: P16: Transparent science! Thanks for making your code and data available!

Response 24: You are welcome. We are happy to share.

Comment 25: P17: It's unclear what a pH response and temperature response function are. Please better define. What is the reader supposed to take away from this information?

Response 25: add "(reaction rate adjustment factor as a function of pH)" and "(reaction rate adjustment factor as a function of temperature)". As we discuss in the introduction and results and discussion sections, the take-away is that these two response functions are an important source of uncertainty.

Comment 26: All tables and figures should be able to stand on their own. Improve caption text and add full legends (colors, symbols, and patterns defined in each figure).

Response 26: improved.

Comment 27: -Please format Table 2.

Response 27: this is reformed (see page 27).

Comment 28: -Figure 2 caption L5 add “as” after “such”

Response 28: added.

Comment 29: -Figure 5 caption text does not match figure. Legend suggests lowest initial biomass results in highest CH4. Please make full legend visible (partially covered up).

Response 29: See Response 20.

Biogeochemical modeling of CO_2 and CH_4 production in anoxic Arctic soil microcosms

Guoping Tang[1], Jianqiu Zheng[2], Xiaofeng Xu[3], Ziming Yang[1], David E. Graham[2,4], Baohua Gu[1], Scott Painter[1,4], and Peter E. Thornton[1,4]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA
[2]Biosciences Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA
[3]Biology Department, San Diego State University, San Diego, CA, 92182 USA
[4]Climate Change Science Institute, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA

Correspondence to: Guoping Tang (guopingtangva@gmail.com)

Abstract. Soil organic carbon turnover to CO_2 and CH_4 is sensitive to soil redox potential and pH conditions. However, land surface models do not consider redox and pH in the aqueous phase explicitly, thereby limiting their use for making predictions in anoxic environments. Using recent data from incubations of Arctic soils, we extend the Community Land Model Carbon Nitrogen (CLM-CN) decomposition cascade to include simple organic substrate turnover, fermentation, Fe(III) reduction, and methanogenesis reactions, and assess the efficacy of various temperature and pH response functions. Incorporating the Windermere Humic Aqueous Model (WHAM) enables us to approximately describe the observed pH evolution without additional parameterization. Although Fe(III) reduction is normally assumed to compete with methanogenesis, the model predicts that Fe(III) reduction raises the pH from acidic to neutral, thereby reducing environmental stress to methanogens and accelerating methane production when substrates are not limiting. The equilibrium speciation predicts a substantial increase in CO_2 solubility as pH increases, and taking into account CO_2 adsorption to surface sites of metal oxides further decreases the predicted headspace gas-phase fraction at low pH. Without adequate representation of these speciation reactions, and the impacts of pH~~,~~ temperature, and pressure, the CO_2 production from closed microcosms can be substantially underestimated based on headspace CO_2 measurements only. Our results demonstrate the efficacy of geochemical models for simulating soil biogeochemistry and provide predictive understanding and mechanistic representations that can be ~~tested~~ incorporated into land surface models to improve climate ~~model~~ predictions.

Key words. anaerobic incubation, Fe(III) reduction, methanogenesis, pH, temperature response

1 Introduction

Global warming is expected to accelerate permafrost thaw, which~~Projected increases in temperature and soil saturation and vegetation shift~~ ~~are widely expected to accelerate~~ may trigger the release of the large amount of frozen soil organic matter (SOM) stored in the Arctic as carbon dioxide (CO_2) and methane (CH_4) into the atmosphere, ~~which may~~possibly forming a positive feedback to climate change (Treat et al., 2015; Knoblauch et al., 2013; Elberling et al., 2013). Permafrost thawing leads to significant changes in soil water saturation, creating favorable conditions for anaerobic respiration and methanogenesis (Lawrence et al., 2015).

Current biogeochemical models predominantly represent SOM decomposition ~~models are developed mostly for~~under aerobic conditions (Manzoni and Porporato, 2009). They ~~and~~ are modified for use under anaerobic conditions. For example, the Community Land Model Carbon Nitrogen (CLM-CN) decomposition cascade is used to implicitly represent anaerobic decomposition with a moisture response function that approaches unity at saturation and an oxygen scalar that has a large unresolved uncertainty (Oleson et al., 2013). In a recent permafrost carbon climate feedback modeling study, the carbon release rate from permafrost soils after thawing under aerobic conditions was assumed to be 3.4 times higher than the release rate under anaerobic conditions (Koven et al., 2015; Schädel et al., 2016). However, in incubations with soils from Alaska and Siberia, carbon release under aerobic conditions was 3.9–10 times greater than ~~release~~ under anaerobic conditions (Lee et al., 2012), and CO_2 production appeared ceased at late times in anaerobic microcosms (Xu et al., 2015; Roy Chowdhury et al., 2015), indicating that these existing models do not adequately represent the anaerobic processes for accurate prediction of SOM turnover and heterotrophic respiration.

In addition, it is important to accurately represent methanogenesis in the context of competing anaerobic processes ~~Because~~ because CH_4 has a 100-year global warming potential that is about 26 times greater than CO_2 (Forster et al., 2007; IPCC, 2013), an atmospheric residence time of approximately 10 years (IPCC, 2013), and methanogenesis rate can be high under favorable conditions,~~it is important to accurately represent methanogenesis in the context of competing anaerobic processes~~. Methanogenesis is carried out by a group of strictly anaerobic Archaea. The free energy of methanogenesis reactions is less favorable than the reduction of O_2, NO_3^-, Mn (IV), Fe(III), and SO_4^{2-} along the redox ladder (Conrad, 1996; Bethke et al., 2011). The accumulation of CH_4 has been widely observed to lag behind CO_2 for periods ranging from days to years in incubations (Knoblauch et al., 2013; Roy Chowdhury et al., 2015; Cui et al., 2015; Hoj et al., 2007; Fey et al., 2004; Jerman et al., 2009; Tang et al., 2013c). The implication is that a first order representation (including constant CO_2 CH_4 ratio parameterization) normally overpredicts CH_4 production rate before methanogenosis initiation and underpredicts CH_4 production rate afterwards, and the uncertain lag time introduces large bias in CH_4 production prediction.

Besides temperature (Fey and Conrad, 2003; Hoj et al., 2007; Jerman et al., 2009; Cui et al., 2015) and initial methanogen abundance (Conrad, 1996; Knoblauch et al., 2013), the wide range of redox buffers provided by the alternative electron acceptors is likely a cause of the wide range of observed lag times ~~that has been observed~~ (Estop-Aragonés and Blodau, 2012; Fey et al., 2004; Jerman et al., 2009; Yao et al., 1999; Conrad, 1996; Knorr and Blodau, 2009). As a result, the ratio of CH_4 to CO_2 ranges from 0.00001 to 0.5 (Wania et al., 2010; Drake et al., 2009; Bridgham et al., 2013), highlighting limitation of the CH_4 CO_2 ratio approach. Nevertheless, some land surface models (LSM) parameterize methanogenesis as a fraction of carbon mineralization (Wania et al., 2013; Oleson et al., 2013; Koven et al., 2015; ~~Tian et al., 2015;~~Cheng et al., 2013). While methanogenesis is explicitly represented in some models (Xu et al., 2015; Grant, 1998) and the reduction of alternative electron acceptors is explicitly represented in others (Fumoto et al., 2008; Segers and Kengen, 1998; Van Bodegom et al., 2001; van Bodegom et al., 2000), these models do not have an aqueous phase that is essential for explicit biogeochemical calculations, e.g., pH, Eh, and thermodynamic calculations. Because methanogenesis is sensitive to redox conditions, the lack of explicit biogeochemical representation of the redox processes contributes to the prediction uncertainty of CH_4 emission.

Anaerobic bacteria and Archaea usually depend on simple substrates such as sugars, alcohols, organic acids, and H_2 as carbon and energy sources~~, sources~~ that are rarely simulated in ecosystem models (Manzoni and Porporato, 2009; Xu et al, 2015). Instead, they are typically lumped together as dissolved organic matter (DOM) or low-molecular-weight organic carbon (LMWOC) (e.g., Tian et al., 2010). The abundance and importance of ~~dissolved organic matter (~~DOM and ~~) and low-molecular-weight organic carbon (~~LMWOC~~)~~ in SOM turnover in the Arctic soils are becoming increasingly recognized (Hodgkins et al., 2014). The DOM concentration in water flowing from collapsing permafrost (thermokarsts) on the North Slope of Alaska ranges from 0.2−8 mM, with biodegradable (degrade in 40 d) DOM accounting for 10-60 % (Abbott et al., 2014; Arnosti, 1998, 2000; Arnosti et al., 1998). Ancient LMWOC was found to fuel rapid CO_2 production upon thawing (Drake et al., 2015). On the other hand, new SOM consists of mostly macromolecules of plant and microbial residues such as carbohydrates (polysaccharides, including cellulose, hemicellulose, ~~lignin,~~ etc.), lipids, nucleic acids, and proteins (Kögel-Knabner, 2002). While conceptual models and measurements connecting SOM with LMWOC have long existed (Drake et al., 2009; Tveit et al., 2013; Tveit et al., 2015; Bridgham et al., 2013), the hydrolysis and fermentation reactions have been poorly represented and quantified in the Arctic as well as temperate and tropical soils. Among ~~the~~ over 250 SOM decomposition models that have been developed in the past 80 years (Manzoni and Porporato, 2009), only a few models explicitly simulate simple substrates (Xu et al., 2016b). Either a simple carbon pool (Cao et al., 1995; Cao et al., 1998; Kettunen, 2003) or a DOM pool (Tian et al., 2010; Xu and Tian, 2012) has been assumed for methanogenesis. The production of ~~Acetate~~ acetate and H_2 ~~have~~ has been ~~added with their production~~ parameterized as a function of carbon mineralization (Van Bodegom et al., 2001; van Bodegom et al., 2000; Grant, 1998; Xu et al., 2015). It is not surprising that CH_4 production prediction is sensitive to simple substrate production (Kettunen, 2003; Weedon et al., 2013). While detailed SOM decomposition models include depolymerization to produce monomers under aerobic conditions (Riley et al., 2014), production and consumption of simple measurable substrates, such as acetate, H_2, formate, etc., are not explicitly represented under anaerobic conditions.

In addition to electron acceptors and substrates, SOM turnover is also sensitive to soil pH. Most methanogens grow over a relatively narrow pH range (6-8), while some adapt to acidic or basic environments (Garcia et al., 2000; Van Kessel and Russell, 1996; Wang et al., 1993; Sowers et al., 1984; Rivkina et al., 2007; Hao et al., 2012; Kotsyurbenko et al., 2004; Kotsyurbenko et al., 2007). Soil pH can change 1-2 logarithmic units in laboratory incubations (Xu et al., 2015; Roy Chowdhury et al., 2015; Peters and Conrad, 1996; Drake et al., 2015) and it can vary significantly through the soil profile and along topographic and vegetation gradients in the field (Cao et al., 1995; Van Bodegom et al., 2001; Lipson et al., 2013b). The pH feedback on methanogenesis could be up to 30% (Xu et al., 2015). ~~The pH response functions in LSMs are empirical and vary substantially (Xu et al., 2016b).~~ ~~Because of the large buffer capacity~~However, soil pH is often fixed in LSMs (Oleson et al., 2013; Tian et al., 2010). ~~But in reality, pH does change 1-2 logarithm units in laboratory incubations (Xu et al., 2015;Roy Chowdhury et al., 2015;Peters and Conrad, 1996;Drake et al., 2015) and in the field, where it can vary significantly through the soil profile and along topographic and vegetation gradients (Cao et al., 1995;Van Bodegom et al., 2001;Lipson et al., 2013b).~~ pH is calculated using soil acidity and soil buffer capacity (Van Bodegom et al., 2001) or as a function of acetate concentration (Xu et al., 2015). It is desirable to use a geochemical model to describe pH evolution mechanistically. The pH response functions (reaction rate adjustment factor as a function of pH) in LSMs are empirical and vary substantially (Xu et al., 2016b). Assessing the efficacy of these functions is needed to better represent pH impacts on carbon mineralization and methanogenesis.

Temperature is another critical factor controlling SOM turnover ~~is also sensitive to temperature~~to CO_2 and CH_4. The reported Q_{10} values for methanogen temperature response vary from 1.5 to 4 (Xu et al., 2016b). Methanogenesis has been widely observed to diminish when the temperature decreases toward 0 °C (Dunfield et al., 1993; Fey et al., 2004; Hoj et al., 2007; Sowers et al., 1984), predicting little CH_4 production from the surface layers of frozen Arctic soils. However, recent observations suggest that CH_4 emissions during the winter season account for ≥ 50 % of the annual emission in the Arctic (Zona et al., 2016). The cold season CH_4 production is among the most uncertain processes for predicting seasonal CH_4 cycle in northern wetlands (Xu et al., 2016a). The temperature response functions (reaction rate adjustment factor as a function of temperature) need to be assessed as well.

Overall, anaerobic SOM turnover is controlled by the hydrolysis of the macromolecules to produce simple substrates and the sequential microbial reduction of electron acceptors along the redox ladder. Because SOM turnover and CO_2 and CH_4 productions are sensitive to redox potential, pH, and temperature, it is desirable to simulate the redox and pH explicitly with geochemical models. With the accumulation of new data on metabolic intermediates, electron acceptors, greenhouse gases, and pH from incubations with Arctic soils at various temperatures (Drake et al., 2015; Herndon et al., 2015a; Herndon et al., 2015b; Yang et al., 2016; Mann et al., 2015), our objectives are to integrate these new data into geochemical models to (1) extend the CLM-CN decomposition cascade to include simple substrates such as sugars and organic acids and add Fe(III) reduction and methanogenesis processes, (2) account for gas, aqueous, and adsorbed phase speciation, (3) describe pH mechanistically, and (4) assess the existing temperature and pH response functions. Unlike previous LSMs, we simulate speciation of CO_2 and CH_4 in the gas, aqueous, and solid phases, and represent sugars, organic acids, Fe(II), Fe(III), Fe reducers, and methanogens, and account for both thermodynamic and kinetic control. Our results provide predictive understanding and mechanistic representations that can be ~~tested~~ incorporated in ~~other~~ LSMs, e.g., CLM-PFLOTRAN (Tang et al., 2016), to improve climate model predictions.

The carbon cycle involves coupled hydrological, geochemical, and biological processes interacting from molecular to global scales. The implicit empirical first order approach used in existing LSMs limits our understanding of the land atmosphere interaction and is a source of prediction uncertainty. To improve our understanding and reduce prediction uncertainty, we attempt to use relatively more explicit mechanistic representations developed in the reactive transport model literature (Tang et al., 2016). Even though explicit representation does not necessarily improve the match between the predictions and observations over well-tuned existing models immediately (e.g., Wieder et al. 2015; Steven et al. 2006), our approach provides a systematic means to incorporate on-going process-rich investigations to improve mechanistic representations in LSMs across scales. As a preliminary study, we constrain our scope to extending CLM-CN with minimum revision to describe anaerobic CO_2 and CH_4 production from several recent microcosm studies in this work. We discuss next steps briefly in the results and discussion section.

2 Materials and methods

We extend the CLM-CN decomposition cascade (Thornton and Rosenbloom, 2005) by adding reactions for hydrolysis to produce sugars, fermentation to produce organic acids and H_2 (Grant, 1998; Xu et al., 2015), Fe(III) reduction, and methanogenesis reactions (Tang et al., 2013c). We add the Windermere Humic Aqueous Model (WHAM) (Tipping, 1994) to simulate the pH buffer by SOM. Recent microcosm data (Herndon et al., 2015a; Roy Chowdhury et al., 2015) are used to assess these representations. While nitrogen (ammonium and nitrate) concentrations can affect carbon mineralization (Lavoie et al., 2011), we do not account for this effect because of a lack of nitrogen measurements from these experiments.

2.1 Soil incubation experiment data

The materials, experimental procedures and results for the microcosm tests were reported previously (Herndon et al., 2015a; Roy Chowdhury et al., 2015). Briefly, three soil cores were taken from center, ridge, and trough locations in a low-center polygon (a typical arctic geographic feature in the low lands with soils surround by ice wedges, see cited references for more information) in the wet tundra of the Barrow Environmental Observatory in Alaska. Soil samples from the organic and mineral horizons of the three cores were analyzed for gravimetric water content, pH, Fe(II), water-extractable organic carbon (WEOC), organic acids, and total organic carbon content (TOTC). For each horizon and location, about 15 g of homogenized wet soil was placed into a 60 ml sterile serum bottle, which was sealed and flushed with pure N_2 gas. The microcosms were incubated at -2, 4, and 8 °C for about 2 months to mimic thawing during the summer season at the site. The headspace CO_2 and CH_4 were sampled and analyzed by gas chromatography. Separate microcosms with 20 g of the homogenized soils were incubated to analyze for pH, Fe(II), water extractable organic carbon~~WEOC~~, and organic acids. Additional soil characterization is available elsewhere (Bockheim et al., 2001; Lipson et al., 2010; Lipson et al., 2013b).

2.2 Model developments

2.2.1 SOM decomposition

The SOM in the Arctic soils was characterized using high-resolution mass spectroscopy (Herndon et al., 2015a; Mann et al., 2015; Hodgkins et al., 2014). However, these characterizations were insufficient to partition SOM into many chemically distinct organic pools (Riley et al., 2014; Kögel-Knabner, 2002). Therefore, we extend the CLM-CN decomposition cascade to produce intermediate metabolites (Fig. 1). To limit the number of new pools, we lump reducing sugars, alcohols, etc. (Yang et al., 2016; Kotsyurbenko et al., 1993; Glissmann and Conrad, 2002; Tveit et al., 2015) into a LabileDOC pool, and the organic acids, such as formate, acetate, propionate, and butyrate, etc. (Herndon et al., 2015a; Kotsyurbenko et al., 1993; Peters and Conrad, 1996; Tveit et al., 2015) into an organic acid pool (Ac) (Xu et al., 2015; Grant, 1998). Assuming that the LabileDOC turns over in 20 h as the Lit1 pool in CLM-CN (Thornton and Rosenbloom, 2005) or glucose fermentation (Rittmann and McCarty, 2001), we split the original respiration factor into a direct and an indirect fraction, with the indirect fraction s_{labile} to produce LabileDOC, which respires through the anaerobic pathway (Fig. 1) to CO_2 or CH_4, and the direct respiration fraction (1- s_{labile}) respires directly to CO_2. We estimate s_{labile} by comparing the predictions with the observations in this work. The fermentation reaction is (Xu et al., 2015; Grant, 1998; van Bodegom and Scholten, 2001; Madigan, 2012)

$$C_6H_{12}O_6 + 4\ H_2O \Rightarrow 2\ CH_3COO^- + 2\ HCO_3^- + 4\ H^+ + 4\ H_2, \qquad \text{(R1)}$$

which lowers the pH and further respires $s_{labile}/3$ of SOM into CO_2.

2.2.2 Fe(III) reduction, methanogenesis, and biomass decay

Because Fe(III) reduction contributes 40-45 % of the ecosystem respiration in some Arctic sites (Lipson et al., 2013b) and NO_3^- and SO_4^{2-} concentrations are typically low in the experiments, we add Fe(III) reduction reactions to represent the reduction of alternative electron acceptors to O_2. We use the microbial reactions formed by combining electron donor (oxidation) half reactions, electron acceptor (reduction) half reactions, and cell synthesis reactions following bioenergetics (Rittmann and McCarty, 2001). Specifically, the Fe(III) reduction reactions are (Istok et al., 2010)

$$2.1\ H_2O + NH_4^+ + 150.2\ Fe^{3+} + 21.3\ CH_3COO^- \Rightarrow C_5H_7O_2N + 150.2\ Fe^{2+} + 167.4\ H^+ + 37.5\ HCO_3^-, \qquad \text{(R2)}$$

$5\ HCO^{3-} + NH_4^+ + 114.8\ Fe^{3+} + 57.4\ H_2 \Rightarrow C_5H_7O_2N + 114.8\ Fe^{2+} + 110.8\ H^+ + 13\ H_2O$, (R3)

where, $C_5H_7O_2N$ represents microbial (iron reducer) mass, and NH_4^+ is assumed not to be limiting (at 1 μM). These two reactions result in dissolution of ferric oxides, for example, $Fe(OH)_{3a}$, to release OH^- to increase pH. The rate is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_{\mathrm{max}} x \frac{k_{surf}}{k_{surf} + x/\mathrm{m}_{\mathrm{surf,avail}}} \frac{m_{\mathrm{D}}}{k_{\mathrm{D}} + m_{\mathrm{D}}} f(G), \qquad (1)$$

where k_{max} is the kinetic rate constant; x is concentration of biomass; $m_{\mathrm{surf,avail}}$ is the microbially-available surface sites taken as the $Fe(OH)_{3a}$ surface sites Hfo associated with H^+, i.e., $m_{\mathrm{surf,avail}} = m_{\mathrm{Hfo\_wOH}} + m_{\mathrm{Hfo\_sOH}}$ in moles per liter pore fluid; k_{surf} accounts for the impact of $x/\mathrm{m}_{\mathrm{surf,avail}}$, which represents the interaction of biomass with available Fe(III) sites on the surface; m_{D} and k_{D} are the concentration and half saturation of the electron donors (acetate or H_2); and $f(G)$ is a thermodynamic factor that goes to zero when the reaction is thermodynamically unfavourable (Jin and Roden, 2011).

The methanogenesis reactions are (Istok et al., 2010)

$1.5\ H^+ + 98.2\ H_2O + NH_4^+ + 103.7\ CH_3COO^- \Rightarrow C_5H_7O_2N + 101.2\ HCO_3^- + 101.2\ CH_4$, (R4)

$84.9\ H^+ + NH_4^+ + 85.9\ HCO_3^- + 333.5\ H_2 \Rightarrow C_5H_7O_2N + 255.6\ H_2O + 80.9\ CH_4$. (R5)

These two reactions consume protons to increase pH. The rate is

$$\frac{dx}{dt} = k_{max} x \frac{m_D}{k_D + m_D} f(G). \qquad (2)$$

We use one pool FeRB for the iron reducers and separate the methanogens into MeGA and MeGH pools for acetoclastic and hydrogenotrophic methanogens (Fig. 1). The biomass decay reaction for FeRB, MeGA, and MeGH is

$0.2\ C_5H_7O_2N \Rightarrow 0.1\ SOM1 + 0.2\ SOM2 + 0.25\ SOM3 + 0.45\ SOM4 + 0.1185\ NH_4^+ + \ldots$. (R6)

Like the SOM pools, the rate is first order.

In this model, iron reducers and methanogens interact in different ways under various conditions. When the electron donors (acetate and H_2) are abundant, iron reducers grow faster than methanogens when Fe(III) is not limiting (depending on the $Fe(OH)_{3a}$ surface sites and iron reducers population), i.e., iron reducers have a short doubling time than methanogens. When the electron donors are limiting, iron reducers are expected to outcompete methanogens, depending on the half saturation (substrate affinity) values. The model also accounts for the thermodynamics. However, it does not account for possible different responses to temperatures and pH for iron reducers and methanogens.

2.2.3 pH

The soil pH is typically buffered by carbonates, clay minerals, metal oxides, and organic matter (Tipping, 1994; Tang et al., 2013a). The Windermere Humic Aqueous Model (WHAM) is used to approximate SOM as humic acid and fulvic acid, with a number of monodentate and bidentate binding sites for protons, to describe the pH buffering due to SOM (Tipping, 1994). The surface complexation model for ferrihydrate is used to describe the sorption of carbonate and proton to metal oxides

(Dzombak and Morel, 1990). Additional aqueous speciation reactions are also included in the reaction database available as supplemental information (also publicly available at https://github.com/t6g/bgcs).

2.2.4 pH and temperature response functions

We use the CLM4Me pH response function (Riley et al., 2011; Meng et al., 2012)

$$log_{10} f(pH) = -0.2235pH^2 + 2.7727pH - 8.6 \quad (3)$$

and the CLM-CN temperature response function (Thornton and Rosenbloom, 2005; Lloyd and Taylor, 1994)

$$\ln f(T) = 308.56\left(\frac{1}{71.02} - \frac{1}{T-227.13}\right). \quad (4)$$

The pH response functions used in DLEM (Tian et al., 2010) and TEM (Raich et al., 1991) and a few other models (Cao et al., 1995; Xu et al., 2015), as described in Appendix 1, and the CENTURY temperature response function, the Q_{10} equation, Arrhenius equation, and Ratkowsky equation, which are described in Appendix 2, are used for comparison.

2.3 Implementation, parameterization, and initialization

2.3.1 Implementation

To calculate the speciation of CO_2, CH_4, H_2, Fe, etc. among gas, aqueous, and solid phases under various temperature, pH, and pressure conditions and explicitly describe pH and redox buffer, we employ the widely used extensively tested geochemical code PHREEQC (Parkhurst and Appelo, 2013) to synthesize the experimental data to develop and parameterize mechanistic representations. The implementation of CLM-CN reactions in a geochemical code is detailed elsewhere (Tang et al., 2016). Guidelines for implementation of the microbial reactions, surface complexation, WHAM, etc., in PHREEQC are available in the user manual (Parkhurst and Appelo, 2013).

2.3.2 Parameterization

The stoichiometric and kinetic rate parameters for the CLM-CN reaction network are specified in Fig. 1. The indirect respiration faction s_{labile} is highly uncertain. We start with $s_{labile} = 0.4$, and check the sensitivity with $s_{labile} = 0.2$ and 0.6. For the decay of biomass, and growth of methanogens, we use the general parameter values in the literature (Rittmann and McCarty, 2001). The half saturation k_D and k_{surf} values are taken from published literature (Jin and Roden, 2011). The parameter values and the references are listed in Table 1.

2.3.3 Initialization

The basic experimental parameters are summarized in Table 2 and Table S1. The amount of water, headspace volume, and temperature are set at the experimental parameter values. The initial pH, organic acids (combined formate, acetate, propionate, and butyrate from Table S1 to Table 2) and Fe(II) concentration are specified as measured.

The measured total organic carbon~~TOTC~~ includes seven carbon pools in the CLM-CN decomposition cascade, as well as simple substrates (such as sugars, alcohols, organic acids), and biomass for FeRB, MeGA, MeGH, and other microbes. Because of the lack of reliable methods in partitioning the measured ~~TOTC~~ total organic carbon into these pools, we combine the Lit1 pool with LabileDOC, Lit2 with SOM1, and Lit3 with SOM2 pools as they have identical turnover times (Fig. 1). That is, we will split the initial ~~TOTC~~ total organic carbon (minus simple substrates) into LabileDOC, SOM1, SOM2, SOM3, SOM4, FeRB, MeGA, and MeGH pools, with fraction $f_{\cancel{\mathrm{l}}\mathrm{LabileDOC}}$, $f_{\cancel{\mathrm{som}}\mathrm{SOM1}}$, $f_{\cancel{\mathrm{som}}\mathrm{SOM2}}$, $f_{\cancel{\mathrm{som}}\mathrm{SOM3}}$, $f_{\mathrm{FeRB}\cancel{\mathrm{ferb}}}$, $f_{\mathrm{MeGA}\cancel{\mathrm{mega}}}$, and $f_{\mathrm{MeGH}\cancel{\mathrm{megh}}}$ (the rest is f_{SOM4}, i.e. $f_{\mathrm{SOM4}} = 1 - f_{\mathrm{LabileDOC}} - f_{\mathrm{SOM1}} - \ldots$). Because the experiments lasted for only 2 months, and predictions are often not very sensitive to the initial biomass (Tang et al., 2013b; Tang et al., 2013c; Xu et al., 2015; Jin and Roden, 2011), the predictions are expected to be sensitive to ~~$f_{\mathrm{labileDOC}}$~~$f_{\mathrm{LabileDOC}}$, $f_{\mathrm{SOM}\cancel{\mathrm{som}}1}$, and $f_{\mathrm{SOM}\cancel{\mathrm{som}}2}$ under the experimental conditions (as the turnover time for SOM3 and SOM4 are 2 and 27 y, respectively, Fig. 1). With a turnover (mean residence) time of 0.2-0.5, 6-9, and >125 years for the fast, slow, and passive pools, respectively, less than 5 % was estimated for the fast pool for 121 individual samples from 23 high-latitude ecosystems located across the northern circumpolar permafrost zone (Schädel et al., 2014). Based on incubation tests with Siberian soils for over 1200 d, the initial labile carbon pools were estimated to comprise 2.22 ± 1.19 and 0.64 ± 0.28 % of the ~~TOTC~~ total organic carbon with turnover times of 0.26±1.56 and 0.21±1.58 y under aerobic and anaerobic conditions, respectively (Knoblauch et al., 2013). We set ~~$f_{\mathrm{labileDOC}}$~~ $f_{\mathrm{LabileDOC}} = 0.0005$, $f_{\mathrm{SOM}\cancel{\mathrm{som}}1} = 0.01$, $f_{\mathrm{SOM}\cancel{\mathrm{som}}2} = 0.02$, $f_{\mathrm{SOM}\cancel{\mathrm{som}}3} = 0.1$, $f_{\mathrm{bio}} = 10^{-6}$~~-~~, $f_{\mathrm{MeGA}\cancel{\mathrm{mega}}} = f_{\mathrm{MeGH}\cancel{\mathrm{megh}}} = f_{\mathrm{bio}}$, and, ~~0.5~~$f_{\mathrm{ferb}} = 2\ f_{\mathrm{bio}}$~~$10^{-6}$ -~~[$f_{\mathrm{bio}} = 10^{-6}$ approximating with *E. coli* with a wet weight 10^{-12} g, 70 % water, and 50 % dry weight carbon (Madigan, 2012), each microbial cell contains ~1.25×10^{-14} mole C, this means ~10^{8} cells in 1 mole ~~TOTC~~total organic carbon, which roughly approximates the range of reported values (Roy Chowdhury et al., 2015)].

Bioavailable ferric oxides are assumed to be in the form of $Fe(OH)_{3a}$, with initial concentration as a fraction f_{fe3} of the dry soil mass. Depending on the season and the age of the drained thawed lake basins, HCl extractable Fe(III) is reported to range between 100 and 700 g Fe(III) m^{-3} in the Barrow soils in a 24 cm soil profile (Lipson et al., 2013a). Using a weighted average of bulk density of 0.26, this translates to 0.2 to 1 % g Fe(III)/g dry soil mass. While bioavailable Fe(III) in soils is not well defined (e.g., Hyacinthe et al. 2006; Poulton and Canfield 2005), ~~We~~ we start with ~~f_{fe3}~~ $f_{\mathrm{Fe3}} = 0.005$ and evaluate the impact with a range of values. Fe(III) reduction dissolves $Fe(OH)_{3a}$ and releases adsorbed protons on the mineral surface, which is described by the surface complexation model (Dzombak and Morel, 1990). The organic content for WHAM is set at ~~TOTC~~total organic carbon. The initial total inorganic carbon (TIC) in the solution is assumed to be in equilibrium with an atmosphere of CO_2 at 400 ppm and 1 atm. The headspace gas starts with N_2 at 1 atm. These parameters are summarized in Table S2. Additional specifics are available in the scripts to produce input files. The reaction database [extended from (Tang et al., 2013b; Tang et al., 2013c)], the python scripts to create input files for various locations, temperatures, and other options (e.g., temperature and pH response functions) and scripts used to make the figures are provided as supplemental information.

3 Results and discussion

3.1 Experimental observations

The experimental results of anoxic soil incubation experiments were published elsewhere (Herndon et al., 2015a; Roy Chowdhury et al., 2015), so we briefly describe the original observed headspace CO_2 and CH_4 concentration, soil Fe(II) and organic acids concentration, and pH (Fig. 2). The variations in the overall observations appear to be better explained by the differences ~~separate~~ between the soil horizons (organic vs. mineral soils) ~~rather~~ than among the microtopographic locations (center, ridge, and trough) of ice-wedge polygons. Up to 20 % CO_2 was observed in the headspace by the end of the 2-month incubations, with higher concentrations in the organic soils than in the mineral soils (Fig. 2a1-3 vs. 4-6). This can be attributed to the higher organic content of the organic soils compared to that of the mineral soils (Table 2, Table S1).

CO_2 in the headspace increased rapidly in the beginning and then the increase slowed (Fig. 2). The initial rapid increase can be attributed to fast decomposition of the easily degradable substrates such as sugars, alcohols, etc. (Yang et al., 2016; Fey and Conrad, 2003; Glissmann and Conrad, 2002; Kotsyurbenko et al., 1993). As the easily degradable substrates were exhausted, the CO_2 production rate decreased. These observations are similar to those for the anaerobic incubations with soils from a trough location in a high center polygon at the same site (Yang et al., 2016) and deep Siberian permafrost soils (Knoblauch et al., 2013). However, CO_2 continued to increase well beyond 2 months in both these previous studies , and the CO_2 production rates stabilized, probably reaching a rate limited by the slow rate of hydrolysis in the Siberian soil microcosms. These observations are different from the observed CO_2 level off in the current microcosms (Fig. 2a2, a4, a5).

CH_4 in the headspace increased slowly at the beginning and then accelerated (Fig. 2b1-5), except the center organic soils. CH_4 accumulation lagged behind CO_2 for about 10 d in most of the microcosms and by a few days for the center organic soil microcosms at 4 and 8 °C. These lag times are shorter than those observed in microcosms with deep Siberian permafrost soils (average 960 ± 300 d) (Knoblauch et al., 2013). This is probably because of the initial abundance of substrates such as organic acids in the Barrow soils (Fig. 2c1-6). In addition, the shallow Barrow soils experience freezing and thawing, and so does microbial activity every year, while the deep Siberian permafrost soils were frozen for extended periods; as a result, the amount of initial biomass in the shallow Barrow soils is probably much higher than that in the deep Siberian soils.

Organic acids generally accumulated at the beginning, decreased as CH_4 concentration increased, and exhausted in the mineral soil microcosms (Fig. 2c1-6). In contrast, organic acids were not exhausted in the center organic soil microcosms (Fig. 2c6). In comparison with similar tests with soils from the high center polygon trough, organic acids accumulated for over 5 months in the organic soils and were not exhausted in the mineral soils (Yang et al., 2016). The accumulation and disappearance of organic acids have been widely observed in the literature (van Bodegom and Stams, 1999; Fey et al., 2004;

Glissmann and Conrad, 2002; Jerman et al., 2009; Kotsyurbenko et al., 1993; Lu et al., 2015; Peters and Conrad, 1996; Yao and Conrad, 1999).

Fe(II) concentrations increased and levelled off (Fig. 2d1-6), with similar trends for pH (Fig. 2e1-6). The ~~pH~~ increase in pH concurred with Fe(III) reduction, which released hydroxides from $Fe(OH)_{3a}$ dissolution. The pH increase is in contrast to the observed pH decrease when Fe(III) reduction was absent (Xu et al., 2015). While Fe(III) reduction was reported to inhibit methanogenesis through direct inhibition (van Bodegom et al., 2004) or substrate competition (Miller et al., 2015; Reiche et al., 2008), the impact appears less significant than expected in these incubations, as well as incubations with the high center polygon trough soils (Yang et al., 2016). This is consistent with the observation that methane production initiated in the presence of oxidants (Roy et al., 1997). In addition, Fe(III) reduction can both inhibit and promote methanogenesis (Zhuang et al., 2015). In the Barrow soils, the initial abundance of organic acids probably mitigates the competition between Fe(III) reducing and methanogenic populations, decreasing the lag time between CH_4 and CO_2 accumulation.

Substantial microbial activity was observed at -2 °C, which is above the soil water freezing point due to osmotic and matric potentials. These incubations led to an increase in CO_2 (Fig. 2a1-6), ~~acetate~~ organic acids (Fig. 2c1-6), Fe(II) (Fig. 2d1-6), and pH (Fig. 2e1-6). CH_4 concentrations were low but detectable in the headspace at -2 °C. The lag time between CH_4 and CO_2 increases with decreasing temperature, which was widely observed in the literature as well (Fey and Conrad, 2003; Hoj et al., 2007; Jerman et al., 2009; van Bodegom and Scholten, 2001; Fey et al., 2004; Kotsyurbenko et al., 1993; Lu et al., 2015). The transition from -2 to 4 and 8 °C appears to be gradual except for the center organic soils, where CH_4 increases were drastic from -2 to 4 °C (Fig.2a1 vs. b1). The observed overall temperature responses are diverse, as manifested by Q_{10} values from 1.6 to 22 (Roy Chowdhury et al., 2015).

3.2 Modeling results

3.2.1 Overall

With the same model parameter values given in Table 1 and Table S2 and different experimental parameter values listed in Table 2, the model roughly predicts the observed trends for different soils at the three temperatures (Fig. 2): CO_2 and CH_4 accumulate in the headspace; CO_2 accumulation slows down while CH_4 speeds up at later times; CH_4 lags behind CO_2; organic acids accumulate and then decrease; Fe(II) accumulates and levels off; pH increases and levels off; and carbon mineralization and methanogenesis rates increase with temperature.

While the model predicts little CO_2 and CH_4 in the headspace at -2 °C, which is similar to what was observed, it predicts little change in Fe(II) and pH as well, which is not consistent with the observations. To improve the prediction at -2 °C, which can be important (Zona et al., 2016; Xu et al., 2016a), it is necessary to understand why little CO_2 or CH_4 was observed to occur with Fe(III) reduction, which was indicated by the increase of Fe(II) and pH.

The same model parameter values describe the observed differences in the mineral soils better than in the organic soils. For the mineral soils, the model overpredicts the increasing trend for CO_2 in the headspace at late times because the observations levelled off (Fig. 2a1-3). The initial rapid CO_2 increases lasted for over 2 months in the 3-year incubations with Siberian permafrost soils under 4 °C and anaerobic conditions (Knoblauch et al., 2013). In these long-term tests, CO_2 increased rapidly at the beginning and the rate stabilized as the carbon release became limited likely by hydrolysis of polymers. The observed sustained CO_2 accumulation in these closed microcosms indicates that the observed trends in Fig. 2a1-6 at later times are probably uncertain. Except for these mismatches, the model predictions generally agree with the observations for the mineral soils reasonably well.

In contrast, the predictions do not agree as well with the observations for the organic soils. For the trough organic soils, the model underpredicts CO_2 in the headspace (Fig. 2a4) but describes the rest of the observations reasonably well. In addition to CO_2 (Fig. 2a5), the model underpredicts Fe(II) and pH increase in the ridge organic soils (Fig 2d5, e5). The prediction of the center organic soils differs from the observations the most (last column in Fig. 2). These mismatches might be explained by model biases in initial Fe(III) content, LabileDOC, and biomasses.

3.2.2 Fe(III) reduction

Agreement between predictions and observations for the Fe(II) and pH increase can be improved for the ridge and center organic soils by increasing the Fe(III) content from $f_{\mathrm{Fe3}} = 0.005$ to 0.01 and 0.02 (Fig. 2d5-6, e5-6). This also increases the predicted CO_2 and CH_4 for the center organic soils (Fig. 2a6, b6) because of the predicted pH increase (Fig. 2e6), which increases the reaction rates as the pH response function increases when the calculated pH increases toward an optimal pH of 6.2 in Eq. (3). For the ridge organic soils, $f_{\mathrm{Fe3}} = 0.01$ increases the predicted CH_4 like the center organic soils, but $f_{\mathrm{Fe3}} = 0.02$ decreases CH_4 prediction because of the competition between methanogens and iron reducers and limited availability of substrates (Fig. 2b5). This provides an explanation as to why Fe(III) reduction can both suppress and promote methanogenesis (rather than strict thermodynamic control, e.g., Bethke et al., 2011; direct inhibition, e.g., van Bodegom et al., 2004; or indirect inhibition through substrate competition, e.g., Mill et al., 2015, Reiche et al. 2008).

As the bioavailable Fe(III) in the organic soils is reported to range from 0.2 to 1 % of dry soil mass (Lipson et al., 2013a), the short-term tests are not expected to be Fe(III) limited for the mineral soils. Increasing bioavailable Fe(III) makes the model overpredict Fe(II) and pH increases at later times for the mineral soils (Fig. 2d1-5, e1-4), and Fe(III) reduction and methanogenesis at later times are predicted to be limited by organic substrate availability at 4 and 8 °C (Fig. 2b1-4). The latter is consistent with the observed very low organic acids concentrations at the end (Fig. 2c1-5). As a result, the model underpredicts CH_4 accumulation, indicating the current parameterizations, in particular the half-saturation and growth rate constants, may over-predict the ability of iron reducing bacteria to outcompete methanogens.

3.2.3 CO_2 distribution among gas, aqueous, and adsorbed phases

While increasing Fe(III) slightly increases the predicted CO_2 for ridge mineral soils (Fig. 2a2), it decreases the predicted CO_2 in the headspace for trough and center mineral soils (Fig. 2a1 and a3). This is because CO_2 solubility is predicted to increase significantly as pH increases, resulting in the dissolution of CO_2 from the headspace into the aqueous phase (Fig. S1). To examine this impact, we conduct numerical simulations with a 45 mL headspace with an initial 1 atm N_2 gas and 10 mL solution with 10 mM total inorganic carbon at various temperature and pH values. CO_2(g) and CO_2(aq) or carbonic acid dominate at a pH lower than 5 (Fig. 3). As the pH increases above the carbonic acid pKa (around 6.3 at standard condition), CO_2(g) in the headspace and $CO_{2(aq)}$ ~~in the aqueous phase~~ decrease as HCO_3^- becomes dominant in the aqueous phase, and the gas-phase fraction decreases dramatically. The gas-phase fraction also decreases with decreasing temperatures (Fig. 3).

In addition, CO_2 was reported to adsorb to surface sites (Appelo et al., 2002; van Geen et al., 1994; Villalobos and Leckie, 2000). With the surface complexation reactions between $Fe(OH)_{3a}$ and carbonate species, we add 1 mmole $Fe(OH)_{3a}$ (about the mean values in Fig. 2 for the case f_{Fe3} = 0.02) to the abovementioned numerical experiments. The calculations show that the adsorption phase can dominate at low pH (Fig. S2), with the total amount dependent on the abundance of surface sites. For the high-temperature high-Fe(III) initial content cases in Fig. 2, adding CO_2 sorption reactions provides a substantial buffer against the early increase in CO_2 in the headspace (Fig. S3). As the $Fe(OH)_{3a}$ is reduced and dissolved, the adsorbed CO_2 is predicted to be released, contributing to an increase in headspace CO_2 increase later on.

In addition to pressure, these calculations suggest the need to appropriately account for pH and its impact on the gas, aqueous, and adsorbed phases CO_2 partition when we use headspace concentration measurements from anaerobic incubations to estimate CO_2 emission. Otherwise, substantial uncertainties can be introduced. A geochemical model with accurate thermodynamic data and accounting for CO_2 sorption can be useful in accurately quantifying CO_2 production in these closed microcosms.

3.2.4 Initial CO_2 accumulation in the organic soil microcosms

The model underpredicts the early CO_2 increase in the headspace for the organic soil microcosms (Fig. 2a4-6), which is mostly apparent in the center organic soil microcosms. The reason is that the organic soil microcosms contain more labile organic carbon than the mineral soil microcosms, as evidenced by water extractable organic carbon~~WEOC~~ (Table 2). In particular, the center organic soil microcosms contain about half ~~the amount of TOTC~~ total organic carbon of the other microcosms, double the water volume, and three to five times water extractable carbon~~WEOC~~ (Table ~~1~~2). As a result, it produces the most CO_2 and CH_4 and has a very short lag time between CH_4 and CO_2. If we increase the initial LabileDOC content f~~$_{\text{l}}$~~$_{\text{LabileDOC}}$ from 0.0005, as shown in Fig. 2, to 0.01, and 0.02 for the organic soil microcosms, the underprediction of the early CO_2 increase in the headspace are more or less mitigated~~model predicts an initial rapid CO_2 increase in the headspace that is comparable to that observed for trough and ridge microcosms but still less than that for the center organic soil microcosms~~ (Fig. 4).

The predicted rapid initial CO_2 increase is due to the fast fermentation reactions (Fig. S4a1-6, e1-6). The predicted steep transition in CO_2 concentration increases appears reasonable for the center and trough soil microcosms, but less so for the ridge soil microcosms. In addition to the 20 h and 14 d turnover time differences, fermentation reactions decrease the pH, further inhibit the predicted SOM1 decomposition reactions, Fe(III) reduction, and methanogenesis, making the predicted transition steeper. The fast fermentation is consistent with the observed rapid disappearance of glucose and increase of CO_2 after glucose addition in similar experiments with soils from a high center polygon trough from the same site (Yang et al., 2016). However, the observed decrease of natural free reducing sugars is gradual, with about one-third of the original reducing sugars left over after 150 d of incubations. Along with the predicted rapid initial LabileDOC decrease and CO_2 increase, the model predicts a rapid initial increase in organic acids, which is close to the observations for the center soil microcosms but much greater than the observations for the trough and ridge soil microcosms. The latter indicates that the ratio of organic acids to CO_2 of 2:1 from the fermentation reaction (R1) may not be accurately representative of the experiments.

Detailed measurements~~ of organic acids~~ showed a rapid initial increase and then a quick decrease of organic acids in the mineral soil microcosms and a gradual increase and slow decrease in the organic soil microcosms from a trough location in ~~the~~ a high center polygon ~~trough near the site~~ in the first 144 d anaerobic incubations (Yang et al., 2016). The rise and fall were fast in both the mineral and organic soil microcosms for ethanol, and were generally more gradual for organic acids than for ethanol (Yang et al., 2016). To explain the various observations for the organic soil microcosms and for accurate predictions, the diversity of the hydrolysis products (Feng and Simpson, 2008), and the subsequent pathways (Tveit et al., 2015) may need to be accounted for. Additional detailed data are needed to support increasingly mechanistic models, e.g., with reducing sugars to represent less rapid fermentation, and additional specific organic acids such as propionate and butyrate to better describe diverse observations in the incubations.

3.2.5 Carbon mineralization

Less than ~~about~~ 1 % of the total initial carbon turned over to CO_2 and CH_4 in about 2 months, which is attributed mostly to decomposition of labile SOM (SOM1), LabileDOC, and organic acids (Fig. S4). Few changes are predicted in the slow pools (SOM3, and SOM4, not shown) even though they comprise a large ~~amount~~ portion of the soil ~~of~~ carbon pool. The small amount of respired carbon~~ turnover~~ is similar to the incubation tests conducted with Siberian permafrost soils under 4 °C, which was estimated to be 3.1 % and 0.55 % under aerobic and anaerobic conditions for 1200 d (Knoblauch et al., 2013), the

1-year aerobic incubations tests (Feng and Simpson, 2008), and the incubations from a wide range of Arctic soils (Schädel et al., 2014). All of these results suggest that the hydrolysis of macromolecular organics by extracellular enzymes ~~is~~ could be a~~the~~ rate-limiting step at late times. To predict the long-term vulnerability of the organic carbons, it is important to understand and describe the hydrolysis of macromolecular components in SOM.

3.2.6 CH_4 accumulation

Besides Fe(III) reduction, the predicted CH_4 production is dependent on the substrate production. With $s_{\text{labile}} = 0.2$, the model generally predicts less CH_4 and more CO_2 than the case with $s_{\text{labile}} = 0.4$ because less SOM is assumed to respire through ~~(or produce substrate for)~~ the anaerobic pathway in the $s_{\text{labile}} = 0.2$ case (Fig. S5). With increased $s_{\text{labile}} = 0.6$, the model predict more CH_4 and less CO_2. The impact on the mineral soils is generally more pronounced than the organic soils because the former is more substrate limiting than the latter. Unlike CO_2, CH_4 solubility and adsorption are much lower. Gas-phase CH_4 in the headspace dominates over aqueous and adsorbed phases. The model predicts the general exponential increase trend with a lag time behind CO_2 (Fig. 2). However, the prediction is sensitive to Fe(III) reduction, pH, temperature (Fig. 2), and labile substrates (Fig. 4). The model substantially underpredicts early fast CH_4 production for the center organic soil microcosms (Fig. 4b3). While the cell count for the center organic soils is not available for day 0, the data did show that the center organic soils had the highest amount of biomass after 100 d incubations (Roy Chowdhury et al., 2015)~~, indicating possible high initial abundance~~. The disagreement between the predictions and the observations can be mitigated by increasing the initial biomass f_{bio} from 10^{-6} to 10^{-5} and 2×10^{-5} for the center organic soil microcosms (Fig. 5). With increased initial biomass, Fe(III) reduction and methanogenesis are predicted to speed up the recovery of the initial pH drop caused by organic acids accumulation so that the model predicts a fast CH_4 increase that is comparable to the observed. However, the model overpredicts the CH_4 increase at late time~~s~~, indicating alternative inhibition mechanisms rather than substrate limitation on methanogenesis at late time~~s~~ or additional CH_4 consumption such as anaerobic oxidation (Caldwell et al., 2008; Smemo and Yavitt, 2011).

3.2.7 pH

With the complexation reactions involving proton or hydroxide anion with carbonate species, ferrihydrite surface, and SOM, the geochemical model describes the observed pH evolution reasonably well (Fig. 2). The initial pH was lower in the mineral soils than in the organic soils (Fig. 2), probably because of less buffering capacity due to less organic matter in the mineral soils and/or more reducing condition in the organic soils as reduction reactions typically consume protons. Because the ridge mineral soils have the lowest initial pH, the CLM4Me pH factor is the lowest (Table S1), contributing to the underprediction of CH_4 (Fig. 2b2). With high organic content, the organic matter dominates the aqueous geochemistry, and the predicted pH is sensitive to the surface sites specified for WHAM. If the specified WHAM organic matter is reduced by 25 %, then the pH buffering capacity is decreased and the predicted pH increases substantially (Fig. S6e1-6) even though the predicted changes in organic acids and Fe(II) are small. For the trough soils, the predicted pH surpasses the optimal of 6.2, and f(pH) (Eq. 3) decreases (Fig. S6e1, e4). As a result, predicted CO_2 and CH_4 are decreased. The pH impact becomes complex around the optimal pH. If we increase the specified WHAM organic matter by 25 %, the predicted pH is lower due to larger pH buffering and the reaction rates are generally smaller. Setting the WHAM sites at measured total organic carbon~~TOTC~~ works reasonably well for the experiments with the CLM4Me pH response function.

Comparing the CLM4Me pH response function with these used in TEM and DLEM, all three response functions show that the reaction rates are sensitive to pH (Fig. 6), which is expected to influence the predictions for these incubation tests as the pH increases from about 5.5 to 7. In this range, CLM4Me and DLEM have a similar slope, but the latter has a greater rate reduction effect. While CLM4Me and TEM have a similar rate reduction effect, CLM4Me has a steeper curve than TEM. These differences translate to substantial differences in model predictions (Fig. S7). All calculated f(pH) values increase during the tests (Fig. S7f1-f6). As the f(pH) calculated by DLEM is the lowest, the predicted changes are the smallest. The f(pH) calculated by TEM is slightly greater than CLM4Me at the beginning and is the opposite at late times (Fig. 6). As a result, TEM generally predicts slightly faster evolution than CLM4Me as the reaction rates at the late time are limited by substrates rather than pH. While the pH ranges from 3.3 to 8.6 in the Arctic soils (Schädel et al., 2014), the range and the variability of the data are limited in the evaluation of these pH response functions. Nevertheless, model predictions are sensitive to pH response functions; the microbes are likely adapted to the site pH conditions such that the response functions are expected to vary among sites and functional groups. Therefore, pH response function can be an important source of prediction uncertainty.

3.2.8 Temperature response

Temperature effects on reactions between inorganic aqueous species, and the aqueous and gas species, are taken into account in the established reaction database. The temperature impact on surface complexation reactions with ferric hydrous oxides, and with SOM in WHAM is not quantified, which can be a potential source of uncertainty. LSMs generally use empirical (e.g., CLM-CN, CENTURY), Q_{10}, or the Arrhenius equations. The CLM-CN temperature response function is compared with the CENTURY, Q_{10} equation, Arrhenius equation, and Ratkowsky equation in Fig. 7 and Fig. S8. All of these temperature response functions describe increasing rate with increasing temperature. When the temperature response functions $f(T)$ are plotted in arithmetical scale, the shapes are similar except for CENTURY, which approaches 1 when the temperature increases above 20 °C; CLM-CN is close to Q_{10} with $Q_{10} = 2.5$, the Arrhenius equation with $E_a = 60$ kJ mol^{-1} and the Ratkowsky equation with $T_m = 260$ K. When $f(T)$ is plotted in log scale (Fig. 7), Q_{10} and Arrhenius equations are approximately linear while the rest have a similar shape; CLM-CN appears close to Ratkowsky equation with $T_m = 260$ K. At our temperatures -2, 4, and 8 °C, CLM-CN is very close to CENTURY, $Q_{10} = 2.5$, $E_a = 60$ kJ mol^{-1}, and $T_m = 260$ K (Fig. 7, Fig. S8). Despite their closeness, the predictions can be different for the different response functions (Fig. S9, Fig. S10), reflecting the sensitivity of the temperature effect on the biogeochemical reaction rates. The difference is amplified when different Q_{10}, E_a, or T_m is used (not shown), introducing potentially large uncertainty in model predictions. Because the temperature response functions are expected to vary for different micro-organisms, extra-cellular vs. intra-cellular enzymes, and geochemical reactions in the soil environment, improved quantification is needed.

3.2.9 Predicted impact of headspace gas accumulation

The accumulation of gases in the headspace may impact the soil carbon mineralization and methanogenesis. Knoblauch et al. (2013) and Yang et al. (2016) flushed the headspace of the microcosms while Roy Chowdhury et al. (2015) and Herndon et al. (2015) did not. The field conditions are likely somewhere between an open system and a closed system because neither the atmospheric pressure nor the hydrostatic pressure is constant, and the produced CO_2 and CH_4 are not always free to release to the atmosphere. To assess the impact of CO_2 accumulation in the headspace on the soil carbon mineralization and methanogenesis, we conduct numerical experiments with 10 and 100 times the headspace volume of the experimental values. With increased headspace volume, the headspace and aqueous CO_2 concentrations are predicted to decrease (Fig. S11 f1-6, g1-6), and the pH increase is predicted to slow down. As a result, the biogeochemical reaction rates are generally slower (Fig. S11e1-6). Eventually, the predicted total CO_2 and CH_4 production generally decrease with lower headspace CO_2 concentration (Fig. S11a1-6,b1-6). However, the impact on CO_2 production is very small for the organic soils in the trough and ridge location, and the CO_2 production is predicted to increase with decrease in headspace CO_2 concentration for the organic center soils. Because of the complicated nonlinear relationships in the biogeochemical processes, the impact of headspace gas accumulation on carbon mineralization and methanogenesis is not linear. While it is debatable that which experimental conditions (flush the headspace or not) reflect the field conditions, biogeochemical models like ours provide a mechanistic method to account for this impact by using boundary conditions that reflect the reality. Additional targeted experiments and mechanistic models are necessary to better understand the impact under different conditions, and develop representations that reflect field conditions.

4 Summary and conclusion

Soil organic carbon turnover and CO_2 and CH_4 production are sensitive to redox potential and pH. However, land surface models typically do not explicitly simulate the redox or pH, particularly in the aqueous phase, introducing uncertainty in greenhouse gas predictions. To account for the impact of availability of electron acceptors other than O_2 on soil organic matter (SOM) decomposition and methanogenesis, we extend the CLM-CN decomposition cascade to link complex polymers with simple substrates and add Fe(III) reduction and methanogenesis reactions. Because pH was observed to change substantially in the laboratory incubation tests and in the field and is a sensitive environmental variable for biogeochemical processes, we use the Windermere Humic Aqueous Model (WHAM) to simulate pH buffering by SOM. To account for the speciation of CO_2 among gas, aqueous, and solid (adsorbed) phases under varying pH, temperature, and pressure values, and the impact on typically measured headspace concentration, we use a geochemical model and an established reaction database to describe observations in recent anaerobic microcosms. Our results demonstrate the efficacy of using geochemical models to mechanistically represent the soil biogeochemical processes for Earth system models.

Together with the speciation reactions from the established geochemical database and surface complexation reactions for ferric hydrous oxides, WHAM enables us to approximately buffer an initial pH drop due to organic acid accumulation caused by fermentation and then a pH increase due to Fe(III) reduction and methanogenesis. The single input parameter for WHAM is total organic carbon content, which is available in any SOM decomposition model. Therefore, adding WHAM does not necessitate any additional characterization. However, the temperature effects on surface complexation reactions with ferric hydrous oxides and organic matter may need to be further quantified.

The equilibrium geochemical speciation reactions predict a substantial increase in CO_2 solubility as the pH increases above 6.3 because the aqueous dominant species shifts from CO_2 to HCO_3^-. Adding CO_2 adsorption to surface sites of metal oxides further increases predicted solubility at low pH. Without taking into consideration of speciation, and pH, temperature and pressure impact with a geochemical model, the carbon mineralization rate can be substantially underestimated from anaerobic microcosms based on headspace CO_2 measurements.

Because ~~different~~ various microbes respond to the temperature and pH change differently, it is challenging to describe observed diverse responses with any single one of the existing response functions. As the microbes adapt to the low temperature and pH conditions in the Arctic, the optimal growth temperature and pH value ~~may need to be adjusted~~ in these response functions may need to be adjusted to account for biological acclimation.

We demonstrate that a geochemical model can mechanistically predict pH evolution and accounts for the impact of pH on biogeochemical reactions, which ~~enhancing~~ enhances our understanding of and ability to quantify the experimental observations. Because pH is an important environmental variable in the ecosystems and land surface models either specify a fixed pH or use simple empirical equations, a geochemical model has the potential to improve model predictability for greenhouse emissions by mechanistically representing the soil biogeochemical processes.

Another following up task can be assessing this new framework of anaerobic SOM decomposition in field studies with CLM-PFLOTRAN. This can be done incrementally, i.e., add/remove reactions one at a time without source code modifications. CLM-PFLOTRAN currently uses CLM4.5 vertical resolved grid. The resolution can be adjusted, possibly in three dimensions, to reflect the heterogeneity of any structural soil column to account for the limitation of electron donors and electron acceptors at individual locations. As we gradually implement more and more processes, such as gas and aqueous transport through soils and aerenchyma, explicitly representing microbial processes for carbon decomposition, we hope the new framework will be useful for future investigation and model developments.

Code availability

PHREEQC is publically available at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.

Data availability

The experimental data, scripts to produce the PHREEQC input files, and plot the figures are archived at https://github.com/t6g/bgcs .

Appendix A Additional pH response functions

With pH_{min}, pH_{opt}, and pH_{max} of 4, 7 and 10 with no microbial activity at pH below pH_{min} or above pH_{max}, the pH response function used in DLEM is (Tian et al., 2010)

$$f(pH) = \frac{1.02}{1.02+10^6 \exp(-2.5pH)}, \tag{A1}$$

for pH < 7; otherwise,

$$f(pH) = \frac{1.02}{1.02+10^6 \exp(-2.5(14-pH))}. \tag{A2}$$

TEM uses a bell-shaped function (Cao et al., 1995;Xu et al., 2015;Raich et al., 1991)

$$f(pH) = \frac{(pH-pH_{min})(pH-pH_{max})}{(pH-pH_{min})(pH-pH_{max})-(pH-pH_{opt})pH_{opt}}, \tag{A3}$$

with pH_{min}, pH_{opt}, and pH_{max} = 5.5, 7.5, and 9, respectively (Cao et al., 1995). Considering the typical acidic conditions in the Arctic and wetlands, we use the DLEM parameter values (Tian et al., 2010) as substantial CH_4 was observed in the incubation tests below pH 5.5 (Roy Chowdhury et al., 2015).

Appendix 2 Additional temperature response functions

The Q_{10} method is the most common temperature response function used in LSMs (Xu et al., 2016b;Berrittella and Van Huissteden, 2009, 2011;Walter and Heimann, 2000;Zhuang et al., 2004;Riley et al., 2011;Oleson et al., 2013). It is

$$f(T) = Q_{10}^{\frac{T-T_{ref}}{10}}, \tag{B1}$$

with T_{ref} as a reference temperature usually at 25 °C. However, the Q_{10} value varies from 1.5 to 28 (Segers, 1998;Mikan et al., 2002), which indicates inadequate representation of the supply of substrates (Davidson and Janssens, 2006;Davidson et al., 2006), and microbial functional groups (Blake et al., 2015;Svensson, 1984;Rivkina et al., 2007;Lu et al., 2015) and necessitates alternative temperature response functions.

The Arrhenius equation (Arah and Stephen, 1998;Wang et al., 2012;Grant, 1998;Grant et al., 1993;Sharpe and DeMichele, 1977;Grant and Roulet, 2002) is

$$f(T) = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right], \qquad \text{(B2)}$$

with E_a as the activation energy, and R as the gas constant. It is related to the Q_{10} method with $\ln(Q_{10}) = \frac{10E_a}{RT_{ref}T}$. The introduced variability by the absolute temperature T is not able to explain the wide range of Q_{10} values either. Consequently, empirical equations are often used (Nicolardot et al., 1994). DayCent, ForCent, and CENTURY use (Parton et al., 2010)

$$f(T) = 0.56 + 0.465 atan[0.097(T - 15.7)]. \qquad \text{(B3)}$$

A temperature response function for microbial growth is (Ratkowsky et al., 1982)

$$f(T) = \left(\frac{T - T_m}{T_{ref} - T_m}\right)^2, \qquad \text{(B4)}$$

with T_m as a conceptual temperature of no metabolic significance between 248-296 °K, depending on the bacterial cultures.

Acknowledgements

This research was funded by the U.S. Department of Energy, Office of Sciences, Biological and Environmental Research, Terrestrial Ecosystem Sciences Program, and is a product of the Next-Generation Ecosystem Experiments in the Arctic (NGEE-Arctic) project. ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. XX is grateful for the supports from the San Diego State ~~References~~University.

Disclaimer

References

Abbott, B. W., Larouche, J. R., Jones, J. B., Bowden, W. B., and Balser, A. W.: Elevated dissolved organic carbon biodegradability from thawing and collapsing permafrost, Journal of Geophysical Research: Biogeosciences, 119, 2049-2063, 10.1002/2014JG002678, 2014.

Appelo, C. A. J., Van Der Weiden, M. J. J., Tournassat, C., and Charlet, L.: Surface Complexation of Ferrous Iron and Carbonate on Ferrihydrite and the Mobilization of Arsenic, Environmental Science & Technology, 36, 3096-3103, 10.1021/es010130n, 2002.

Arah, J. R. M., and Stephen, K. D.: A model of the processes leading to methane emission from peatland, Atmospheric Environment, 32, 3257-3264, 10.1016/S1352-2310(98)00052-1, 1998.

Arnosti, C.: Rapid potential rates of extracellular enzymatic hydrolysis in Arctic sediments, Limnology and Oceanography, 43, 315-324, 10.4319/lo.1998.43.2.0315, 1998.

Arnosti, C., Jørgensen, B. B., Sagemann, J., and Thamdrup, B.: Temperature dependence of microbial degradation of organic matter in marine sediments: polysaccharide hydrolysis, oxygen consumption, and sulfate reduction, Marine Ecology-Progress Series, 165, 59-70, 10.3354/meps165059, 1998.

Arnosti, C.: Substrate specificity in polysaccharide hydrolysis: Contrasts between bottom water and sediments, Limnology and Oceanography, 45, 1112-1119, 10.4319/lo.2000.45.5.1112, 2000.

Berrittella, C., and Van Huissteden, J.: Uncertainties in modelling CH4 emissions from northern wetlands in glacial climates: effect of hydrological model and CH4 model structure, Climate of the Past, 5, 361-373, 10.5194/cp-5-361-2009, 2009.

Berrittella, C., and van Huissteden, J.: Uncertainties in modelling CH4 emissions from northern wetlands in glacial climates: the role of vegetation parameters, Climate of the Past, 7, 1075-1087, 10.5194/cp-7-1075-2011, 2011.

Bethke, C. M., Sanford, R. A., Kirk, M. F., Jin, Q., and Flynn, T. M.: The thermodynamic ladder in geomicrobiology, Am J Sci, 311, 183-210, 10.2475/03.2011.01, 2011.

Blake, L. I., Tveit, A., Øvreås, L., Head, I. M., and Gray, N. D.: Response of Methanogens in Arctic Sediments to Temperature and Methanogenic Substrate Availability, PLoS ONE, 10, e0129733, 10.1371/journal.pone.0129733, 2015.

Bockheim, J. G., Hinkel, K. M., and Nelson, F. E.: Soils of the Barrow region, Alaska, Polar Geography, 25, 163-181, 10.1080/10889370109377711, 2001.

Bridgham, S. D., Cadillo-Quiroz, H., Keller, J. K., and Zhuang, Q.: Methane emissions from wetlands: biogeochemical, microbial, and modeling perspectives from local to global scales, Global Change Biology, 19, 1325-1346, 10.1111/gcb.12131, 2013.

Caldwell, S. L., Laidler, J. R., Brewer, E. A., Eberly, J. O., Sandborgh, S. C., and Colwell, F. S.: Anaerobic Oxidation of Methane: Mechanisms, Bioenergetics, and the Ecology of Associated Microorganisms, Environmental Science & Technology, 42, 6791-6799, 10.1021/es800120b, 2008.

Cao, M., Dent, J. B., and Heal, O. W.: Modeling methane emissions from rice paddies, Global Biogeochemical Cycles, 9, 183-195, 10.1029/94GB03231, 1995.

Cao, M., Gregson, K., and Marshall, S.: Global methane emission from wetlands and its sensitivity to climate change, Atmospheric Environment, 32, 3293-3299, 10.1016/S1352-2310(98)00105-8, 1998.

Cheng, K., Ogle, S. M., Parton, W. J., and Pan, G.: Predicting methanogenesis from rice paddies using the DAYCENT ecosystem model, Ecological Modelling, 261–262, 19-31, 10.1016/j.ecolmodel.2013.04.003, 2013.

Conrad, R.: Soil microorganisms as controllers of atmospheric trace gases (H2, CO, CH4, OCS, N2O, and NO), Microbiological Reviews, 60, 609-640, 1996.

Cui, M., Ma, A., Qi, H., Zhuang, X., Zhuang, G., and Zhao, G.: Warmer temperature accelerates methane emissions from the Zoige wetland on the Tibetan Plateau without changing methanogenic community composition, Scientific Reports, 5, 11616, 10.1038/srep11616, 2015.

Davidson, E. A., and Janssens, I. A.: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change, Nature, 440, 165-173, 2006.

Davidson, E. A., Janssens, I. A., and Luo, Y.: On the variability of respiration in terrestrial ecosystems: moving beyond Q10, Global Change Biology, 12, 154-164, 10.1111/j.1365-2486.2005.01065.x, 2006.

Drake, H. L., Horn, M. A., and Wüst, P. K.: Intermediary ecosystem metabolism as a main driver of methanogenesis in acidic wetland soil, Environmental Microbiology Reports, 1, 307-318, 10.1111/j.1758-2229.2009.00050.x, 2009.

Drake, T. W., Wickland, K. P., Spencer, R. G. M., McKnight, D. M., and Striegl, R. G.: Ancient low–molecular-weight organic acids in permafrost fuel rapid carbon dioxide production upon thaw, Proceedings of the National Academy of Sciences, 2015.

Dunfield, P., knowles, R., Dumont, R., and Moore, T. R.: Methane production and consumption in temperate and subarctic peat soils: Response to temperature and pH, Soil Biology and Biochemistry, 25, 321-326, 10.1016/0038-0717(93)90130-4, 1993.

Dzombak, D. A., and Morel, F.: Surface complexation modeling: hydrous ferric oxide, Wiley, 1990.

Elberling, B., Michelsen, A., Schadel, C., Schuur, E. A. G., Christiansen, H. H., Berg, L., Tamstorf, M. P., and Sigsgaard, C.: Long-term CO2 production following permafrost thaw, Nature Clim. Change, 3, 890-894, 10.1038/nclimate1955, 2013.

Estop-Aragonés, C., and Blodau, C.: Effects of experimental drying intensity and duration on respiration and methane production recovery in fen peat incubations, Soil Biology and Biochemistry, 47, 1-9, 10.1016/j.soilbio.2011.12.008, 2012.

Feng, X., and Simpson, M. J.: Temperature responses of individual soil organic matter components, Journal of Geophysical Research: Biogeosciences, 113, G03036~~n/a-n/a~~, 10.1029/2008JG000743, 2008.

Fey, A., and Conrad, R.: Effect of temperature on the rate limiting step in the methanogenic degradation pathway in rice field soil, Soil Biology and Biochemistry, 35, 1-8, 10.1016/S0038-0717(02)00175-X, 2003.

Fey, A., Claus, P., and Conrad, R.: Temporal change of 13C-isotope signatures and methanogenic pathways in rice field soil incubated anoxically at different temperatures, Geochimica et Cosmochimica Acta, 68, 293-306, 10.1016/S0016-7037(03)00426-5, 2004.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., and Myhre, G.: Changes in atmospheric constituents and in radiative forcing. Chapter 2, in: Climate Change 2007. The Physical Science Basis, 2007.

Fumoto, T., Kobayashi, K., Li, C., Yagi, K., and Hasegawa, T.: Revising a process-based biogeochemistry model (DNDC) to simulate methane emission from rice paddy fields under various residue management and fertilizer regimes, Global Change Biology, 14, 382-402, 10.1111/j.1365-2486.2007.01475.x, 2008.

Garcia, J.-L., Patel, B. K. C., and Ollivier, B.: Taxonomic, Phylogenetic, and Ecological Diversity of Methanogenic Archaea, Anaerobe, 6, 205-226, 10.1006/anae.2000.0345, 2000.

Glissmann, K., and Conrad, R.: Saccharolytic activity and its role as a limiting step in methane formation during the anaerobic degradation of rice straw in rice paddy soil, Biol Fertil Soils, 35, 62-67, 10.1007/s00374-002-0442-z, 2002.

Grant, R. F., Juma, N. G., and McGill, W. B.: Simulation of carbon and nitrogen transformations in soil: Mineralization, Soil Biology and Biochemistry, 25, 1317-1329, 10.1016/0038-0717(93)90046-E, 1993.

Grant, R. F.: Simulation of methanogenesis in the mathematical model ecosys, Soil Biology and Biochemistry, 30, 883-896, 10.1016/S0038-0717(97)00218-6, 1998.

Grant, R. F., and Roulet, N. T.: Methane efflux from boreal wetlands: Theory and testing of the ecosystem model Ecosys with chamber and tower flux measurements, Global Biogeochemical Cycles, 16, 1054, 10.1029/2001gb001702, 2002.

Hao, L.-P., Lü, F., Li, L., Shao, L.-M., and He, P.-J.: Shift of pathways during initiation of thermophilic methanogenesis at different initial pH, Bioresource Technology, 126, 418-424, 10.1016/j.biortech.2011.12.072, 2012.

Herndon, E. M., Mann, B. F., Chowdhury, T. R., Yang, Z., Wullschleger, S. D., Graham, D., Liang, L., and Gu, B.: Pathways of anaerobic organic matter decomposition in tundra soils from Barrow, Alaska, Journal of Geophysical Research: Biogeosciences, n/a-n/a, 10.1002/2015JG003147, 2015a.

Herndon, E. M., Yang, Z., Bargar, J., Janot, N., Regier, T. Z., Graham, D. E., Wullschleger, S. D., Gu, B., and Liang, L.: Geochemical drivers of organic matter decomposition in arctic tundra soils, Biogeochemistry, 126, 397-414, 10.1007/s10533-015-0165-5, 2015b.

Hodgkins, S. B., Tfaily, M. M., McCalley, C. K., Logan, T. A., Crill, P. M., Saleska, S. R., Rich, V. I., and Chanton, J. P.: Changes in peat chemistry associated with permafrost thaw increase greenhouse gas production, Proceedings of the National Academy of Sciences of the United States of America, 111, 5819-5824, 10.1073/pnas.1314641111, 2014.

Hoj, L., Olsen, R. A., and Torsvik, V. L.: Effects of temperature on the diversity and community structure of known methanogenic groups and other archaea in high Arctic peat, ISME J, 2, 37-48, 2007.

Hyacinthe C., Bonneville S., and Van Cappellen P.: Reactive iron in sediments: chemical versus microbial extractions, Geochimica Cosmochimica Acta, 70, 4166-4180, 10.1016/j.gca.2006.05.018, 2006.

IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., 2013.

Istok, J. D., Park, M., Michalsen, M., Spain, A. M., Krumholz, L. R., Liu, C., McKinley, J., Long, P., Roden, E., Peacock, A. D., and Baldwin, B.: A thermodynamically-based model for predicting microbial growth and community composition coupled to system geochemistry: Application to uranium bioreduction, Journal of Contaminant Hydrology, 112, 1-14, 10.1016/j.jconhyd.2009.07.004, 2010.

Jerman, V., Metje, M., Mandić-Mulec, I., and Frenzel, P.: Wetland restoration and methanogenesis: the activity of microbial populations and competition for substrates at different temperatures, Biogeosciences, 6, 1127-1138, 10.5194/bg-6-1127-2009, 2009.

Jin, Q., and Roden, E. E.: Microbial physiology-based model of ethanol metabolism in subsurface sediments, Journal of Contaminant Hydrology, 125, 1-12, 10.1016/j.jconhyd.2011.04.002, 2011.

Kettunen, A.: Connecting methane fluxes to vegetation cover and water table fluctuations at microsite level: A modeling study, Global Biogeochemical Cycles, 17, n/a-n/a, 10.1029/2002GB001958, 2003.

Knoblauch, C., Beer, C., Sosnin, A., Wagner, D., and Pfeiffer, E.-M.: Predicting long-term carbon mineralization and trace gas production from thawing permafrost of Northeast Siberia, Global Change Biology, 19, 1160-1172, 10.1111/gcb.12116, 2013.

Knorr, K.-H., and Blodau, C.: Impact of experimental drought and rewetting on redox transformations and methanogenesis in mesocosms of a northern fen soil, Soil Biology and Biochemistry, 41, 1187-1198, 10.1016/j.soilbio.2009.02.030, 2009.

Kögel-Knabner, I.: The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter, Soil Biology and Biochemistry, 34, 139-162, 10.1016/S0038-0717(01)00158-4, 2002.

Kotsyurbenko, O. R., Nozhevnikova, A. N., and Zavarzin, G. A.: Methanogenic degradation of organic matter by anaerobic bacteria at low temperature, Chemosphere, 27, 1745-1761, 10.1016/0045-6535(93)90155-X, 1993.

Kotsyurbenko, O. R., Chin, K.-J., Glagolev, M. V., Stubner, S., Simankova, M. V., Nozhevnikova, A. N., and Conrad, R.: Acetoclastic and hydrogenotrophic methane production and methanogenic populations in an acidic West-Siberian peat bog, Environmental Microbiology, 6, 1159-1173, 10.1111/j.1462-2920.2004.00634.x, 2004.

Kotsyurbenko, O. R., Friedrich, M. W., Simankova, M. V., Nozhevnikova, A. N., Golyshin, P. N., Timmis, K. N., and Conrad, R.: Shift from Acetoclastic to H2-Dependent Methanogenesis in a West Siberian Peat Bog at Low pH Values and Isolation of an Acidophilic Methanobacterium Strain, Applied and Environmental Microbiology, 73, 2344-2348, 2007.

Koven, C. D., Schuur, E. A. G., Schädel, C., Bohn, T. J., Burke, E. J., Chen, G., Chen, X., Ciais, P., Grosse, G., Harden, J. W., Hayes, D. J., Hugelius, G., Jafarov, E. E., Krinner, G., Kuhry, P., Lawrence, D. M., MacDougall, A. H., Marchenko, S. S., McGuire, A. D., Natali, S. M., Nicolsky, D. J., Olefeldt, D., Peng, S., Romanovsky, V. E., Schaefer, K. M., Strauss, J., Treat, C. C., and Turetsky, M.: A simplified, data-constrained approach to estimate the permafrost carbon–climate feedback, Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 373, 2015.

Lavoie, M., Mack, M. C., and Schuur, E. A. G.: Effects of elevated nitrogen and temperature on carbon and nitrogen dynamics in Alaskan arctic and boreal soils, Journal of Geophysical Research: Biogeosciences, 116, n/a-n/a, 10.1029/2010JG001629, 2011.

Lawrence, D. M., Koven, C. D., Swenson, S. Cl, Riley, W. J., and Slater, A. G. : Permafrost thaw and resulting soil moisture changes regulate projected high-latitude CO_2 and CH_4 emissions, Environmental Research Letters, 10, 094011, 10.1088/1748-9326/10/9/094011, 2015.

Lee, H., Schuur, E. A. G., Inglett, K. S., Lavoie, M., and Chanton, J. P.: The rate of permafrost carbon release under aerobic and anaerobic conditions and its potential effects on climate, Global Change Biology, 18, 515-527, 10.1111/j.1365-2486.2011.02519.x, 2012.

Lipson, D. A., Jha, M., Raab, T. K., and Oechel, W. C.: Reduction of iron (III) and humic substances plays a major role in anaerobic respiration in an Arctic peat soil, Journal of Geophysical Research: Biogeosciences, 115, n/a-n/a, 10.1029/2009JG001147, 2010.

Lipson, D. A., Haggerty, J. M., Srinivas, A., Raab, T. K., Sathe, S., and Dinsdale, E. A.: Metagenomic Insights into Anaerobic Metabolism along an Arctic Peat Soil Profile, PLoS ONE, 8, e64659, 10.1371/journal.pone.0064659, 2013a.

Lipson, D. A., Raab, T. K., Goria, D., and Zlamal, J.: The contribution of Fe(III) and humic acid reduction to ecosystem respiration in drained thaw lake basins of the Arctic Coastal Plain, Global Biogeochemical Cycles, 27, 399-409, 10.1002/gbc.20038, 2013b.

Lloyd, J., and Taylor, J. A.: On the Temperature Dependence of Soil Respiration, Functional Ecology, 8, 315-323, 1994.

Lu, Y., Fu, L., Lu, Y., Hugenholtz, F., and Ma, K.: Effect of temperature on the structure and activity of a methanogenic archaeal community during rice straw decomposition, Soil Biology and Biochemistry, 81, 17-27, 10.1016/j.soilbio.2014.10.031, 2015.

Madigan, M. T.: Brock biology of microorganisms, Benjamin Cummings, San Francisco, 2012.

Mann, B. F., Chen, H., Herndon, E. M., Chu, R. K., Tolic, N., Portier, E. F., Roy Chowdhury, T., Robinson, E. W., Callister, S. J., Wullschleger, S. D., Graham, D. E., Liang, L., and Gu, B.: Indexing Permafrost Soil Organic Matter Degradation Using High-Resolution Mass Spectrometry, PLoS ONE, 10, e0130557, 10.1371/journal.pone.0130557, 2015.

Manzoni, S., and Porporato, A.: Soil carbon and nitrogen mineralization: Theory and models across scales, Soil Biology and Biochemistry, 41, 1355-1379, 10.1016/j.soilbio.2009.02.031, 2009.

Meng, L., Hess, P. G. M., Mahowald, N. M., Yavitt, J. B., Riley, W. J., Subin, Z. M., Lawrence, D. M., Swenson, S. C., Jauhiainen, J., and Fuka, D. R.: Sensitivity of wetland methane emissions to model assumptions: application and model testing against site observations, Biogeosciences, 9, 2793-2819, 10.5194/bg-9-2793-2012, 2012.

Mikan, C. J., Schimel, J. P., and Doyle, A. P.: Temperature controls of microbial respiration in arctic tundra soils above and below freezing, Soil Biology and Biochemistry, 34, 1785-1795, 10.1016/S0038-0717(02)00168-2, 2002.

Miller, K. E., Lai, C.-T., Friedman, E. S., Angenent, L. T., and Lipson, D. A.: Methane suppression by iron and humic acids in soils of the Arctic Coastal Plain, Soil Biology and Biochemistry, 83, 176-183, 10.1016/j.soilbio.2015.01.022, 2015.

Nicolardot, B., Fauvet, G., and Cheneby, D.: Carbon and nitrogen cycling through soil microbial biomass at various temperatures, Soil Biology and Biochemistry, 26, 253-261, 10.1016/0038-0717(94)90165-1, 1994.

Oleson, K., Lawrence, D., Bonan, G., Levis, S., Swenson, S., Thornton, P., Bozbiyik, A., Fisher, R., Heald, C., Kluzek, E., Lamarque, J.-F., Lawrence, P., Lipscomb, W., Muszala, S., and Sacks, W.: Technical description of version 4.5 of the Community Land Model (CLM), NCAR, 2013.

Parkhurst, D. L., and Appelo, C.: Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, US Geological Survey2328-7055, 2013.

Parton, W. J., Hanson, P. J., Swanston, C., Torn, M., Trumbore, S. E., Riley, W., and Kelly, R.: ForCent model development and testing using the Enriched Background Isotope Study experiment, J. Geophys. Res., 115, G04001, 10.1029/2009jg001193, 2010.

Peters, V., and Conrad, R.: Sequential reduction processes and initiation of CH4 production upon flooding of oxic upland soils, Soil Biology and Biochemistry, 28, 371-382, 10.1016/0038-0717(95)00146-8, 1996.

Poulton, S. W. and Canfield, D. E.: Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates, Chemical Geology, 214, 209-221, 10.1016/j.chemgeo.2004.09.003, 2005.

Raich, J. W., Rastetter, E. B., Melillo, J. M., Kicklighter, D. W., Steudler, P. A., Peterson, B. J., Grace, A. L., Moore Iii, B., and Vorosmarty, C. J.: Potential net primary productivity in South America: application of a global model, Ecological Applications, 1, 399-429, 10.2307/1941899, 1991.

Ratkowsky, D. A., Olley, J., McMeekin, T. A., and Ball, A.: Relationship between temperature and growth rate of bacterial cultures, Journal of Bacteriology, 149, 1-5, 1982.

Reiche, M., Torburg, G., and Küsel, K.: Competition of Fe(III) reduction and methanogenesis in an acidic fen, FEMS Microbiology Ecology, 65, 88-101, 2008.

Riley, W. J., Subin, Z. M., Lawrence, D. M., Swenson, S. C., Torn, M. S., Meng, L., Mahowald, N. M., and Hess, P.: Barriers to predicting changes in global terrestrial methane fluxes: analyses using CLM4Me, a methane biogeochemistry model integrated in CESM, Biogeosciences, 8, 1925-1953, 10.5194/bg-8-1925-2011, 2011.

Riley, W. J., Maggi, F., Kleber, M., Torn, M. S., Tang, J. Y., Dwivedi, D., and Guerry, N.: Long residence times of rapidly decomposable soil organic matter: application of a multi-phase, multi-component, and vertically resolved model (BAMS1) to soil carbon dynamics, Geosci. Model Dev., 7, 1335-1355, 10.5194/gmd-7-1335-2014, 2014.

Rittmann, B. E., and McCarty, P. L.: Environmental biotechnology: principles and applications, McGraw-Hill, 2001.

Rivkina, E., Shcherbakova, V., Laurinavichius, K., Petrovskaya, L., Krivushin, K., Kraev, G., Pecheritsina, S., and Gilichinsky, D.: Biogeochemistry of methane and methanogenic archaea in permafrost, FEMS Microbiology Ecology, 61, 1-15, 2007.

Roy Chowdhury, T., Herndon, E. M., Phelps, T. J., Elias, D. A., Gu, B., Liang, L., Wullschleger, S. D., and Graham, D. E.: Stoichiometry and temperature sensitivity of methanogenesis and CO2 production from saturated polygonal tundra in Barrow, Alaska, Global Change Biology, 21, 722-737, 10.1111/gcb.12762, 2015.

Roy, R., Klüber, H. D., and Conrad, R.: Early initiation of methane production in anoxic rice soil despite the presence of oxidants, FEMS Microbiology Ecology, 24, 311-320, 10.1016/S0168-6496(97)00072-X, 1997.

Schädel, C., Schuur, E. A. G., Bracho, R., Elberling, B., Knoblauch, C., Lee, H., Luo, Y., Shaver, G. R., and Turetsky, M. R.: Circumpolar assessment of permafrost C quality and its vulnerability over time using long-term incubation data, Global Change Biology, 20, 641-652, 10.1111/gcb.12417, 2014.

Schädel, C., Bader, M., Schuur, E. A., Bracho, R., Capek, P., De-Baets, S., Diakova, K., Ernakovich, J., Estop-Aragones, C., Graham, D. E., Hartley, I. P., Iversen, C. M., Kane, E., Knoblauch, C., Lupascu, M., Natali, S., Norby, R. J., O'Donnell, J. A., Roy Chowdhury, T., Šantrůčková, H., Shaver, G., Sloan, V. L., Treat, C. C., Turetsky, M. R., Waldrop, M., and Wickland, K. P.: Potential carbon emissions dominated by carbon dioxide from thawed permafrost soils, . Nature Climate Change, in press, 2016.

Segers, R.: Methane production and methane consumption: a review of processes underlying wetland methane fluxes, Biogeochemistry, 41, 23-51, 10.1023/A:1005929032764, 1998.

Segers, R., and Kengen, S. W. M.: Methane production as a function of anaerobic carbon mineralization: A process model, Soil Biology and Biochemistry, 30, 1107-1117, 10.1016/S0038-0717(97)00198-3, 1998.

Sharpe, P. J. H., and DeMichele, D. W.: Reaction kinetics of poikilotherm development, Journal of Theoretical Biology, 64, 649-670, 10.1016/0022-5193(77)90265-X, 1977.

Smemo, K. A., and Yavitt, J. B.: Anaerobic oxidation of methane: an underappreciated aspect of methane cycling in peatland ecosystems?, Biogeosciences, 8, 779-793, 10.5194/bg-8-779-2011, 2011.

Sowers, K. R., Baron, S. F., and Ferry, J. G.: Methanosarcina-Acetivorans Sp-Nov, An Acetotrophic Methane-Producing Bacterium Isolated from Marine-Sediments, Applied and Environmental Microbiology, 47, 971-978, 1984.

Svensson, B. H.: Different Temperature Optima for Methane Formation When Enrichments from Acid Peat Are Supplemented with Acetate or Hydrogen, Applied and Environmental Microbiology, 48, 389-394, 1984.

Tang, G., Luo, W., Watson, D. B., Brooks, S. C., and Gu, B.: Prediction of Aluminum, Uranium, and Co-Contaminants Precipitation and Adsorption during Titration of Acidic Sediments, Environmental Science & Technology, 47, 5787-5793, 10.1021/es400169y, 2013a.

Tang, G., Watson, D. B., Wu, W.-M., Schadt, C. W., Parker, J. C., and Brooks, S. C.: U(VI) Bioreduction with Emulsified Vegetable Oil as the Electron Donor – Model Application to a Field Test, Environmental Science & Technology, 47, 3218-3225, 10.1021/es304643h, 2013b.

Tang, G., Wu, W.-M., Watson, D. B., Parker, J. C., Schadt, C. W., Shi, X., and Brooks, S. C.: U(VI) Bioreduction with Emulsified Vegetable Oil as the Electron Donor – Microcosm Tests and Model Development, Environmental Science & Technology, 47, 3209-3217, 10.1021/es304641b, 2013c.

Tang, G., Yuan, F., Bisht, G., Hammond, G. E., Lichtner, P. C., Kumar, J., Mills, R. T., Xu, X., Andre, B., Hoffman, F. M., Painter, S. L., and Thornton, P. E.: Addressing numerical challenges in introducing a reactive transport code into a land surface model: a biogeochemical modeling proof-of-concept with CLM–PFLOTRAN 1.0, Geosci. Model Dev., 9, 927-946, 10.5194/gmd-9-927-2016, 2016.

Thornton, P. E., and Rosenbloom, N. A.: Ecosystem model spin-up: Estimating steady state conditions in a coupled terrestrial carbon and nitrogen cycle model, Ecological Modelling, 189, 25-48, 10.1016/j.ecolmodel.2005.04.008, 2005.

Tian, H., Xu, X., Liu, M., Ren, W., Zhang, C., Chen, G., and Lu, C.: Spatial and temporal patterns of CH4 and N2O fluxes in terrestrial ecosystems of North America during 1979–2008: application of a global biogeochemistry model, Biogeosciences, 7, 2673-2694, 10.5194/bg-7-2673-2010, 2010.

Tian, H., Chen, G., Lu, C., Xu, X., Ren, W., Zhang, B., Banger, K., Tao, B., Pan, S., Liu, M., Zhang, C., Bruhwiler, L., and Wofsy, S.: Global methane and nitrous oxide emissions from terrestrial ecosystems due to multiple environmental changes, Ecosystem Health and Sustainability, 1, 1-20, 10.1890/EHS14-0015.1, 2015.

Tipping, E.: WHAM—A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances, Computers & Geosciences, 20, 973-1023, 10.1016/0098-3004(94)90038-8, 1994.

Treat, C. C., Natali, S. M., Ernakovich, J., Iversen, C. M., Lupascu, M., McGuire, A. D., Norby, R. J., Roy Chowdhury, T., Richter, A., Šantrůčková, H., Schädel, C., Schuur, E. A. G., Sloan, V. L., Turetsky, M. R., and Waldrop, M. P.: A pan-Arctic synthesis of CH4 and CO2 production from anoxic soil incubations, Global Change Biology, 21, 2787-2803, 10.1111/gcb.12875, 2015.

Tveit, A., Schwacke, R., Svenning, M. M., and Urich, T.: Organic carbon transformations in high-Arctic peat soils: key functions and microorganisms, The ISME Journal, 7, 299-311, 10.1038/ismej.2012.99, 2013.

Tveit, A. T., Urich, T., Frenzel, P., and Svenning, M. M.: Metabolic and trophic interactions modulate methane production by Arctic peat microbiota in response to warming, Proceedings of the National Academy of Sciences of the United States of America, 112, E2507-E2516, 10.1073/pnas.1420797112, 2015.

Van Bodegom, P., Goudriaan, J., and Leffelaar, P.: A mechanistic model on methane oxidation in a rice rhizosphere, Biogeochemistry, 55, 145-177, 10.1023/a:1010640515283, 2001.

van Bodegom, P. M., and Stams, A. J. M.: Effects of alternative electron acceptors and temperature on methanogenesis in rice paddy soils, Chemosphere, 39, 167-182, 10.1016/S0045-6535(99)00101-0, 1999.

van Bodegom, P. M., Leffelaar, P. A., Stams, A. J. M., and Wassmann, R.: Modeling methane emissions from rice fields: Variability, uncertainty, and sensitivity analysis of processes involved, Nutrient Cycling in Agroecosystems, 58, 231-248, 10.1023/a:1009854905333, 2000.

van Bodegom, P. M., and Scholten, J. C. M.: Microbial processes of CH4 production in a rice paddy soil: model and experimental validation, Geochimica et Cosmochimica Acta, 65, 2055-2066, 10.1016/S0016-7037(01)00563-4, 2001.

van Bodegom, P. M., Scholten, J. C. M., and Stams, A. J. M.: Direct inhibition of methanogenesis by ferric iron, FEMS Microbiology Ecology, 49, 261-268, 10.1016/j.femsec.2004.03.017, 2004.

van Geen, A., Robertson, A. P., and Leckie, J. O.: Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters, Geochimica et Cosmochimica Acta, 58, 2073-2086, 10.1016/0016-7037(94)90286-0, 1994.

Van Kessel, J. A. S., and Russell, J. B.: The effect of pH on ruminal methanogenesis, FEMS Microbiology Ecology, 20, 205-210, 10.1016/0168-6496(96)00030-X, 1996.

Villalobos, M., and Leckie, J. O.: Carbonate adsorption on goethite under closed and open CO2 conditions, Geochimica et Cosmochimica Acta, 64, 3787-3802, 10.1016/S0016-7037(00)00465-8, 2000.

Walter, B. P., and Heimann, M.: A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate, Global Biogeochemical Cycles, 14, 745-765, 10.1029/1999gb001204, 2000.

Wang, G., Post, W. M., and Mayes, M. A.: Development of microbial-enzyme-mediated decomposition model parameters through steady-state and dynamic analyses, Ecological Applications, 23, 255-272, 10.1890/12-0681.1, 2012.

Wang, Z. P., DeLaune, R. D., Patrick, W. H., and Masscheleyn, P. H.: Soil Redox and pH Effects on Methane Production in a Flooded Rice Soil, Soil Science Society of America Journal, 57, 10.2136/sssaj1993.03615995005700020016x, 1993.

Wania, R., Ross, I., and Prentice, I. C.: Implementation and evaluation of a new methane model within a dynamic global vegetation model: LPJ-WHyMe v1.3.1, Geosci. Model Dev., 3, 565-584, 10.5194/gmd-3-565-2010, 2010.

Wania, R., Melton, J. R., Hodson, E. L., Poulter, B., Ringeval, B., Spahni, R., Bohn, T., Avis, C. A., Chen, G., Eliseev, A. V., Hopcroft, P. O., Riley, W. J., Subin, Z. M., Tian, H., van Bodegom, P. M., Kleinen, T., Yu, Z. C., Singarayer, J. S., Zurcher, S., Lettenmaier, D. P., Beerling, D. J., Denisov, S. N., Prigent, C., Papa, F., and Kaplan, J. O.: Present state of global wetland extent and wetland methane modelling: methodology of a model inter-comparison project (WETCHIMP), Geoscientific Model Development, 6, 617-641, 10.5194/gmd-6-617-2013, 2013.

Weedon, J. T., Aerts, R., Kowalchuk, G. A., van Logtestijn, R., Andringa, D., and van Bodegom, P. M.: Temperature sensitivity of peatland C and N cycling: Does substrate supply play a role?, Soil Biology & Biochemistry, 61, 109-120, 10.1016/j.soilbio.2013.02.019, 2013.

Xu, X., and Tian, H.: Methane exchange between marshland and the atmosphere over China during 1949–2008, Global Biogeochemical Cycles, 26, GB2006, 10.1029/2010GB003946, 2012.

Xu, X., Elias, D. A., Graham, D. E., Phelps, T. J., Carroll, S. L., Wullschleger, S. D., and Thornton, P. E.: A microbial functional group-based module for simulating methane production and consumption: Application to an incubated permafrost soil, Journal of Geophysical Research: Biogeosciences, 120, 1315-1333, 10.1002/2015JG002935, 2015.

Xu, X., Riley, W. J., Koven, C. D., Billesbach, D. P., Chang, R. Y. W., Commane, R., Euskirchen, E. S., Hartery, S., Harazono, Y., Iwata, H., McDonald, K. C., Miller, C. E., Oechel, W. C., Poulter, B., Raz-Yaseef, N., Sweeney, C., Torn, M., Wofsy, S. C., Zhang, Z., and Zona, D.: A multi-scale comparison of modeled and observed seasonal methane cycles in northern wetlands, Biogeosciences Discuss., 2016, 1-30, 10.5194/bg-2016-167, 2016a.

Xu, X., Yuan, F., Hanson, P. J., Wullschleger, S. D., Thornton, P. E., Riley, W. J., Song, X., Graham, D. E., Song, C., and Tian, H.: Reviews and syntheses: Four Decades of Modeling Methane Cycling in Terrestrial Ecosystems, Biogeosciences~~ Discuss.~~, ~~2016, ~~13, 3735-3755, 1-56, 10.5194/bg-13-3735-2016~~2016-37~~, 2016b.

Yang, Z., Wullschleger, S. D., Liang, L., Graham, D. E., and Gu, B.: Effects of warming on the degradation and production of low-molecular-weight labile organic carbon in an Arctic tundra soil, Soil Biology and Biochemistry, 95, 202-211, 10.1016/j.soilbio.2015.12.022, 2016.

Yao, H., and Conrad, R.: Thermodynamics of methane production in different rice paddy soils from China, the Philippines and Italy, Soil Biology and Biochemistry, 31, 463-473, 10.1016/S0038-0717(98)00152-7, 1999.

Yao, H., Conrad, R., Wassmann, R., and Neue, H. U.: Effect of soil characteristics on sequential reduction and methane production in sixteen rice paddy soils from China, the Philippines, and Italy, Biogeochemistry, 47, 269-295, 10.1007/BF00992910, 1999.

Zhuang, L., Xu, J., Tang, J., and Zhou, S.: Effect of ferrihydrite biomineralization on methanogenesis in an anaerobic incubation from paddy soil, Journal of Geophysical Research: Biogeosciences, 120, 876-886, 10.1002/2014JG002893, 2015.

Zhuang, Q., Melillo, J. M., Kicklighter, D. W., Prinn, R. G., McGuire, A. D., Steudler, P. A., Felzer, B. S., and Hu, S.: Methane fluxes between terrestrial ecosystems and the atmosphere at northern high latitudes during the past century: A retrospective analysis with a process-based biogeochemistry model, Global Biogeochemical Cycles, 18, GB3010, 10.1029/2004gb002239, 2004.

Zona, D., Gioli, B., Commane, R., Lindaas, J., Wofsy, S. C., Miller, C. E., Dinardo, S. J., Dengel, S., Sweeney, C., Karion, A., Chang, R. Y. W., Henderson, J. M., Murphy, P. C., Goodrich, J. P., Moreaux, V., Liljedahl, A., Watts, J. D., Kimball, J. S., Lipson, D. A., and Oechel, W. C.: Cold season emissions dominate the Arctic tundra methane budget, Proceedings of the National Academy of Sciences, 113, 40-45, 2016.

Table 1. Model parameter values for base scenario

Reaction	k_{max} (d^{-1})	k_D (μM)	k_{surf}	Reported k_{max} range
R1	0.83			
R2	0.5	12[1]	0.062[1]~~[1]~~	0.96-2.16[2], 0.55 and 2.38[3], 0.34[4]
R3	0.8	11[1]~~[1]~~	0.062[1]~~[1]~~	
R4	0.3[5]	23[1]~~[1]~~		
R5	0.5[5]~~[5]~~	4.7[1]~~[1]~~		
R6	0.05[5]~~[5]~~			

For
Sup

For
Sup

For
Sup

For
Sup

For
Sup

For
Sup

For
Sup

---

[1] Jin, Q., and Roden, E. E.: Microbial physiology-based model of ethanol metabolism in subsurface sediments, J. Contam. Hydrol., 125, 1-12, 10.1016/j.jconhyd.2011.04.002, 2011.

[2] Esteve-Núñez, A., Rothermich, M., Sharma, M., and Lovley, D.: Growth of Geobacter sulfurreducens under nutrient-limiting conditions in continuous culture, Environmental Microbiology, 7, 641-648, 10.1111/j.1462-2920.2005.00731.x, 2005.

[3] Cord-Ruwisch, R., Lovley, D. R., and Schink, B.: Growth of Geobacter sulfurreducens with Acetate in Syntrophic Cooperation with Hydrogen-Oxidizing Anaerobic Partners, Applied and Environmental Microbiology, 64, 2232-2236, 1998.

[4] Holmes, D. E., Giloteaux, L., Barlett, M., Chavan, M. A., Smith, J. A., Williams, K. H., Wilkins, M., Long, P., and Lovley, D. R.: Molecular Analysis of the In Situ Growth Rates of Subsurface Geobacter Species, ibid., 79, 1646-1653, 2013.

[5] Rittmann, B. E., and McCarty, P. L.: Environmental biotechnology: principles and applications, McGraw-Hill, 2001.

Table 2. Experimental parameter values summarized from (Herndon et al., 2015;Roy Chowdhury et al., 2015). TOTC = total organic carbon. WEOC = water extractable organic carbon.

Location	Horizon	Depth (cm)	pH	Soil (dwt g)	Water (g)	TOTC (g)	WEOC (mg)	~~Acetate~~ Organic acids (mgC)	Fe(II) (mmol)	Bulk den. (g/cm^3)	Headspace (ml)
Center	Oa	6-21.5	5.02	1.412	13.588	0.542	9.585	2.079	0.0107	0.9106	42.5282
	Bgh	21.5-53.5	4.84	9.146	5.854	1.260	3.845	0.394	0.1302		
Ridge	Oe	0-8	5.21	3.212	11.788	1.249	6.790	0.016	0.0190	1.0003	44.0051
	Bh	8-42	4.54	8.621	6.379	1.263	3.282	0.409	0.1466		
Trough	Oe	0-19	5.23	4.310	10.690	0.886	3.324	0.022	0.1675	0.9724	43.5745
	Bh/ice	25-69	4.95	8.380	6.620	0.670	2.013	0.292	0.0475		

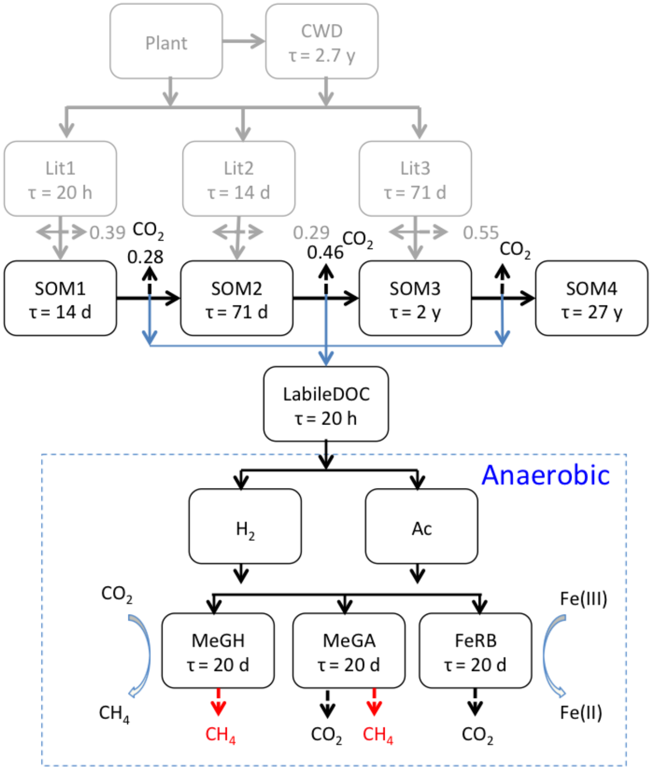


Figure 1: Extension of the CLM-CN decomposition cascade (Thornton and Rosenbloom, 2005) to include a LabileDOC pool. A portion of the original respiration fraction is assumed to produce LabileDOC, which undergoes fermentation, Fe reduction and methanogenesis to release CO_2 and CH_4. FeRB, MeGA, and MeGH denote microbial mass pools for Fe reducers, acetoclastic and hydrogenotrophic methanogens, respectively. τ is the turnover time.

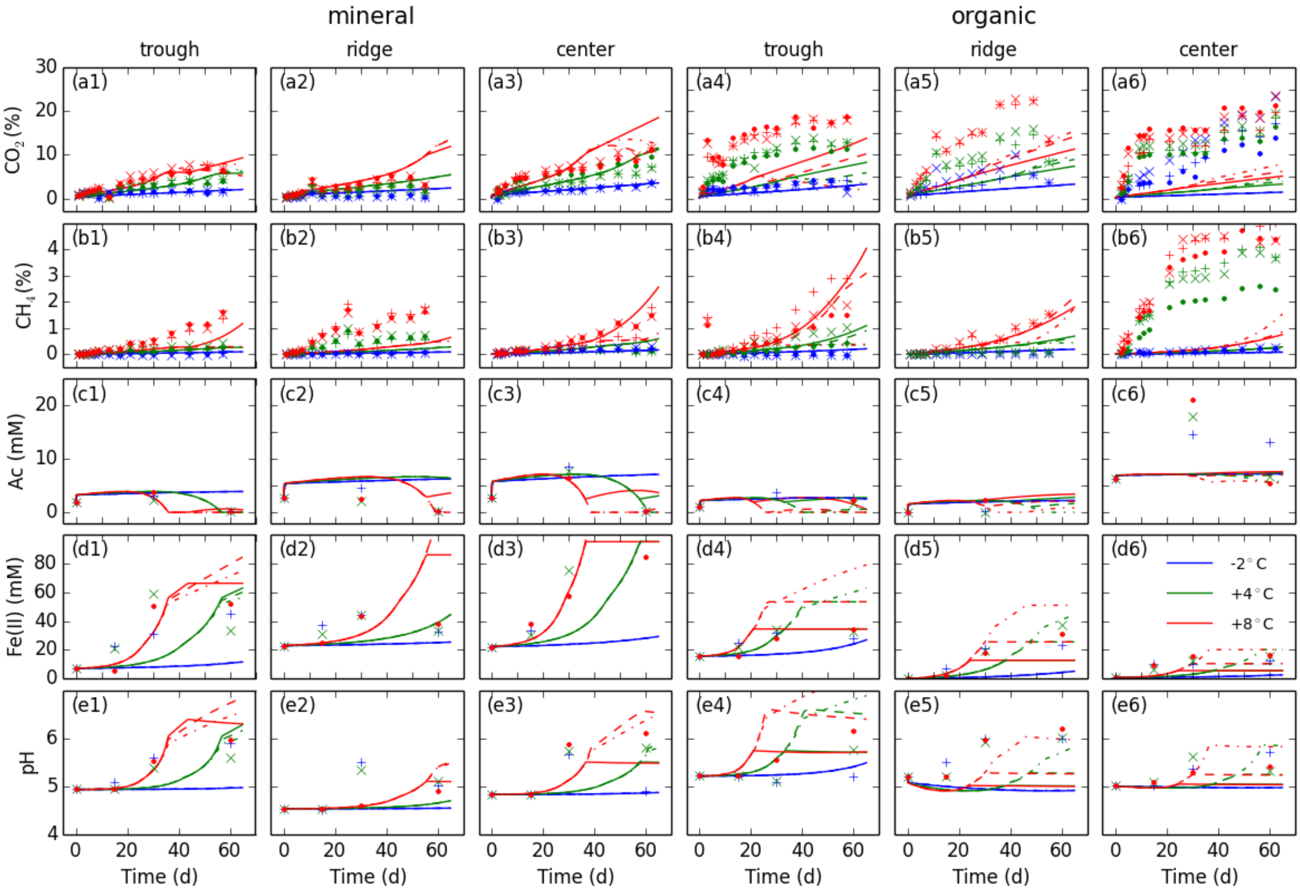


Figure 2: Comparison of observed and modeled CO$_2$ (a1-6) and CH$_4$ (b1-6) in the headspace, organic acid (Ac, c1-6), extractable Fe(II) (d1-6), and pH (e1-6) in the incubation tests with soils from an Arctic lower center polygon. Symbols represent observations with blue, green and red for -2, 4, and 8 °C. For CO$_2$ and CH$_4$, different symbols of the same color represent duplicates. The organic acids, such as formate, acetate, propionate, and butyrate, reported by (Herndon et al., 2015) are combined as Ac in c1-6. The rest of the data were taken from (Roy Chowdhury et al., 2015). The curves are calculations based on model parameter values listed in Table 1 and experimental parameter values listed in Table 2. Trough, ridge, and center denote the microtopographic locations in the polygon, and mineral and organic denote soil horizons. Increasing the initial bioavailable Fe(III) f_{Fe} from 0.005 (continuous) to 0.01 (dash) and 0.02 (dashdot) brings the predictions close to the observations for Fe(II) and pH for center and ridge organic soils.

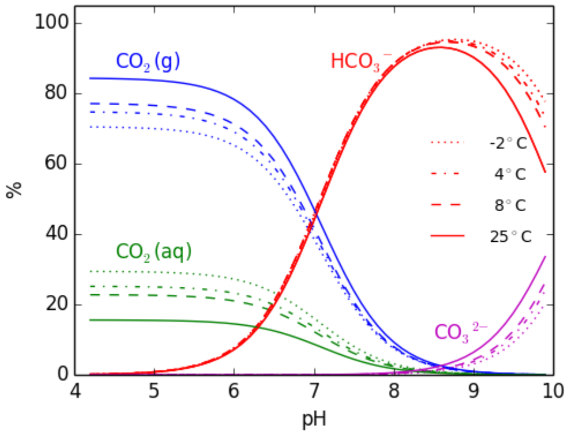


Figure 3: Partition of CO_2 among gas and aqueous phase species under various temperatures. The calculations are conducted with 45 ml headspace with N_2 and 10 ml solution with 10 mM total inorganic carbon using PHREEQC. Gas phase dominates at lower pH and high temperature. As pH increases, gas phase CO_2 fraction is very low after pH 7, implicating potential underestimation of carbon mineralization based on headspace CO_2 concentration measurement only.

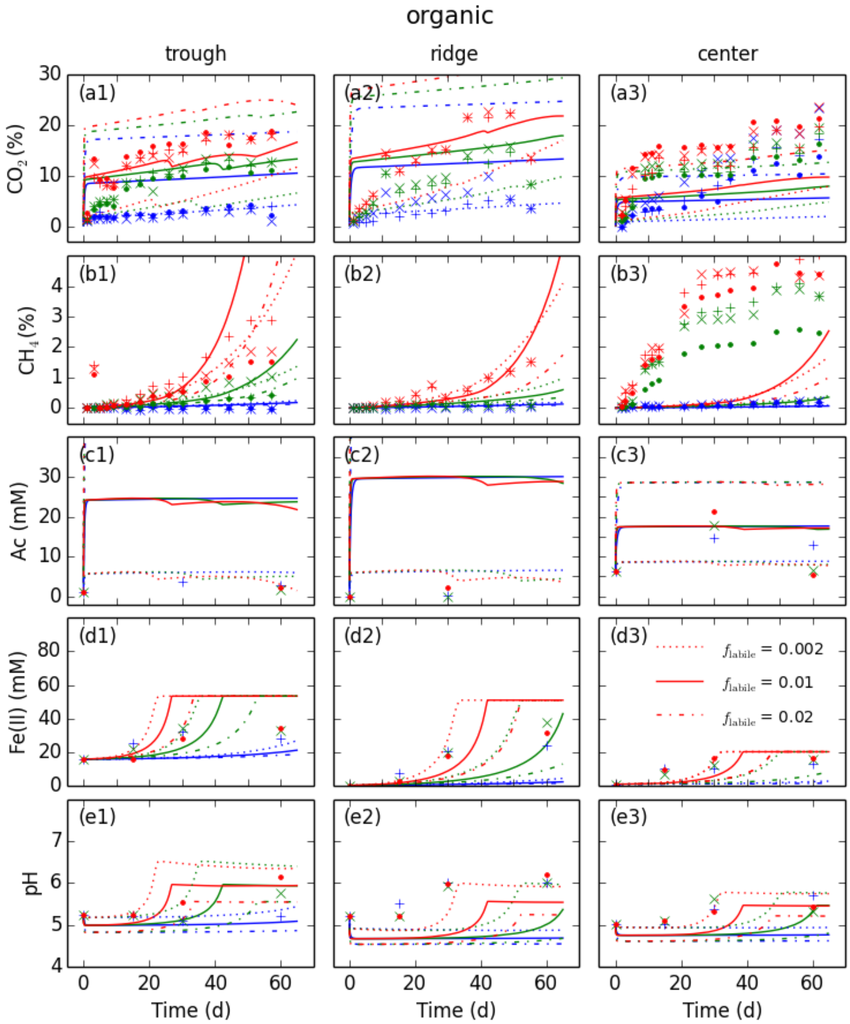
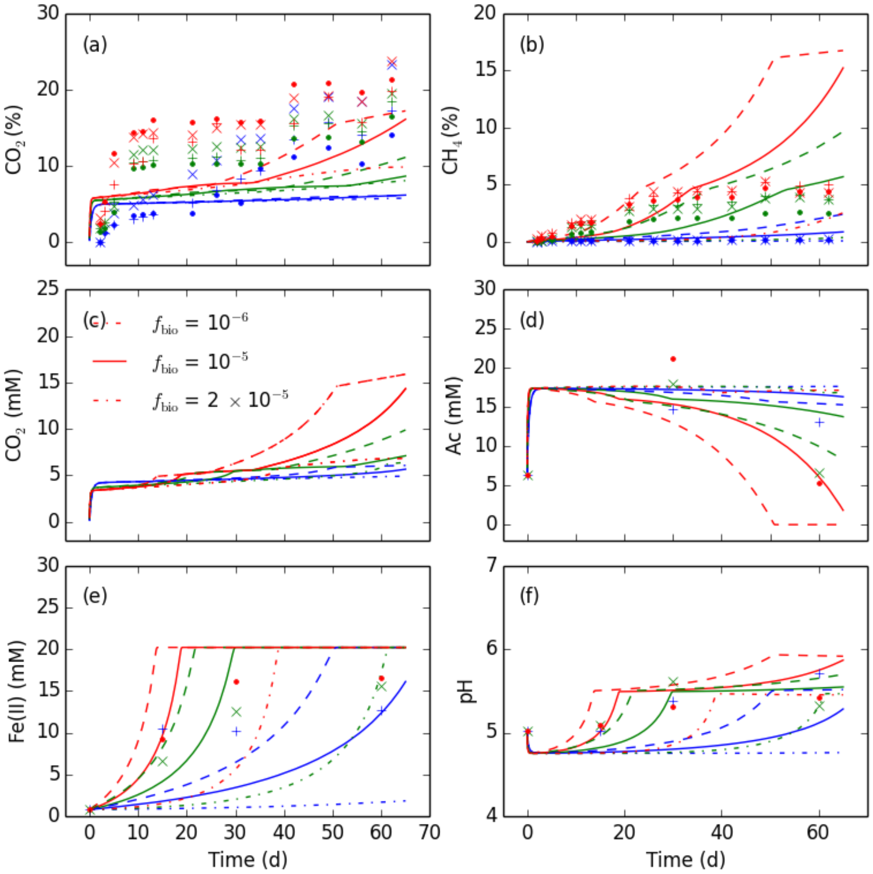


Figure 4: Increasing initial LabileDOC better describes the observed initial rapid CO$_2$ increase in the headspace for the organic soils. See Figure 2 caption for more information.



(a)
CO$_2$ (%)
0
10
20
30
(b)
CH$_4$ (%)
0
5
10
15
20
(c)
CO$_2$ (mM)
0
5
10
15
20
25
$f_{\rm bio} = 10^{-6}$
$f_{\rm bio} = 10^{-5}$
$f_{\rm bio} = 2 \times 10^{-5}$
(d)
Ac (mM)
0
5
10
15
20
25
30
(e)
Fe(II) (mM)
0
5
10
15
20
25
30
0
10
20
30
40
50
60
70
Time (d)
(f)
pH
4
5
6
7
0
20
40
60
Time (d)

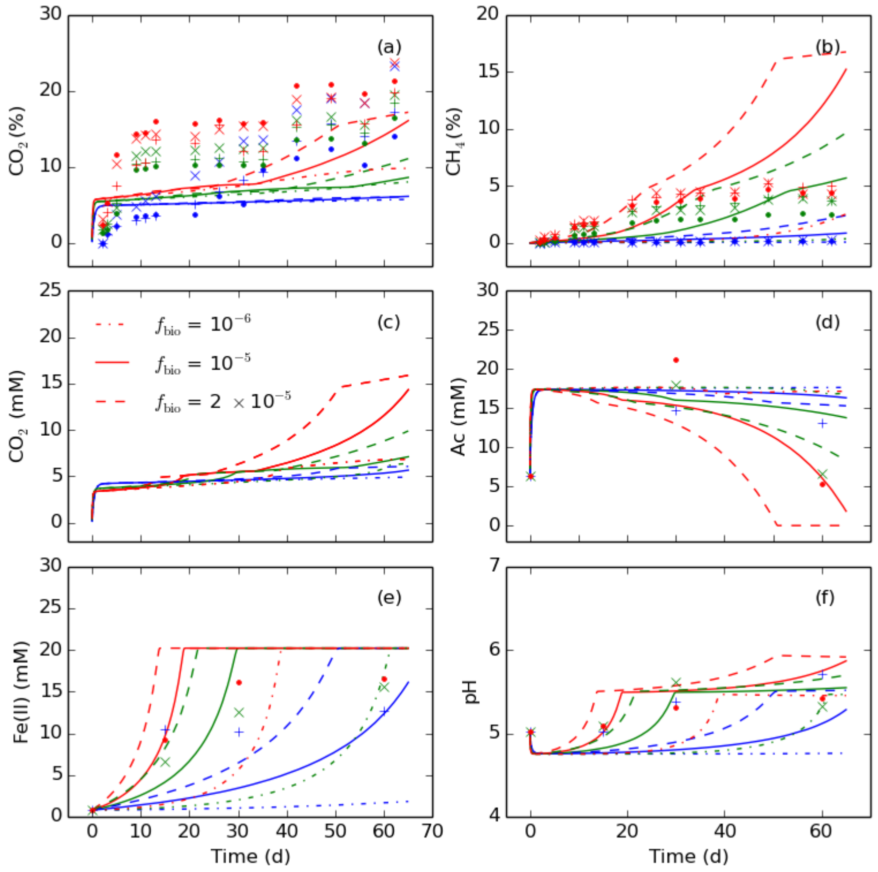


Figure 5: Increasing the initial biomass predicts rapid CH_4 accumulation at early times that is close to the observations but misses the level-off trend at late time for the center organic soils. **See Figure 2 caption for more information.**

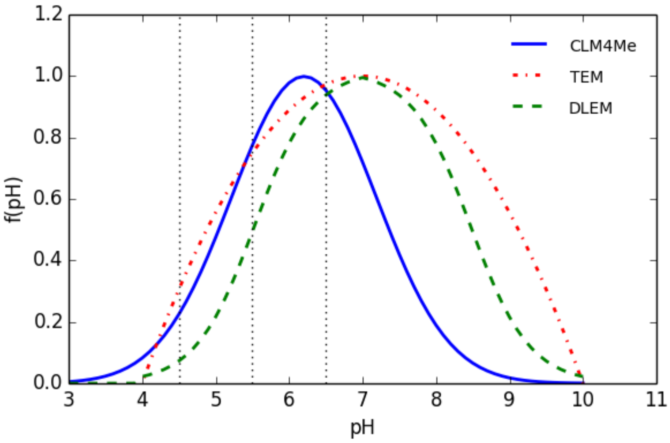


Figure 6: Comparison of pH response functions used in CLM4Me (Riley et al., 2011), TEM (Raich et al., 1991), and DLEM (Tian et al., 2010) as described by Eqs. 3, A1-3. Reaction rates are sensitive to pH and pH response functions vary substantially, introducing prediction uncertainty.

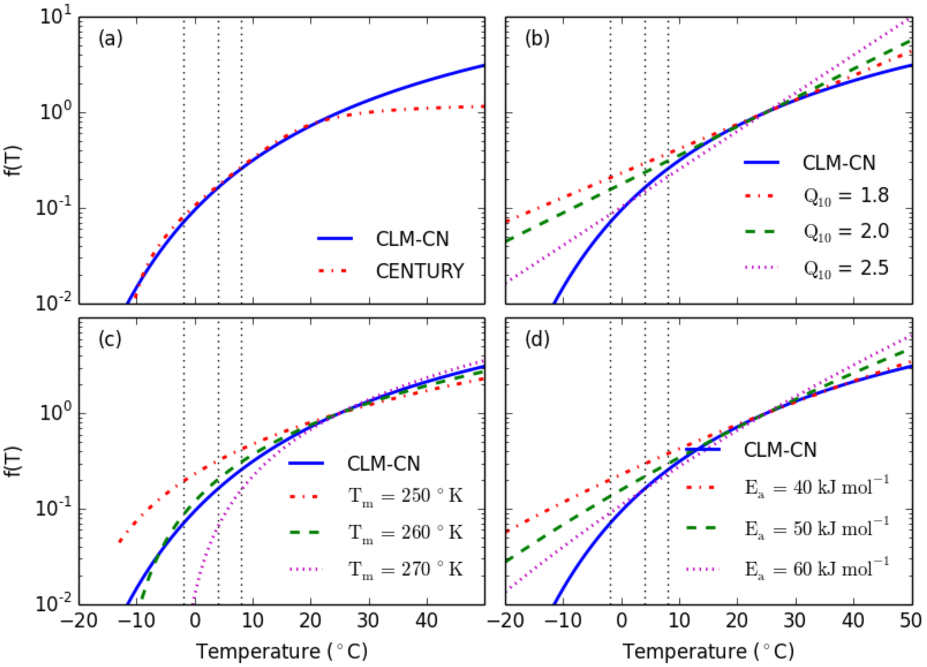


Figure 7: Comparison of temperature response functions used in (a) land surface models CLM-CN (Thornton and Rosenbloom, 2005), CENTURY (Parton et al., 2010), (b) Q_{10} (Oleson et al., 2013), (c) Ratkowsky equation (Ratkowsky et al., 1982) and (d)

Arrhenius equation (Wang et al., 2013) described by Eq. (4, B1-B4). Reaction rates are sensitive to temperature and temperature response functions vary substantially, introducing prediction uncertainty.

Supplement Information

Biogeochemical modeling of CO_2 and CH_4 production in anoxic Arctic soil microcosms

Guoping Tang[1], Jianqiu Zheng[2], Xiaofeng Xu[3], Ziming Yang[1], David E. Graham[2,4], Baohua Gu[1], Scott Painter[1,4], and Peter E. Thornton[1,4]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA
[2]Biosciences Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA
[3]Biology Department, San Diego State University, San Diego, CA, 92182 USA
[4]Climate Change Science Institute, Oak Ridge National Laboratory, Oak Ridge TN, 37831 USA

Correspondence to: Guoping Tang (guopingtangva@gmail.com)

Table S1. Additional experimental parameter values summarized from (Herndon et al., 2015;Roy Chowdhury et al., 2015) (TOTC = total organic carbon; WEOC = water extractable organic carbon; Acids = organic acids, f(pH) = pH factor).

Location	Horizon	Formate (mgC)	Acetate (mgC)	Propionate (mgC)	TOTC/dwt Soil	WEOC /TOTC	Acids/WEOC	f(pH)
Center	Oa	0.3162	1.7185	0.0445	38.35%	1.77%	21.69%	0.486
	Bgh	0.0198	0.3524	0.0213	13.78%	0.31%	10.23%	0.384
Ridge	Oe	0.0012	0.0046	0.0104	38.89%	0.54%	0.24%	0.601
	Bh	0.0270	0.3420	0.0399	14.65%	0.26%	12.46%	0.241
Trough	Oe	0.0016	0.0062	0.0140	20.55%	0.38%	0.66%	0.614
	Bh/ice	0.0204	0.2617	0.0104	7.99%	0.30%	14.53%	0.445

Table S2. Model parameter values for base scenario

Symbol	Value	Description
~~f_{labile}~~$f_{LabileDOC}$	0.0005	Initial fraction of LabileC in total organic carbon ~~TOTC~~
~~f_{som1}~~f_{SOM1}	0.01	Initial fraction of SOM1 in total organic carbon~~TOTC~~
~~f_{som2}~~f_{SOM2}	0.02	Initial fraction of SOM2 in total organic carbon~~TOTC~~
~~f_{som3}~~f_{SOM3}	0.1	Initial fraction of SOM3 in total organic carbon ~~TOTC~~
F_{FeRB}~~$_{ferb}$~~	2×10^{-6}	Initial fraction of Fe reducers in total organic carbon~~TOTC~~
F_{Mega}~~$_{mega}$~~	10^{-6}	Initial fraction of acetoclastic methanogens in total organic carbon~~TOTC~~
F_{MegH}~~$_{megh}$~~	10^{-6}	Initial fraction of hydrogenotrophic methanogens in total organic carbon~~TOTC~~
~~f_{mega}~~	~~10^{-6}~~	~~Initial fraction of SOM4 in TOTC~~
~~f_{fe3}~~f_{Fe3}	0.0025	Initial Fe(III) as a fraction of soil dry weight
~~s_{labile}~~s_{Labile}	0.4	Fraction of the original CLM-CN respiration factor goes through labile pool.

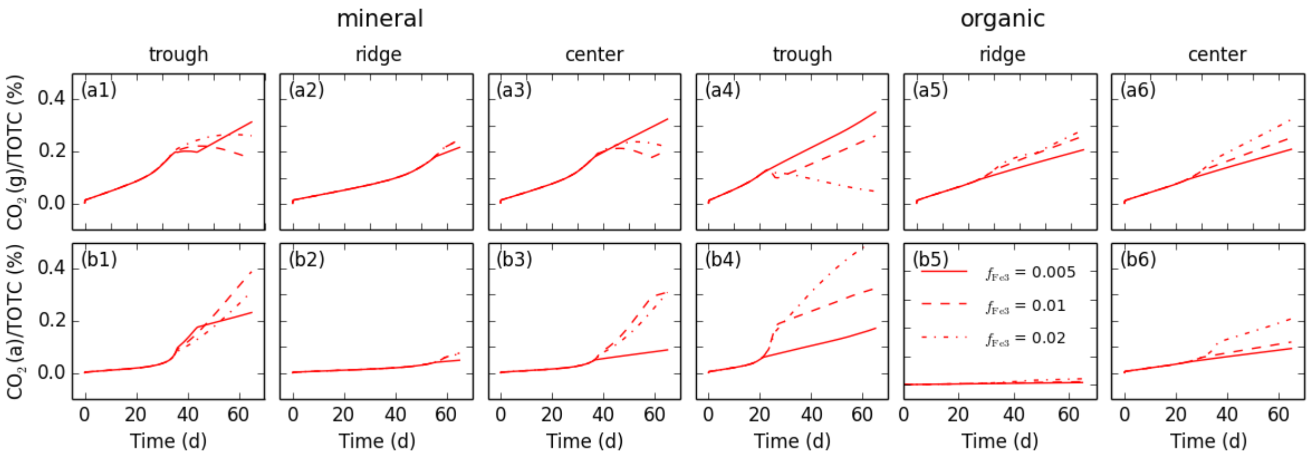


Figure S1: Calculated partition of CO_2 in gas and aqueous phases as a percentage of initial TOTC with different f_{Fe3} values. The results correspond to Fig. 2 for temperature 8 °C. With increasing f_{Fe3}, the pH increases at the late times, as does the CO_2 solubility. See Figure 2 caption for more information.

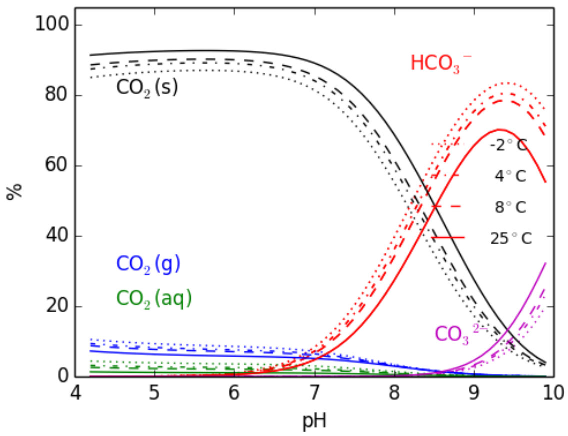


Figure S2: Adding 1 mmol $Fe(OH)_{3a}$ into the numerical experiments shown in Fig. 3, the gas-phase fraction is decreased at low pH values as the sorbed phase dominates. See Fig. 3 caption for more information.

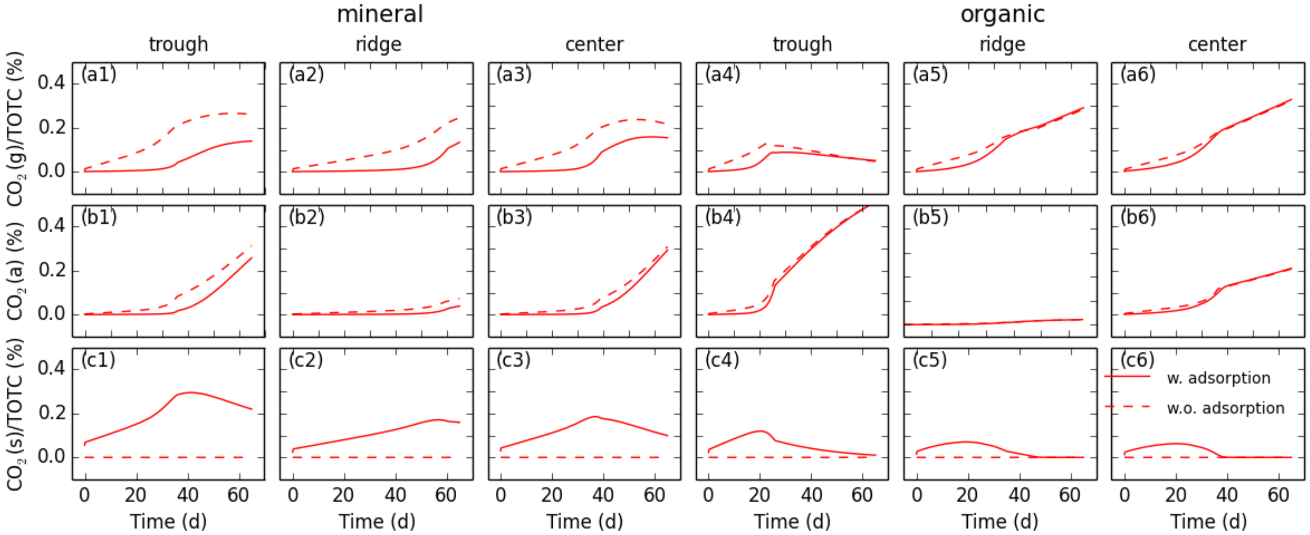


Figure S3: Impact of adsorption of CO_2 to ferric oxide surfaces on the distribution among gas, aqueous and solid phases. The gas phase concentration is predicted to be buffered by adsorption at the beginning. At late times, reduction and dissolution of $Fe(OH)_{3a}$ sites may release CO_2. See caption for Fig. 2 and Fig. S1 for more information.

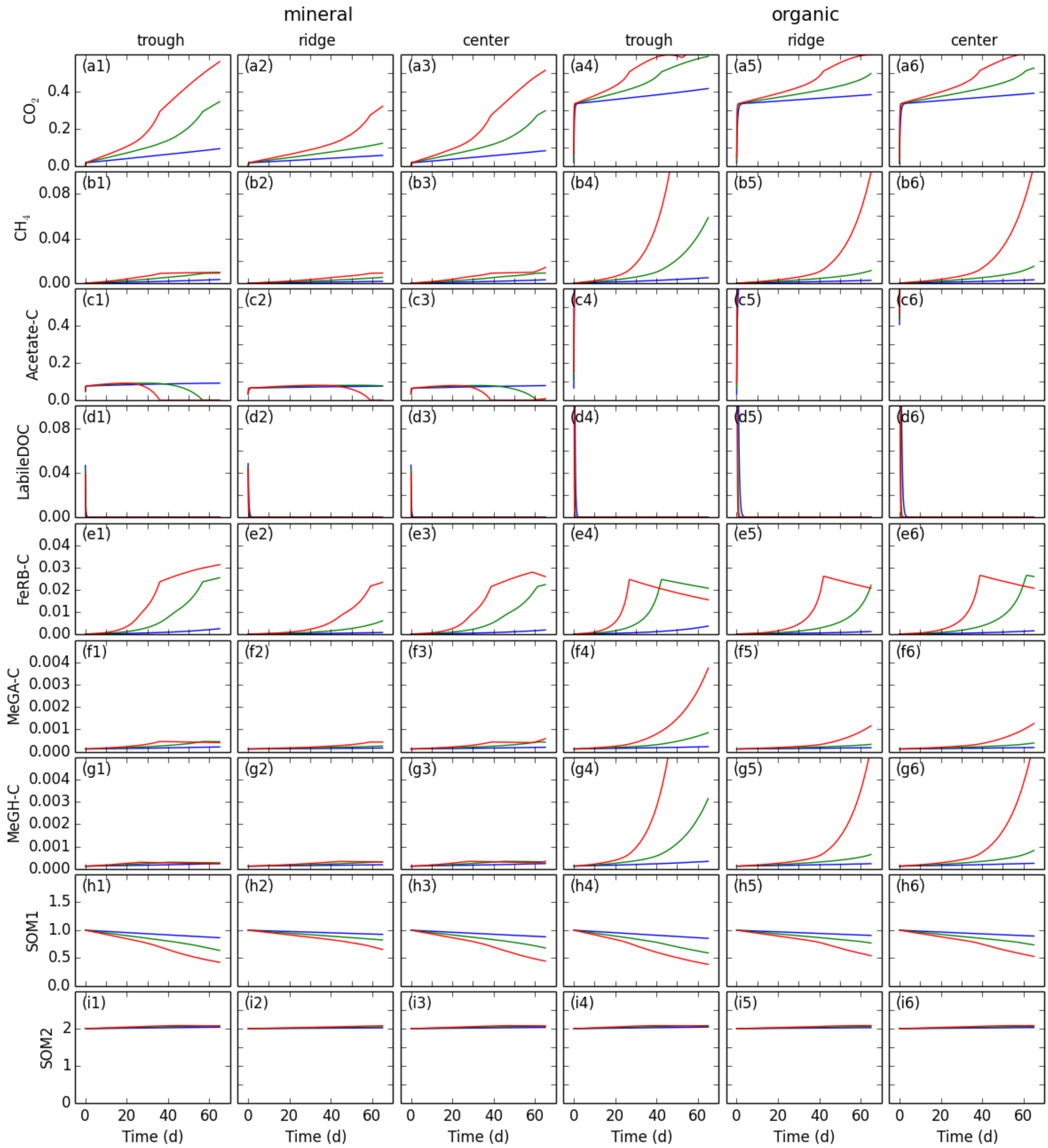


Figure S4: Partition of carbon among various organic pools. a, and b~~, and c~~ are for total CO$_2$ ~~distribution in the gas (head space), aqueous (water), and adsorbed (sorption to Fe(OH)3a)~~and CH$_4$ in aqueous and gas phases. The recalcitrant pools (SOM3 and

SOM4) are the major fractions of soil organic carbon but have a slow turnover time relative to the experiment duration, therefore, not shown. See Fig.2 caption for more description about the model and experimental parameters.

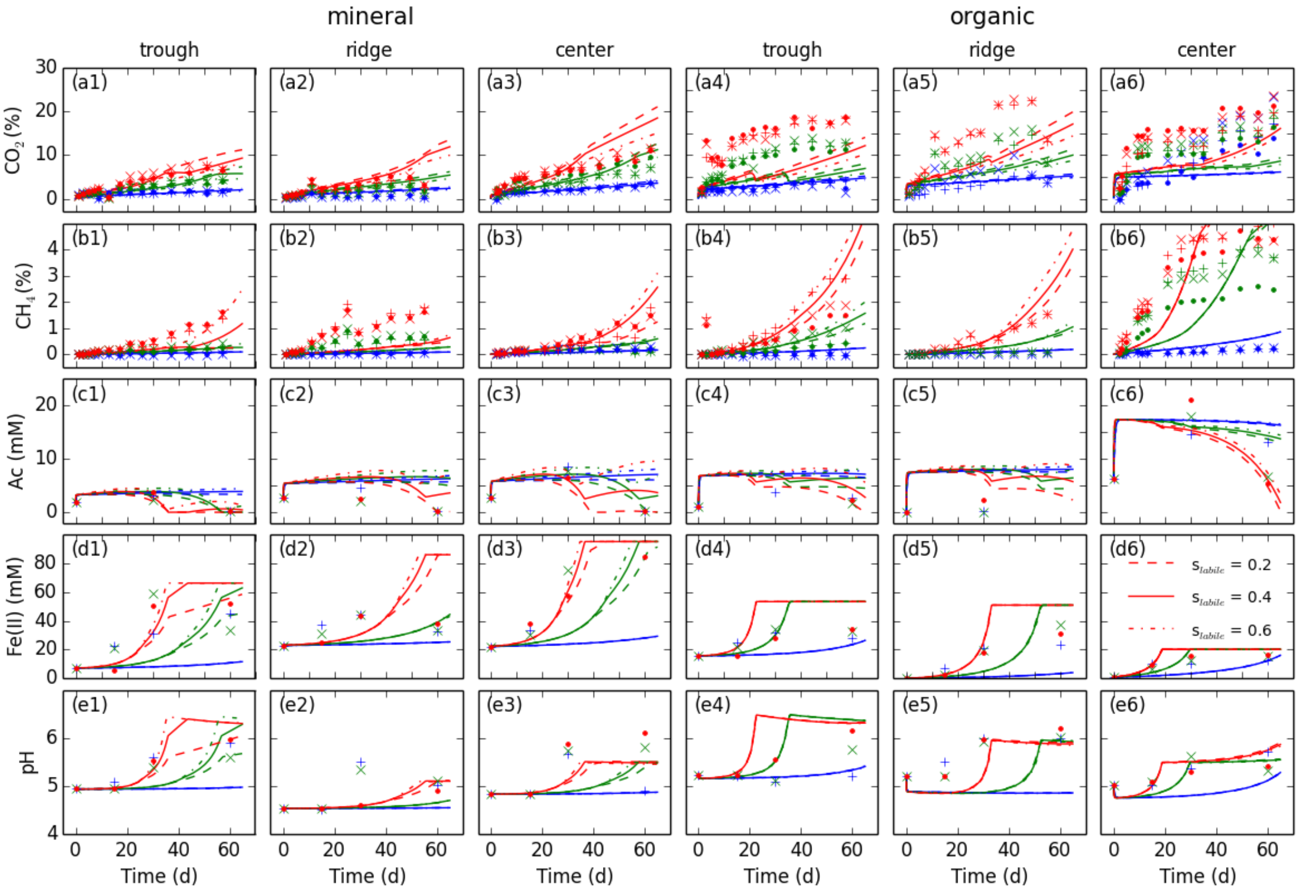


Figure S5: Impact of indirect respiration fraction (s_{labile}) on predictions: less direct respiration means more simple substrates for iron reduction and methanogenesis . See Fig.2 caption for more description about the model and experimental parameters.

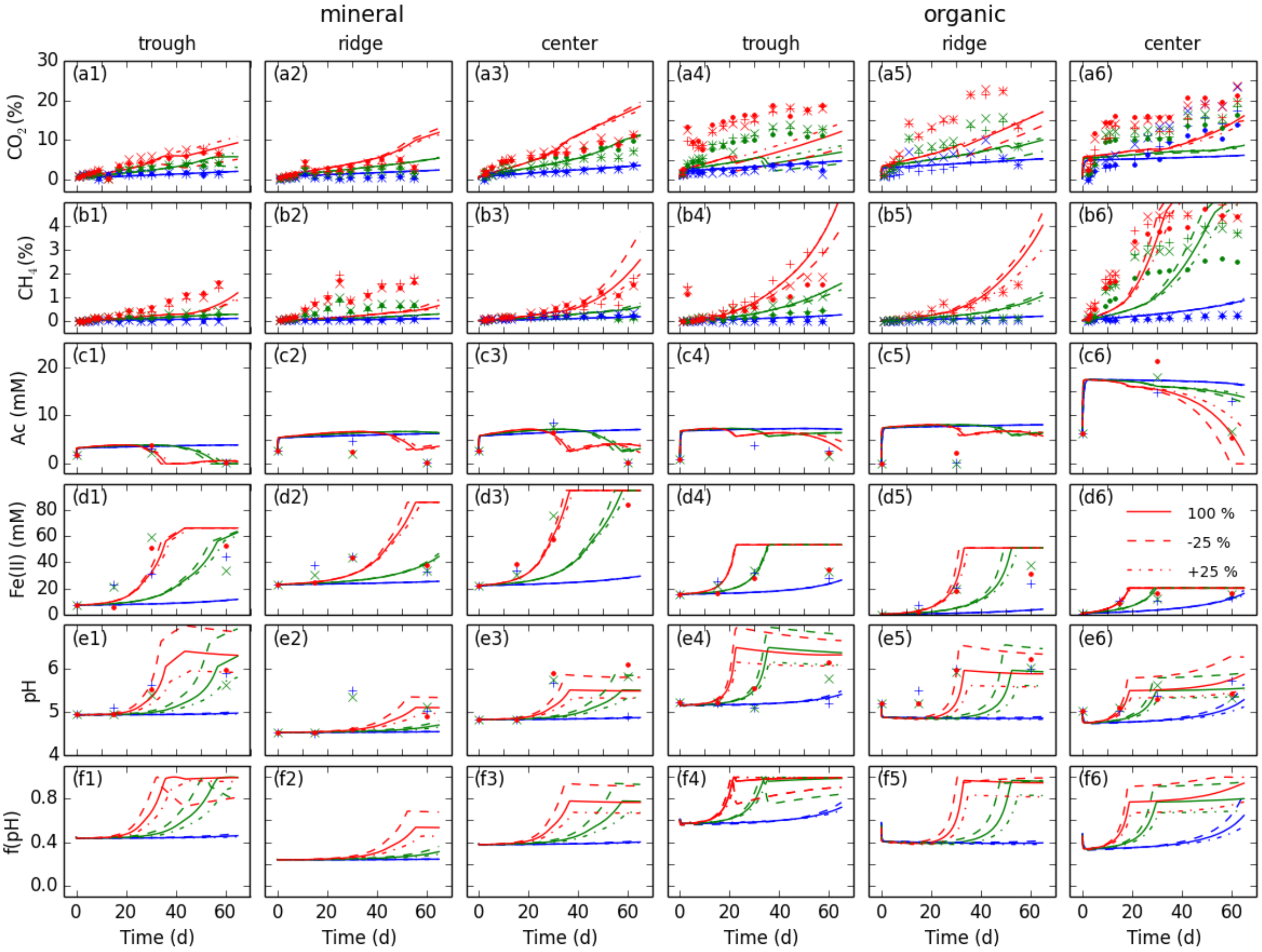


Figure S6: Impact of specified organic matter in WHAM on predictions~~.~~: more organic matter means more pH buffer. See Fig.2 caption for more description about the model and experimental parameters.

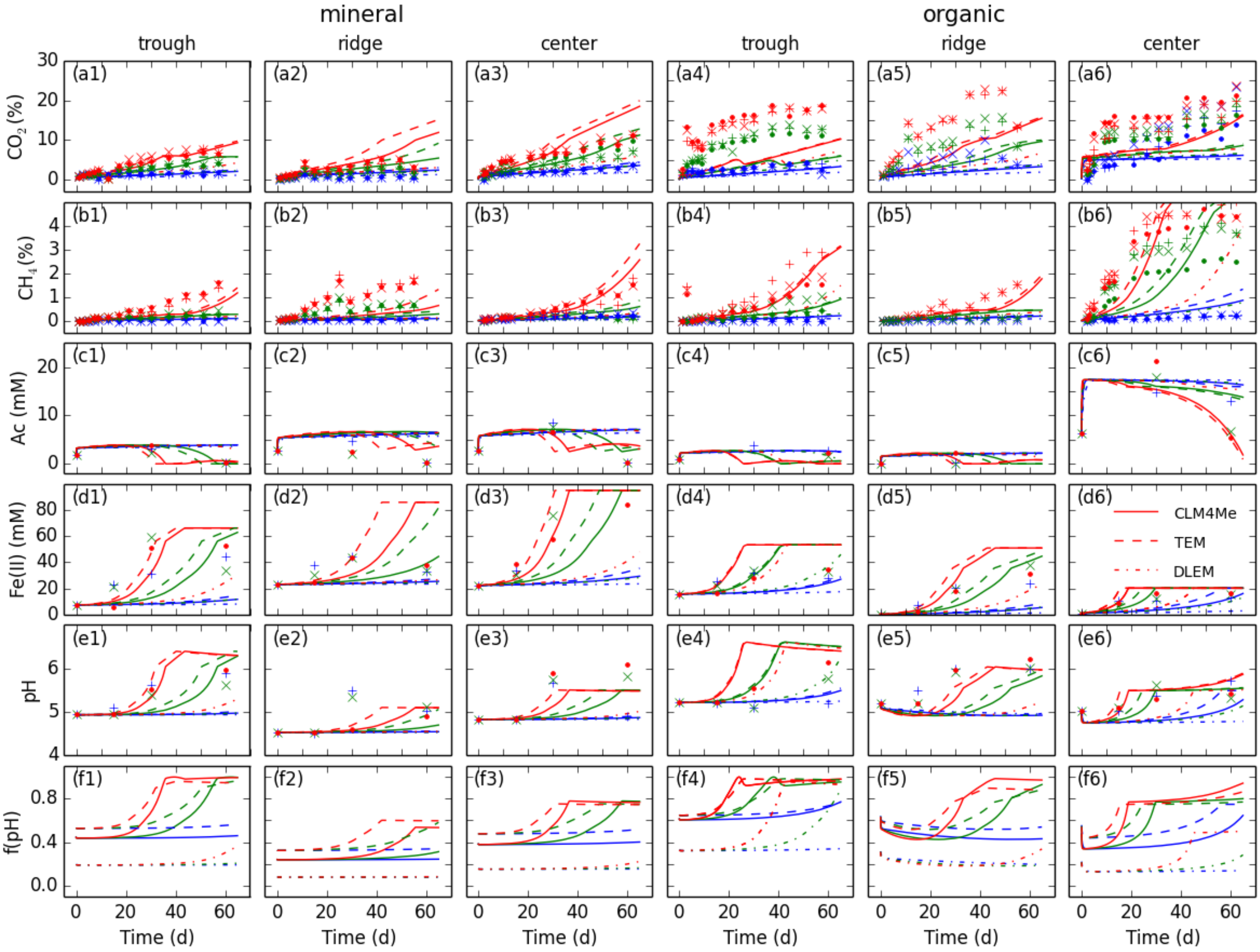


Figure S7: Comparison of the impact of different pH response functions (CLM4Me, TEM, and DLEM) on predictions. pH response function can be a substantial source of prediction uncertainty. See Fig.2 caption for more description about the model and experimental parameters.

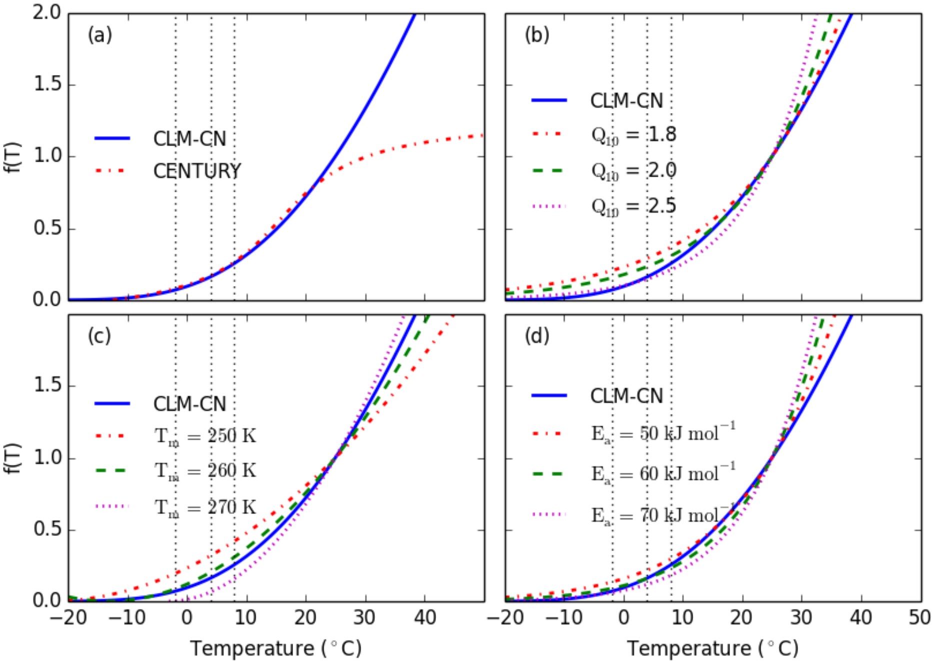


Figure S8: Fig. 7 with arithmetic vertical scale.

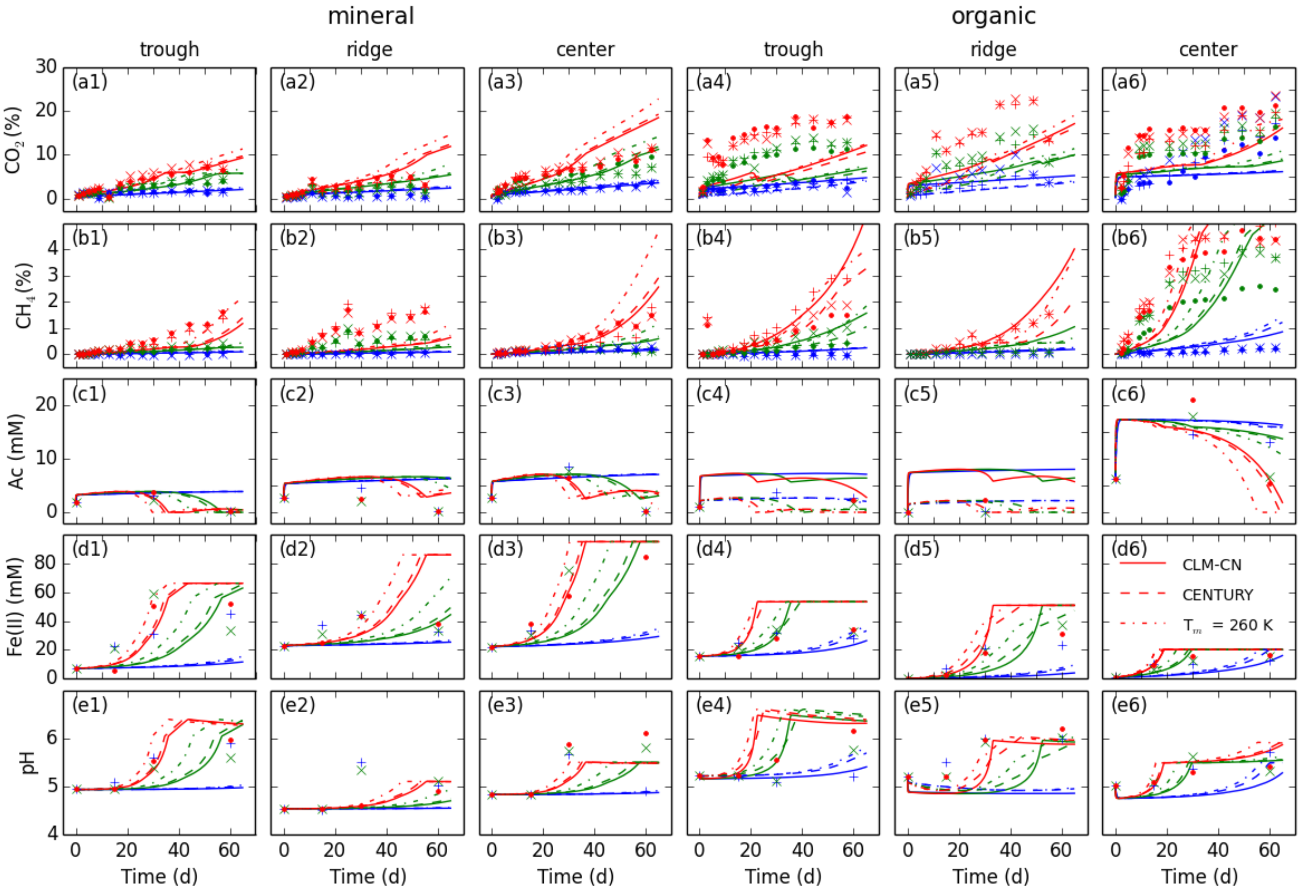


Figure S9: Comparison of impact of different temperature response functions (CLM-CN, CENTURY, Ratkowsky Equation with T$_m$ =260) on predictions. Predictions are sensitive to temperature response function, which can introduce large prediction uncertainty. See Fig.2 caption for more description about the model and experimental parameters.

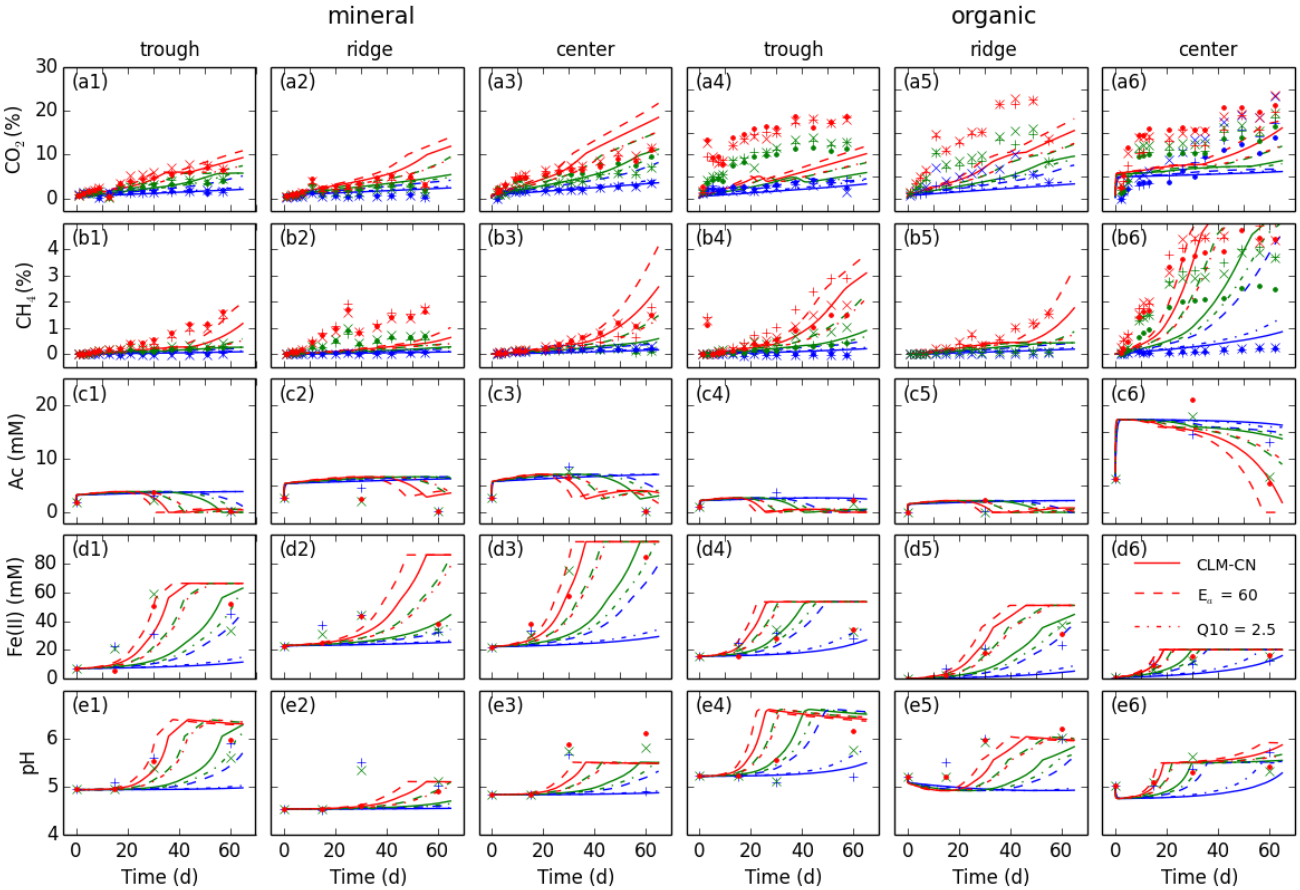


Figure S10: Comparison of impact of different temperature response functions (CLM-CN, Arrhenius equation (*E_a*), Q_{10} Equation) on predictions. Predictions are sensitive to temperature response function, which can introduce large prediction uncertainty. See Fig.2 caption for more description about the model and experimental parameters.

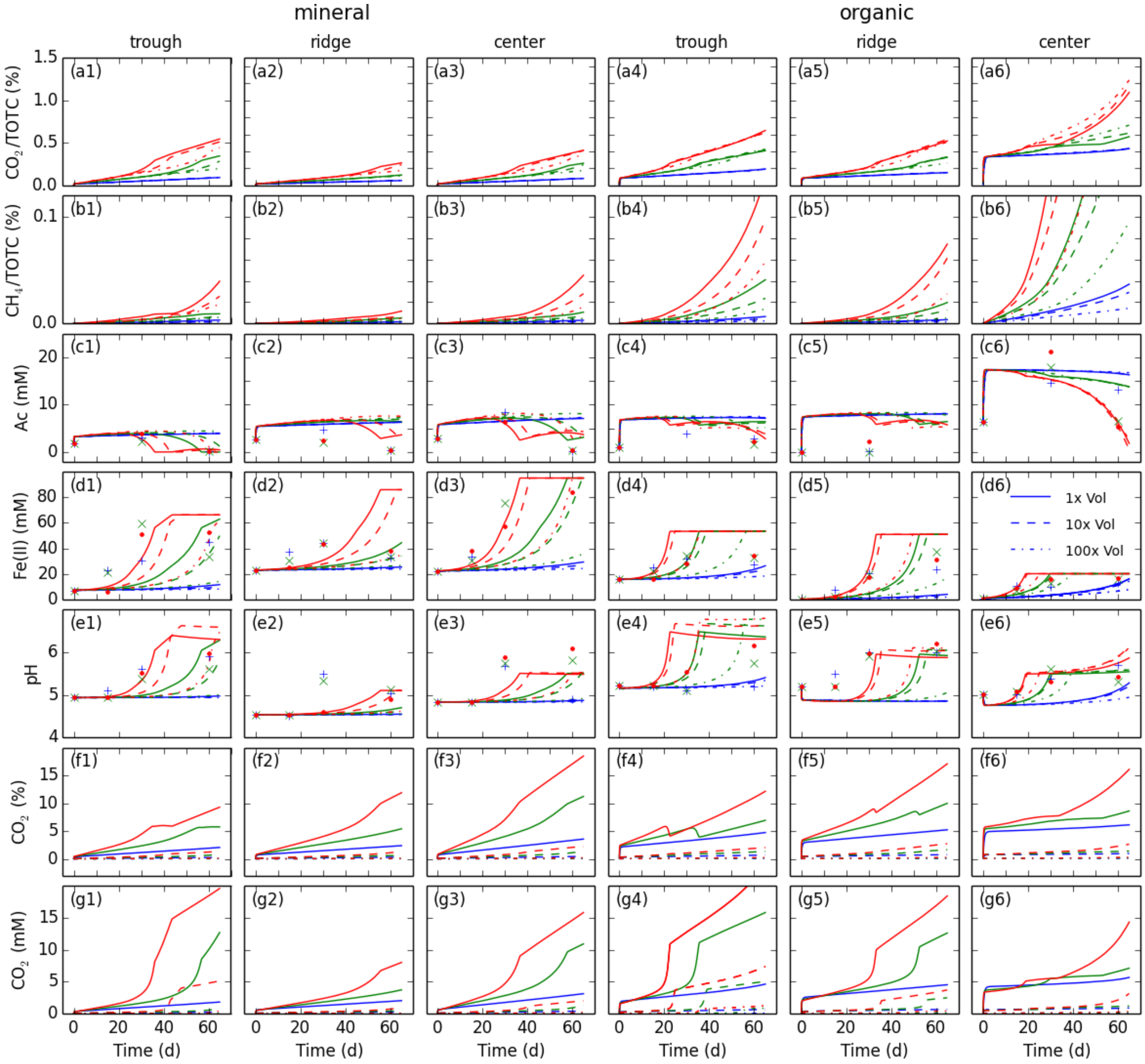


Figure S11: Impact of headspace volume on predictions: increase in headspace volume results in decrease in headspace (f1-6) and aqueous (g1-6) CO$_2$ concentration, slower pH increase and biogeochemical reaction rates, and generally less CO$_2$ and CH$_4$ production prediction. As an exception, predicted CO$_2$ production is increases with increasing headspace volume for the center oganic soils. The impact is not linear as the underlying biogeochemical processes are nonlinear. TOTC = initial total organic carbon. Ac = organic acids as acetate. See Fig.2 caption for more description about the model and experimental parameters. 5

References

Herndon, E. M., Mann, B. F., Chowdhury, T. R., Yang, Z., Wullschleger, S. D., Graham, D., Liang, L., and Gu, B.: Pathways of anaerobic organic matter decomposition in tundra soils from Barrow, Alaska, Journal of Geophysical Research: Biogeosciences, n/a-n/a, 10.1002/2015JG003147, 2015.

Roy Chowdhury, T., Herndon, E. M., Phelps, T. J., Elias, D. A., Gu, B., Liang, L., Wullschleger, S. D., and Graham, D. E.: Stoichiometry and temperature sensitivity of methanogenesis and CO2 production from saturated polygonal tundra in Barrow, Alaska, Global Change Biology, 21, 722-737, 10.1111/gcb.12762, 2015.