

## ***Interactive comment on “Biogeochemical model of CO<sub>2</sub> and CH<sub>4</sub> production in anoxic Arctic soil microcosms” by Guoping Tang et al.***

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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<sub>2</sub> 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

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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 CO<sub>2</sub> and CH<sub>4</sub> are not always free to release to the atmosphere. To assess the impact of CO<sub>2</sub> 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<sub>2</sub> 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. S11 e1-6). Eventually, the pre-

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dicted total CO<sub>2</sub> and CH<sub>4</sub> production generally decrease with lower headspace CO<sub>2</sub> concentration (Fig. S11a1-6,b1-6). However, the impact on CO<sub>2</sub> production is very small for the organic soils in the trough and ridge location, and the CO<sub>2</sub> production is predicted to increase with decrease in headspace CO<sub>2</sub> 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 S11: Impact of headspace volume on predictions: increase in headspace volume results in decrease in headspace and aqueous CO<sub>2</sub> concentration, slower pH increase and biogeochemical reaction rates, and generally less CO<sub>2</sub> and CH<sub>4</sub> production prediction. As an exception, predicted CO<sub>2</sub> production is increases with increasing headspace volume for the center organic 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.

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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<sub>2</sub> and CH<sub>4</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> 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 CH<sub>4</sub>, while the following sentences switched the focus away from simple substrates.

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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 H2 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

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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. We attempt to be balanced. We hope this is acceptable.

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

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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<sub>2</sub>) are abundant, iron reducers grow faster than methanogens when Fe(III) is not limiting (depending on the Fe(OH)<sub>3</sub>a 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) Biogeo-sciences, 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<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, Fe, etc.”

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

Response 15: revise " $f_{\text{mega}} = f_{\text{megh}} = 0.5f_{\text{ferb}} = 10^{-6}$ " to " $f_{\text{bio}} = 10^{-6}$ ,  $f_{\text{MeGA}} = f_{\text{MeGH}} = f_{\text{bio}}$ , and  $f_{\text{FeRB}} = 2 f_{\text{bio}}$ ".  $\text{som}_1$ ,  $\text{som}_2$ ,  $\text{som}_3$ ,  $\text{megh}$ ,  $\text{mega}$ , and  $\text{ferb}$  in the subscripts are changed to consistent forms as normal text throughout the manuscript.  $f_{\text{FeRB}}$  is twice  $f_{\text{MeGA}}$  or  $f_{\text{MeGH}}$  because  $\text{FeRB}$  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  $\text{HCl-Fe(III)}$  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  $f_{\text{Fe}} = 0.005$ " to "While bioavailable  $\text{Fe(III)}$  in soils is not well defined (e.g., Hyacinthe et al. 2006; Poulton and Canfield 2005), we start with  $f_{\text{Fe}} = 0.005$  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."

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Comment 18: P8L28, it appears that soil microcosms were not flushed after gas sampling. Without flushing headspace, CO<sub>2</sub> 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<sub>2</sub> on microbial activities likely explained why the CO<sub>2</sub> 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 CH<sub>4</sub> production. The center organic soils had the highest CH<sub>4</sub> 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

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where methanogenesis does not occur until all alternative electron acceptors that are more favorable than CO<sub>2</sub> 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 CO<sub>2</sub> production. Thus, it is not surprising that the models appeared to overestimate CO<sub>2</sub> 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 CO<sub>2</sub> concentration reached 3%.

Response 25: see response 1.

Comment 26: P12L6, Figure 3S, adsorption of CO<sub>2</sub> 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)<sub>3</sub> 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 CO<sub>2</sub> production.

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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  $-2^{\circ}\text{C}$ .

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.

Figure S11: Impact of headspace volume on predictions: increase in headspace volume results in decrease in headspace and aqueous  $\text{CO}_2$  concentration, slower pH increase and biogeochemical reaction rates, and generally less  $\text{CO}_2$  and  $\text{CH}_4$  production prediction. As an exception, predicted  $\text{CO}_2$  production is increases with increasing headspace volume for the center organic 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.

Marked revised manuscript will be available in response to referee #1.

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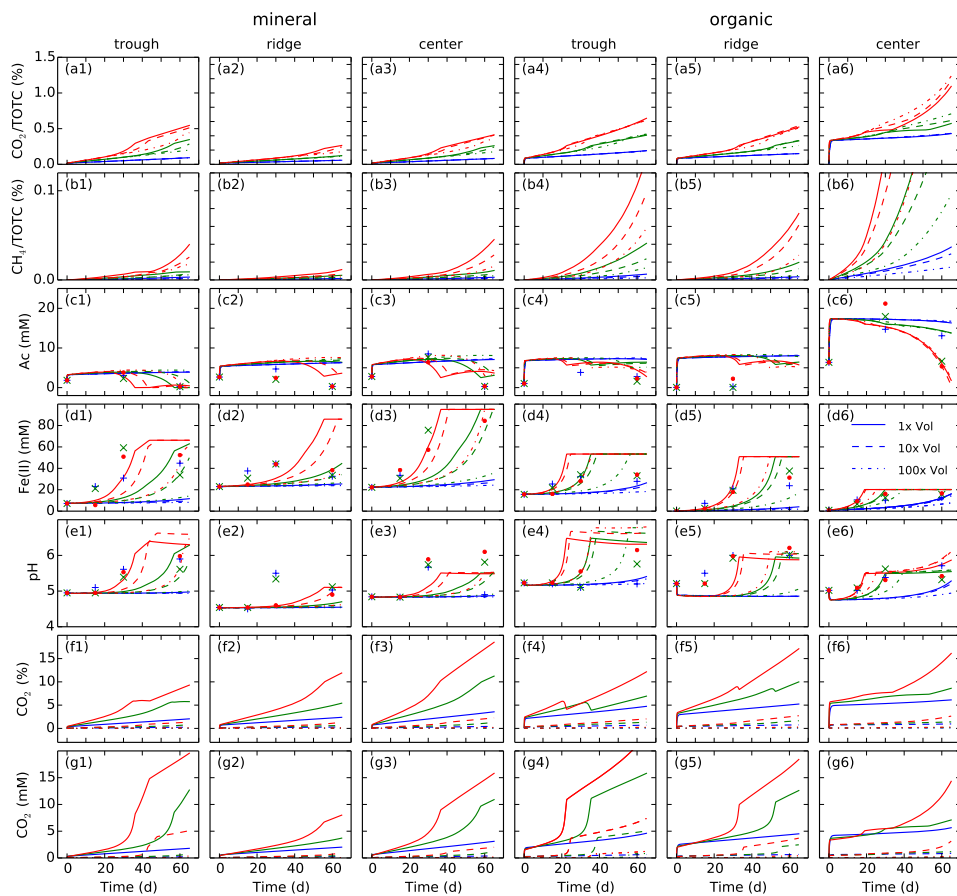


Fig. 1.