Biogeosciences
Discussions
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Responses to (in italic font):

Interactive comment on "Representing methane emissions from wet tropical forest soils using microbial functional groups constrained by soil diffusivity" *by* Debjani Sihi et al.

Anonymous Referee #1

Received and published: 22 August 2020

The study "Representing methane emissions from wet tropical forest soils using microbial functional groups constrained by soil diffusivity" by Sihi et al. tries to explain soil methane emission dynamics in tropical forest soils of Puerto Rico during normal and drought conditions. They combine field measurements with modelling efforts (Microbial Model for Methane Dynamics-Dual Arrhenius and Michaelis Menten (M3D-DAMM). Overall, I think it is a really nice study that tries to combine microbial with biogeochemical data to investigate ecosystem methane dynamics. However, I have some general and some minor comments.
Thank you kindly for the positive comments and for the constructive suggestions that really strengthened our paper.

The authors should describe the concept of "microsites" more in detail. The authors focused on the top 10 or 10-30 cm of their Ultisol although methane production/consumption dynamics in the deeper clay-accumulating horizons may be more important for the overall net methane emissions from their Ultisols. The authors do not discuss that and do not compare with other soils. How does the abundance of microsites change with soil type, soil depth and other ancillary variables?
Our sampling strategy, both of soils and of soil water, are geared to accompany the greenhouse gas flux measurements which are taken on the soil surface. Past studies (Silver et al. 1999) have taken methane concentrations at depth in similar soils, and found that concentrations are higher at 10 versus 35 cm. Examination of the soils in the Luquillo mountains have found that SOC maximums are around 35 cm depth (Johnson et al. 2014). For this site, clay is abundant at shallow depths, e.g., 20-30% clay at 0 to 10 cm depth (L177). Therefore, we designed our sampling strategy for shallow depths. We added text and the Johnson citation to a revision to ensure readers also understand this concurrence of sampling strategy and past observations (L189-194).Thanks for pointing this out; adding these details helps the manuscript.

There are no specific measurements of microsites at any depth at this site; microsites are inferred because of many observations of co-occurrences of oxygen concentrations in the soil along with CH_4 fluxes; and because of the rich clay, iron oxides, and visible redox mottling, particularly evident in the valley and slope soils (papers cited in L111-134). Techniques for measuring microsite activities remain very limited to date, here or elsewhere (L134). We added this information to in a new methods section 2.4.3 devoted to microsite modeling (L457-462).

We will address the issue of comparison to other soils in response to a more detailed question below.

Minor comments: L22-25: Is it important to give this information? I would only include the most significant ones that support your guiding questions! What is the difference between "<" and "«". The abstract should self-explanatory.
Good point thank you. We simplified the abstract and the manuscript throughout by using only < or >; it was a subjective difference between "<" and "<<". The geochemical parameters in L23-25 were measured and are key model inputs, so we rephrased to say they were measured at the field site, but we removed the parenthetical material regarding differences in their values with respect to topographic

positions which is not germane to the abstract.

L33: write aceticlastic methanogenesis instead of "acetotrophic" and "acetoclastic" (check the whole manuscript)
Thank you for catching these typos; corrected as suggested.

L43: what are wet tropical forest soils? What are wet tropical forests and what is the difference between wet tropical forest soils and upland soils? How do you define that?
The soils are classified as wet tropical forest soils according to the Holdridge life zone system, which considers rainfall, elevation, latitude, humidity, and evapotranspiration, as described specifically regarding the Luquillo Experimental Forest (Harris et al. 2012). Upland refers only to topography. The soils in our current study (including the valley soils) could be referred to as "upland" in that they are all located in a lower montane region (~350 m elevation). We added the Harris citation and a description of what is meant by "wet" tropical forest soils to the methods (L156). See also L88 that mentions that upland tropical soils can produce methane.

L53-65: What are the soil types in the different studies? Since methanogenesis and methanotrophy are substrate-limited, the soil type with its specific biogeochemistry is very important. The authors mention that there are several studies that report effects of drought on net methane emissions across different wet tropical forest soils. Consequently, they should mention the different soil types.
We added the soil type (below) when the studies were mentioned in L97-105 and elsewhere as relevant.
Aronson et al. 2019 (Costa Rica) Oxisols
Davidson et al. 2004, 2008 (Brazil) Oxisols
Wood and Silver 2012 (Puerto Rico) Ultisols with a similar climate and parent material
O'Connell et al. 2018 (Puerto Rico) Ultisols, same soils as current study

L66-74: Oxygen may not be the only factor for methane emissions upon rewetting. The observed rapid flush of methane in response to a wetting event may be driven by rapid depletion of other electron acceptors, as well. The major focus of this paragraph is on oxygen but what is with acetate, H2 and CO2?
We concur with the reviewer's suggestions; in fact, that is part of the reason we initiated this study. We wanted additional data on acetate concentrations, and to use a predictive model to better understand the conflicting/collaborating roles of oxygen, substrate, and microbial biomass in controlling methane emissions. In the revision, we clarified the role of these different substrates in controlling methane emissions in this paragraph so it does not appear we are only focused on oxygen. We also discussed their availability in terms of soil moisture and diffusion limitations (L113-125).

L85-86: and why not H2 and CO2? How do you account for acetate formation during fermentation and homoacetogenesis? How do you account for syntrophic acetate oxidation? How can you explain the "contrasting patterns of observed CH4 emissions", when sources and sinks of acetate etc. is not measured or simply not known?
Here, we use the model to provide quantitative answers in accordance with specific hypotheses stemming from the O'Connell et al. 2018 paper. The idea of this paper is to consider a relatively simple set of mechanisms and see how well a model that quantitatively represents these mechanisms can explain the complex observations. This study used a model where the production of methane is modeled by acetoclastic and hydrogenotrophic mechanisms only, and consumption by methanotrophy. Acetate is based on measurements of soil water. There are not measurements to constrain H2 concentrations, but CO_2 concentrations in water are estimated according to the pH. Acetate is formed by fermentation and by homoacetogenesis as defined in Xu et al. (2015) in Eq A15 and 16 in their appendix, see also our revised Fig. 1b and caption. There is a pH feedback to acetate production that affects methanogenesis (Eqn 7) that is also described in Fig 1b caption. The model is not completely comprehensive and syntrophic acetate oxidation is neglected. In modeling, we balance parsimony and mechanisms and data limitations; we have made choices here mostly following the original model design (Xu et al. 2015). We describe the impact of some neglected processes in Section 4.3. We added that homoacetogenesis is included and that syntrophic acetate oxidation is neglected in the methods Section 2.4.1 in the revision (L280-281).

L97-105: The dominant soil type in the current study is Ultisol. I guess the whole

methane cycling will be very different in other tropical soils (What is with Oxisols?) What are the soil types in the other studies mentioned in the introduction? It would be great to see a more detailed description of the soil type. How did bulk density change with depth? At what depth does clay accumulation (subsurface zone) start? How big is the eluvial horizon?

The response to this comment also includes response to the first detailed review comment (request for comparison to other soils). The soil types of the other tropical studies of methane releases from the introduction are mentioned in a reply above. The studies in Costa Rica and Brazil on Oxisols were specific in showing that methane consumption was the major effect of the seasonal El Niño cycle (Costa Rica) or imposed drought manipulation (Brazil), which was similar to here. Only the O'Connell et al. (2018) study showed the enhanced released of CH_4 during post-drought recovery. We cannot say for certain if the O'Connell observations are related to soil type. Oxisols, because of their high oxide and clay contents, may also have microsites. In particular, hematite clay minerals (found in both soil types) enhances formation of soil aggregates because of their high surface area and charge properties. Soil organic matter can also enhance aggregation and at the same time consume O_2. So we added a statement in the introduction (with the soil type mentions) to note that these mechanisms for aggregate formation might also lead to anaerobic microsites in Oxisols and Ultisols (L131-134).

We have data on bulk density up to 1 m that are in press with Ecology and Evolution (K. Cabugao et al., in press). In that manuscript we find that on the surface, bulk density ranges from 0.5 to 0.7 g/cm3. By 25 cm depth, bulk density is 0.8 to 1.1 g/cm3. These results are similar to those published by Johnson et al. (2014) and Silver et al. (1999) at nearby sites in the same forest. See L185-185.

A publication that provides a detailed soil survey in the immediate vicinity of the field site (Soil Survey Staff, 1995) lists the following soils: Zarzal, Cristol, and Prieto soils. For all soils, the litter layer is minimal due to very rapid litter decomposition rates (Parton et al. 2007, Cusack et al. 2009). For the Zarzal soil, the surface (A) horizon is usually 4 cm thick, and the B horizon is around 150 cm thick. The Cristol soil surface horizon is listed as 6 cm thick, and B horizon to around 150 cm thick. The Prieto soil surface horizon is listed as 6 cm thick, and B horizon to around 130 cm thick. We added this information and the citation to the site description (L181-183).

L107: Why was soil only sampled from the top 10 cm of the soil? I guess methane consumption dominates at the surface due to oxic conditions while in the deeper soil horizons methane production dominates due to more anoxic conditions.

These soils are very rich in clays with high NPP and high surface C inputs (Weaver and Murphy, 1990), beginning at the interface with the atmosphere, and are often very wet, and many lab- and field-scale studies by the Silver group (see various citations in the manuscript) confirm that methane production can occur in soils at shallow depths, especially in the valley soils and to a lesser extent in the slope and ridgetop soils. The soil flux chambers are on the soil surface and the sampling strategy was designed to focus on near-surface measurements that are relevant to surface monitoring, as described above and in another comment response below.

L111-114: What was the detection limit for acetate?
We assumed it was equivalent to the lowest standard by HPLC analysis, i.e., 0.5 μM.

L117-120: The chemical data (what chemical data? Only pH?) for bulk soil is from the 0-10 cm soil depth and acetate and DOC from the pore water from 10-30 cm soil depth? I do not understand how you relate this information, taken from different soil depths, to each other. Finally, where do you find or where do you assume these microsites? (only in the top 10 cm or below? Or may be even below 30 cm?

We assume that soil flux chambers placed on the top of the soil surfaces are dominated by fluxes from relatively shallow depths. A summary of fluxchamber methods by two experts in this field states that it is usually assumed surface chambers measure fluxes from about 25 cm in depth (Rochette and Hutchinson 2005). Given this perspective, we collected soil and soil water measurements from the 0 to 30 cm depth to best relate to surface flux chamber measurements. The chemical data used in this study consisted of acetate and DOC from the lysimeters located at a minimum depth of 5-10 cm and a maximum depth of 25-30 cm (the lysimeters are 5 cm in length). The soil samples on which pH were measured were collected from 0-10 cm depth. See L189-194 and L259.

Microsites are inferred by observations such as originally presented in O'Connell et al. (2018), i.e., sudden releases of methane during post-drought recovery; and from seminal publications such as Silver et al. (1999). In the latter, co-occurrences of soil oxygen and methane in bulk soils presume the abundance of anaerobic microsites in the soils. Because the soils have abundant clay and iron oxides at all depths, it is likely that microsites are pervasive throughout. This has also been observed repeatedly in soil incubation studies using surface soils from this. See section 2.4.3.

L144-148: What is with methylotrophic methanogenesis. You should discuss about the potential contribution of methylotrophic methanogenesis (see Norrow et al. 2019).
Our model does not include methylotrophic methanogenesis. We will add this to the mention of several other processes not considered in our model in Section 2.4.1 and cite the relevant paper (L282).

L173-174: Why not?

We believe the reviewer is asking why iron reduction and oxidation are not included in this study. As explained in L300 in the methods and in Section 4.3, we chose to take a more simplified approach to start, just focusing on substrates and microbial functional groups for methanogenesis (both aceticlastic and hydrogenotrophic) and methanotrophy. We feel that our model does a reasonable job at reproducing the data, considering "normal" and "drought" conditions, and involving two different time frames of data collection, and we consider that as confirmation of the validity of our approach. We acknowledged in Section 4.3 that iron reduction can alter the pH of the soils and soil water and enhance methane emissions; and that iron reduction can also support anaerobic methane oxidation, as well as using acetate as a substrate and thereby reducing net methane emissions. We acknowledge that our model fits are not perfect, as you can see from Fig 3, the model misses the highest methane fluxes seen during the post drought. This could be a result of not considering the pH effects of iron reduction that enhance methanogenesis. However, other processes in the iron cycle reduce methanogenesis, so the benefit of including unconstrained iron cycling processes is unclear without additional information to constrain the model. Therefore, we felt it was appropriate to focus only on the mechanisms covered in this study.

L206: Why 15 cm?

This is the average depth sampled (ranges from 0 to 30 cm).

L214: How do calculate "total microsites"? I would assume that there are way more microsites in clayey horizons below 15 or even 30 cm soil depth? Overall, I think you have to explain the concept of microsites, more in detail? You are scratching only the soil surface at the moment but in my opinion the biggest methane production potential occurs in deeper parts of the Ultisol.
A seminal study in 1999 by Silver et al (cited in our manuscript) in a nearby Ultisol soil took measurements of methane and oxygen at 10 and 35 cm depth, as well as surface chamber flux measurements. The authors found that CH_4 concentrations were higher at the shallower depths. Most of the subsequent papers from Luquillo Experimental Forest used surface chamber measurements and focused on shallow soil depths, pls see L189-193 We surmise that perhaps diffusion would be quite slow at greater depth in these rich clays, that substrate (SOC) availability which is maximum at 0-30 cm would also be lessened, and that microbial biomass would be lower (Hall et al. 2016). Therefore, we focused on shallow depths.
We assumed that size of the microsites should be at least an order magnitude lower than the bulk soil measurements we had for soil CH_4 fluxes. Using this logic, we decided that "diameter" of microsites should be in "mm" scale as the diameter of soil chambers we used are in "cm" scale (15.24 cm). Thus, we did the math to come up with the number of "total microsites" (i.e. 10000) such that the diameter of microsites below each chamber meets our criteria, following Sihi et al. 2020a. We added this to the methods Section 2.4.3.

L270-272: Why are acetate and hydrogen production decreasing when aceticlastic and hydrogenotrophic methanogenesis also decrease? Aceticlastic and hydrogenotrophic methanogens consume acetate and hydrogen, respectively. So, if there is a decrease in aceticlastic methanogens, I would first assume an increase in acetate concentration and thereafter a sharp decrease if oxygen levels further increase.
Good catch, thank you, the cause and effect in that sentence was inverted (L611). It

now reads: "Simulated decreased production of acetate and hydrogen during the 2015 drought in the ridge and slope positions resulted in decreased biomass of aceticlastic methanogens and hydrogenotrophic methanogens (Figs. S5, S6)."

L280: How do explain that?
We believe the reviewer is referring to predicted changes in the biomass of different microbial functional groups during drought, drought recovery, and post-drought. These are model predictions, that are based upon the mechanisms within the model, and the input data that constrains model behavior (pH, acetate, DOC, and CH_4 fluxes). Although we lack measurements of the microbial biomass of specific microbial taxonomies or functional groups during the events in this paper (as we acknowledged), microbes can respond rapidly to changes in their environment. It is important to distinguish that the model is predicting changes in biomass of a particular microbial functional group and is not predicting large changes of the bulk microbial biomass in the soil. Bulk microbial biomass in the soil is likely to double or perhaps quadruple in response to changes in conditions, but individuals can grow exponentially (Goberna et al. 2010; Pavlov and Ehrenberg 2013; Roussel et al. 2015; Buan 2018). Please see L866.

L286-287: Why does the increasing production of acetate lowers the pH?
Acetate production is a source of proton (Eq 7 and Fig. 1).

L301-306: If the diffusion of H2 increases during drought, one may think that hy- drogenotrophic methanogenesis should increase as well. However, it does not in- crease because of increasing oxygen levels. That should be made clear!
This is true, particularly for the ridge and slope soils, please see clarification in L657 in Section 3.3. It is somewhat less true for valley soils, L669, so no changes were made there.

L304-309: The diffusion of acetate increases upon rewetting but that of H2 decreases. Why do you observe an increase in overall gross methane production. First, I would assume that under relatively acid conditions, hydrogenotrophic methanogenesis dom- inates. I think the overall increase of methane emissions upon rewetting is because of oxygen depletion and therefore the stimulation of methanogenesis in general . . .. and not because of increasing acetate concentrations or a shift in the methanogenic pathway of methane formation. If it is really aceticlastic methanogenesis that is stimu- lated, you should provide some isotopic data. There is competition for acetate between several microorganisms. In the end it could be simply stimulation or inhibition of fer- mentation or homoacetogenesis that drives changes in the amount of observed acetate concentrations.
The main issue is that CH4 emissions are not normally found in the ridge and slope soils (eg, see 2016 data), so a response of a simple increase in methanogenesis cannot explain the observations. The mechanism of hydrogenotrophic methanogenesis does not well explain the observations because as the soils wetted, hydrogen gas would become less available as its diffusion rate will decrease strongly (Fig. S8). Further, the turnover rate of H_2 in shallow soils is very high, so it is less likely (than a solute) to accumulate in microsites (Xu et al. 2015). Acetate diffusion in solution, however, more readily explains the observations (Fig. S8). As wetting commenced and progressed, acetate in solution may become more available to microorganisms and can enhance methanogenesis. At the same time, wetting decreases O_2 availability, decreasing the role of methanotrophy (Fig. S8) and allowing more methane to escape the subsurface, despite limitations in gas diffusion. Methanogenesis is definitely enhanced in response to decreasing O_2 as the reviewer points out. Text in the discussion supporting this interpretation (L732): "The return to dominantly reducing conditions also was predicted to stimulate fermentation and the production of acetate through homoacetogenesis (Fig. S6). Enhanced production and diffusion of acetate during recovery (Fig. S8) triggered growth in the predicted biomass of aceticlastic methanogens (Fig. S5), which in turn, increased rates of aceticlastic methanogenesis (Fig. S9)." See also L737: "Although secondary to aceticlastic methanogenesis, simulated rates of hydrogenotrophic methanogenesis also increased in anaerobic microsites (Figs. S9, S10), mediated by increased production of H_2 and subsequent stimulation of the biomass of hydrogenotrophic methanogens during the drought recovery in 2015 (Fig. S5)." The sensitivity analysis (Fig. 8) shows a stronger control by aceticlastic methanogenesis that by hydrogenotrophic methanogenesis. Both are important, however.

Unfortunately, there were not isotopic data available for the field study; these type of data are rarely available at the field scale. Assessing patterns in isotopic fractionation or even

isotope tracing (gross rates or label chasing) would make an interesting experiment for future research.

L318: Again, how do you define the microsites?
In addition to revising the methods section 2.4.3 as suggested above, we have revised Fig. 1 caption as follows:
"Top panel (a) shows the model representation of soil microsite distribution (modified from Sihi et al., 2020a, also see Eq. 14). The cylinder refers to the volume beneath the soil chambers. The intensity of different cylinder colors figure refers to rate of a process or the intensity of a concentration inside microsites in each theoretical cylinder, e.g., a dark color means a higher rate/intensity, and a light color means a lower rate/intensity for a given process. The 2D graph on the right refers to the probability density function of the rate of the process or intensity of the concentration in the bulk soil. A wide distribution skewed to the right (dark line) implies higher bulk rates of the process or higher concentrations, and a narrow distribution skewed to the left (light line) implies lower bulk rates of the process or lower concentrations, of any of the following: solute concentration [S_i], gas concentration [G_i], soil moisture ($SoilM_i$), gas and solute diffusion ($Diff_i$), methane production ($Prod_i$), and methane oxidation (Ox_i)."

We have revised the figure from the original as follows: Add an arrow on the x axis pointing towards the right, denoting increasing concentrations or rates. Moved the light-colored probability-density function to the left of the dark-colored probability-density function and make it much more narrow and signify less impact on bulk rates/concentrations compared to the dark-colored function (more impact on bulk rates/concentrations).

L346-348: Again, what makes you so sure that it is acetate that drives net methane emissions and not H2/CO2 and a decrease in oxygen?
All of these processes are happening simultaneously. Our model simulation suggests that acetate is driving most of the CH_4 increases, and that decreases in methanotrophy due to decreases in oxygen, are both more important than hydrogenotrophic methanogenesis. Please see also the sensitivity analysis in Fig 8. Fig S5 shows that both kinds of methanogens increase during drought recovery and post-drought, but that acetotrophic methanogens are two orders of magnitude more abundant than hydrogenotrophic methanogens. Additionally, the acetate hypothesis is supported under drought condition as acetate may accumulate in microsites. During wetting, the acetate may become more available to the methanogens as solute diffusion becomes enhanced (Fig. S8), resulting in higher CH_4 production. The model simulations suggest that hydrogen diffusion is lessened under wetting conditions which is consistent with what we might expect for a gas diffusing through a liquid versus diffusing through air (Fig. S8). So, hydrogen substrate availability does not completely explain the observations of higher CH_4 production under wetting conditions, but it is a contributor. The low contribution of H_2/CO_2 is also caused by low concentration and high turnover rate of H_2 in soil; particularly in the top soil, which is where this experiment was carried out. Please see L737-752 for improved explanation.

L369-372: and homoacetogenesis?
Yes, please see L733.

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Discussions

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Responses to (in italic font):

Interactive comment on "Representing methane emissions from wet tropical forest soils using microbial functional groups constrained by soil diffusivity" *by* Debjani Sihi et al.

Anonymous Referee #3

Received and published: 26 August 2020

The manuscript of Debjani Sihi and colleagues brings up a very interesting topic on disentangling gross methane emission and uptake from wet tropical forest soil using a combination of microbial functional group CH4 model and a diffusivity module. This work clearly shows how landscape topography and climate affect net CH4 emissions due to shift of substrate production, soil redox conditions, and diffusivity of O2, H2, and acetate under drought and recovery phases. The experimental work is well performed, convincing and well discussed in the context of previous literature. The manuscript is well organized and clearly written and I enjoyed reading it. I only have a few comments that should be addressed:
Thank you kindly for the positive comments and for the constructive suggestions, all of which we have adopted.

Line 54 Should it be "increased consumption of atmospheric CH4"?
Good catch. Thank you, the manuscript is corrected as suggested (L99 in the tracked version [note: all line numbers refer to tracked version).

Line258 The correlation seems stronger and more negative in 2015 (-0.36) than 2016 (-0.61).
The reviewer is correct. The sentence L601 is changed to "The correlation between CH4 emissions and O2 concentrations was stronger and more negative in 2015 than 2016."

Line 321-322 You defined pre-drought period from DOY 57-115 instead of DOY 200. The details in results should be checked.
Yes, we mean to say "during the drought period (DOY 200) (L688)". We will double-check all other similar references and ensure there are no additional errors. Thank you.

Fig. 1 I appreciate the conceptual figures herein, but it looks a bit confusion and I do not well understand what means in panel a. How to relate microsite frequency with soil properties?
*We agree this figure and its description could use some revisions. Our caption says currently: **Top panel (a) shows the model representation of soil microsite distribution (modified from Sihi et al., 2020, also see Eq. 13). Different shades indicate substrate concentration [Si], soil moisture (SoilMi), diffusion (Diffi) of solutes and gases, production (Prodi) and oxidation (Oxi) processes at each microsite.***

We revised the caption, extensively, as follows:
"Top panel (a) shows the model representation of soil microsite distribution (modified from Sihi et al., 2020a, also see Eq. 14). The cylinder refers to the volume beneath the soil chambers. The intensity of different cylinder colors figure refers to rate of a process or the intensity of a concentration inside microsites in each theoretical cylinder, e.g., a dark color means a higher rate/intensity, and a light color means a lower rate/intensity for a given process. The 2D graph on the right refers to the probability density function of the rate of the process or intensity of the concentration

in the bulk soil. A wide distribution skewed to the right (dark line) implies higher bulk rates of the process or higher concentrations, and a narrow distribution skewed to the left (light line) implies lower bulk rates of the process or lower concentrations, of any of the following: solute concentration [S_i], gas concentration [G_i], soil moisture ($SoilM_i$), gas and solute diffusion ($Diff_i$), methane production ($Prod_i$), and methane oxidation (Ox_i)."

We also revised the figure from the original as follows: Add an arrow on the x axis pointing towards the right, denoting increasing concentrations or rates. Moved the light-colored probability-density function to the left of the dark-colored probability-density function and make it much narrower and signify less impact on bulk rates/concentrations compared to the dark-colored function (more impact on bulk rates/concentrations).

Do substrate concentration, soil moisture, diffusivity of solute and gas present the similar pattern for one kind of microsite?
The frequency distribution for the microsites is the same for all of these, according to Eq 14. But, the diffusivity of liquids is according to Eq 11 and 12; diffusivity of gasses according to Eq 8, 9, and 10. Here is a little more information on the microsites that is included in a new methods Section 2.4.3 devoted to microsites: We assumed that size of the microsites should be at least an order magnitude lower than the bulk soil measurements we had for soil methane fluxes. Using this logic, we decided that "diameter" of microsites should be in "mm" scale as the diameter of soil chambers we used are in "cm" scale (15.24 cm). Thus, we did the math to come up with the number of "total microsites" (i.e. 10000) under each fluxchamber such that the diameter of microsites meets our criteria, following Sihi et al. 2020a. This is why the frequency of microsites is the same for both low rate/intensities (light yellow line Fig 1a) and high rate/intensities (dark line Fig 1a) (see also Fig. 7 in manuscript and Fig. S10 in SI)."

Why this figure links to Eq.13?
This figure 1 should link to Eq 14; apologies for the confusion and thank you for the catch. It is corrected in the revision.

Also in panel b, it would be more clear for readers if you could adjust it to a better shape or based on the clue of the present study. Can you try to improve the conceptual figure and clarify this in the legend?
We removed the Air/Soil diagram at the top of this figure, and the word "solute diffusion" from the figure. Panel b should only represent the geochemical pathways that the model is representing, and we should rely on panel (a) to address diffusion. We hope that makes the content of both panels more understandable.

We revised the caption from the current version: **Bottom panel (b) is the schematic of the microbial functional group-based model coupled with a diffusivity module (Microbial Model for Methane Dynamics-Dual Arrhenius and Michaelis Menten, M3D-DAMM) for simulating soil methane (CH_4) dynamics in field soils (Modified from Xu et al., 2015), where SOM = soil organic matter, CO_2 = carbon dioxide, DOC = dissolved organic carbon, H^+ is the hydronium ion, and H_2 = dihydrogen molecule.**
Revised figure caption: Bottom panel (b) is the schematic of the microbial functional group-based model for simulating soil methane (CH_4) dynamics in field soils (modified from Xu et al., 2015). The schematic represents the decomposition of soil organic matter (SOM) and plant litter into carbon dioxide (CO_2) and dissolved organic matter (DOC); the production of acetate and hydronium ion (H^+) from decomposition and fermentation of DOC which also decreases pH, the production of acetate and hydronium ion (H^+) from homoacetogenesis which decreases pH; and the production of dihydrogen ion (H_2) and CO_2 from decomposition of DOC. The intermediary products then have three possible non-mutually exclusive pathways (1) acetoclastic methanogenesis, which is the production of methane from aqueous acetate found in soil solutions, (2) hydrogenotrophic methanogenesis, which is the production of methane from hydrogen, and (3) methanotrophy, which is the oxidation of methane into carbon dioxide.

Fig.3 and 4 The label of y-axis for soil moisture and oxygen should between 0-1 rather than 0-100, as the unit is V V-1. Otherwise, the unit should change to %.
Thank you for pointing this out. We adjusted the unit of the axes in Figs 3 and 4,

S8(g)(h)(i), and S10(i)(j) in the revision.

Fig.4 and 6 The unit of CH4 emission should be uniform. Some of them are nmol m-2 S-1, while others are nmole m-2 S-1. Also the unite of acetate (Fig. 2).
Thank you, we should use nmol and μmol (and not "mole"). Corrections are made to figures 2,3,4,7, and S5,S6,S7,S8,S9,S10 in the revision.

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C2

Representing methane emissions from wet tropical forest soils using microbial functional groups constrained by soil diffusivity

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Abstract. Tropical ecosystems contribute significantly to global emissions of methane (CH_4) and landscape topography influences the rate of CH_4 emissions from wet tropical forest soils. However, extreme events such as drought can alter normal topographic patterns of emissions. Here we explain the dynamics of CH_4 emissions during normal and drought conditions across a catena in the Luquillo Experimental Forest, Puerto Rico. Valley soils served as the major source of CH_4 emissions in a normal precipitation year (2016), but drought recovery in 2015 resulted in dramatic pulses in CH_4 emissions from all topographic positions. Geochemical parameters including dissolved organic carbon (C), acetate, and soil pH, and hydrological parameters like soil moisture and oxygen (O_2) concentrations, varied across the catena. During the drought, soil moisture decreased in the slope and ridge and O_2 concentrations increased in the valley. We simulated the dynamics of CH_4 emissions with the Microbial Model for Methane Dynamics-Dual Arrhenius and Michaelis Menten (M3D-DAMM) which couples a microbial functional group CH_4 model with a diffusivity module for solute and gas transport within soil microsites. Contrasting patterns of soil moisture, O_2, acetate, and associated changes in soil pH with topography regulated simulated CH_4 emissions, but emissions were also altered by rate-limited diffusion in soil microsites. Changes in simulated available substrate for CH_4 production (acetate, CO_2, and H_2) and oxidation (O_2 and CH_4) increased the predicted biomass of methanotrophs during the drought event and methanogens during drought recovery, which in turn affected net emissions of CH_4. A variance-based sensitivity analysis suggested that parameters related to aceticlastic methanogenesis and methanotrophy were most critical to simulate net CH_4 emissions. This study enhanced the predictive capability for CH_4 emissions associated with complex topography and drought in wet tropical forest soils.

1 Introduction

Wet tropical forest soils contribute significantly to global emissions of methane (CH_4; Pachauri et al., 2014). Although net emissions of CH_4 from upland soils are infrequent in temperate climates, studies show that CH_4 emissions are common in wet tropical forests, even in upland soils (Cattânio et al., 2002; Keller and Matson, 1994; Silver et al., 1999; Teh et al., 2005; Verchot et al., 2000). Landscape topography can strongly influence the proportions of CH_4 production and oxidation in mountainous tropical regions, affecting net emissions (Silver et al., 1999; O'Connell et al., 2018). Climate, and specifically patterns in rainfall, also affect emissions from tropical forests. Climate change may increase the frequency and severity of extreme rainfall and drought events, altering the spatial and temporal dynamics of CH_4 emissions through changes in redox dynamics and substrate availability (Silver et al., 1999; Chadwick et al., 2016; Neelin et al., 2006). Thus, accurately estimating CH_4 emissions under a variety of climatic and topographic conditions is important for predicting soil carbon-climate feedbacks in the humid tropical biome.

Several studies have reported the effect of drought events on biogenic CH_4 emissions across different wet tropical forest soils. For example, Aronson et al. (2019) demonstrated that the lower soil moisture conditions during 2015-16 El Niño event increased consumption of atmospheric CH_4 in a wet tropical forest Oxisol of Costa Rica. Similarly, a large-scale, 5-year throughfall exclusion experiment in a moist tropical forest Oxisol in Brazil also reported increased consumption of atmospheric CH_4 under the drought treatment, followed by a recovery of CH_4 emissions to pre-treatment values after the experiment ceased (Davidson et al., 2004, 2008). Using rainout shelters, Wood and Silver (2012) found spatial variability in CH_4 oxidation rates, with an increase of 480% uptake in valleys in an Ultisol in Puerto Rico. More recently, in a similar Puerto Rico Ultisol, O'Connell et al. (2018) reported increasing consumption of atmospheric CH_4 during a Caribbean drought event, followed by increased production of CH_4 after the drought was over. The post-drought net CH_4 emission rates were higher than the pre-drought emissions, such that the benefits to atmospheric radiation imparted by the lowered emissions during the drought were eliminated. The sharp differences between pre- and post-drought emissions suggested that drought affected the balance of methanogenesis and methanotrophy in the soils, but the study lacked analysis of the microbial community's contributions to these two separate processes.

The concept of "microsites" inside soil aggregates or within soil micropores can help explain the coexistence of oxidative and reductive processes in soils (Silver et al., 1999; Teh and Silver, 2006), which may have occurred in the post-drought period in the O'Connell et al. (2018) study. Oxygen can remain inside micropores during saturated conditions and thereby maintain aerobic microbial respiration; likewise, hypoxic conditions can persist in microsites under extended droughts and thereby maintain anaerobiosis. Additionally, liquid substrates for methanogenesis such as acetate can accumulate in microsites under dry conditions because their diffusion to hungry microbial

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communities may be restricted. Conversely, gaseous substrates such as CO_2 and H_2 may accumulate in microsites under saturated conditions because gaseous diffusion can be limited. The observed rapid flush of CH_4 in response to a post-drought wetting event (O'Connell et al., 2018) suggests methanogenesis continued during the drought in the Ultisol's microsites, despite low soil moisture and high O_2 supply (Andersen et al., 1998; Bosse and Frenzel, 1998; Teh et al., 2005; von Fischer and Hedin, 2002). Finely-textured soils common to the humid tropics can facilitate the co-existence of reduced solute and gas species with O_2 because the rate of solute and gaseous exchanges is controlled by diffusion into and out of microaggregates (Hall and Silver, 2013; Liptzin et al., 2010; Silver et al., 2013). In particular, hematite precipitation on clay minerals, found in both Oxisols and Ultisols, can enhance formation of soil aggregates because of their high surface area and charge properties (Hall et al., 2016). Soil organic matter can also enhance aggregation and at the same time consume O_2 (Six et al., 2004). However, few if any measurements of microsites exist in real field soils.

To explain the diverse observations of CH_4 emissions during and after drought across a wet tropical forest catena, we hypothesized that explicit representations of diffusion into and out of microsites for gas and solute transport would be required. To account for the balance of methanotrophy and methanogenesis, separate microbial functional groups for CH_4 production and oxidation would need to be defined. Therefore, a microbial functional group model for CH_4 production and consumption (Xu et al., 2015) was merged with a soil diffusivity module (Davidson et al., 2012; Sihi et al., 2018) to simulate the dynamics of net *in situ* CH_4 emissions from soil microsites (Sihi et al., 2020a). This module considers three key mechanisms for CH_4 production and consumption: aceticlastic methanogenesis (production from acetate) and hydrogenotrophic methanogenesis (production from H_2 and CO_2), and aerobic methanotrophy (oxidation of CH_4 and reduction of O_2) (Fig. 1). Here we report a modeling experiment to explain contrasting patterns of observed CH_4 emissions following a severe drought in 2015 and we provide new data to describe CH_4 emissions under non-drought conditions in 2016. We explicitly account for changes in soil moisture, O_2, acetate, and microbial functional group dynamics within soil microsites in the model.

2 Materials and methods

2.1 Study site

The study was conducted across a tropical forest catena near the El Verde Research Station in the Luquillo Experimental Forest (LEF) in northeastern Puerto Rico in the United States (Latitude 18°19'16.83" N, Longitude 65°49'10.13" W). The site is part of a National Science Foundation Long-Term Ecological Research (LTER) and Critical Zone Observatory (CZO) site and is also part of the U.S. Department of Energy's Next Generation Ecosystem Experiment-Tropics. The mean annual temperature at the site is 23 °C and the long-term mean rainfall is approximately 3500 mm yr^{-1} with low seasonality (Scatena, 1989). Inter-annual variability of rainfall ranges between 2600 mm yr^{-1} to 5800 mm yr^{-1}, sometimes associated with extreme rainfall events (approximately 100 mm day^{-1}) from Caribbean storm systems (Heartsill-Scalley et al., 2007). The LEF is classified as a wet tropical forest according to the Holdridge life zone system, which considers rainfall, elevation, latitude, humidity, and evapotranspiration (Harris et al., 2012).

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The landscape at the field site is highly dissected with short catenas, characterized by a land surface distance of < 30 m from ridgetop to valley (O'Connell et al., 2018). This study partitioned sampling along a catena from ridgetop, slope, and valley topographic positions (Fig. S1). The soils are clay-rich Ultisols, which were derived from basaltic and andesitic volcanoclastic parent materials. Soils are acidic (average pH is 4.3 and 5.1 in ridge and valley topographic positions, respectively, Fig. 2). The valley soils have approximately 30% clay and approximately 15% sand, while the ridge soils have approximately 22% clay and approximately 30% sand (Brenner et al., 2019). The soils contain high concentrations of iron (Fe) and aluminum (Al) (oxy)hydroxides where their relative concentrations vary along the catena and differences in Fe speciation are associated with variable redox conditions (Hall and Silver, 2013, 2015). A detailed soil survey in the immediate vicinity lists three soil types (Zarzal, Cristol, and Prieto) with a minimal litter layer due to rapid decomposition (Parton et al. 2007, Cusack et al. 2009), surface (A) horizons 5 cm thick, and B horizons of 130 to 150 cm thick (Soil Survey Staff, 1995). The surface soil bulk density ranged from 0.5 to 0.7 g cm^{-3}, and by 25 cm depth was 0.8 to 1.1 g cm^{-3} (Cabugao et al., in press), similar to previous observations (Johnson et al., 2014; Silver et al., 1999). The forest composition is relatively diverse with the mature Tabonuco (*Dacryodes excelsa* Vahl) and Sierra palm (*Prestoea montana*) trees being most dominant (Scatena and Lugo, 1995; Wadsworth et al., 1951).

2.2 Soil and porewater sampling

Previous CH$_4$ measurements in the LEF at the soil surface, 10 cm depth, and 35 cm depth, found the highest CH$_4$ concentrations at 10 cm depth (Silver et al. 1999), while 30 cm depth was the location of maximum soil organic carbon (SOC) concentrations (Johnson et al., 2014). To initialize the model, soil and soil water samples were collected from depths ranging from 0 to 30 cm in accordance with these previous studies. Soil samples were collected in triplicate from a depth of 0-10 cm and on a quarterly timeframe from the ridgetop, slope, and valley positions for over two years. The soil pH was determined using a 1:2 ratio of soil:solution using a glass electrode with 0.005 M CaCl$_2$ as the equilibrated soil solution (Thomas, 1996; Sihi et al. 2020b). Porewater samples were collected approximately weekly for over two years using macro-rhizon soil water samplers (length = 5 cm) (Rhizosphere Research Products B.V.; Wageningen, The Netherlands) installed at both 5-10 cm and 25-30 cm depth in triplicate in the ridge, slope, and valley topographic positions (Sihi et al., 2020c). The soil water samples were analyzed for organic acid concentrations (acetate) using High Performance Liquid Chromatography (Dionex ICS-5000+ Thermo-Fisher Waltham, MA, USA) with the Dionex IonPac AS11-HC column using a potassium hydroxide eluent and gradient elution. The samples were analyzed for total dissolved organic carbon (DOC) using a Shimadzu total organic C analyzer (Shimadzu TOC-L CSH/CSN Analyzer Baltimore, MD, USA). The soil and porewater measurements were conducted in 2017-2018 (the number of samples *n* ranged between 20 to 35, Fig. 2) to initialize different model parameters for the catena, because measurements were not available for 2015-2016. To that end, the chemical data were used as the reference characteristics of the bulk soil, and the temporal evolution of DOC, acetate, and soil pH at the microsites were calculated using probability distributions of soil moisture and O$_2$ across soil microsites over the two-year measurement window. Soil bulk density and particle density values were taken from O'Connell et al. (2018).

2.3 In situ methane flux and soil driver measurements

Campbell Scientific CS 655 soil moisture and temperature sensors and Apogee SO-110 O_2 sensors were co-located with soil gas flux chambers at 15 cm soil depth along the catena, each with five replications along five transects (Fig. S1) (O'Connell et al., 2018). Following Liptzin et al. (2011), soil O_2 sensors were installed in gas-permeable soil equilibration chambers (295 cm^3). Data from these sensors were collected hourly using Campbell Scientific CR10000 data loggers and AM16/32B multiplexers (Campbell Scientific, Logan, UT, USA), which were processed using site-based calibration equations.

Soil flux chambers were placed on the top of the soil surface. Soil CH_4 emissions along the catena were measured during 2015 (February 26 to December 23, O'Connell et al., 2018; Silver, 2018) and 2016 (April 5 to July 18) (Sihi et al., 2020d) using a Cavity Ring-Down Spectroscopy gas analyzer (Picarro G2508, Santa Clara, CA, USA) connected to 12 automated eosAC closed dynamic soil chambers (Pumpanen et al., 2004) using a multiplexer (Eosense Inc., Dartmouth, Nova Scotia, Canada). Data for soil CH_4 emissions were processed using eosAnalyze-AC (v3.5.0) software followed by a series of quality control protocols (O'Connell et al., 2018). We used daily average values of drivers (soil temperature, soil moisture, and O_2 concentrations) and CH_4 emissions in the modeling exercise. See O'Connell et al (2018) for more information on the soil sensor, chamber arrays, and the data analysis pipeline.

The data from the 2015 Caribbean drought was partitioned into four distinct periods (O'Connell et al., 2018): (1) pre-drought from day of year (DOY) 57 to 115 (dark gray on Fig. 3), (2) the drought from DOY 116 to 236 (medium gray on Fig. 3), (3) drought recovery from DOY 237 to 328 (light gray on Fig. 3), and (4) post-drought from DOY 329 to 354 (white on Fig. 3). Total precipitation during the drought period was 700 mm in 2015 and 1088 mm during the same time frame in 2016 (Meteorological data from El Verde Field Station: NADP Tower, available at https://luq.lter.network/data/luqmetadata127).

2.4 Modelling approach

2.4.1 Microbial functional group model for methane production and oxidation

An existing microbial functional group-based model for CH_4 production and consumption (Xu et al., 2015) was adopted for this research (Sihi, 2020). As shown in Fig. 1, acetate and H_2/CO_2 represent substrate [Substrate$_{func_i}$] (nM cm^{-3}) for aceticlastic and hydrogenotrophic methanogenesis reactions, respectively. On the other hand, CH_4 and O_2 concentrations represent substrate for the methanotrophy reaction. Acetate and CO_2 are inputs based on measurements of soil water and pH described in Section 2.2. In the model, acetate is formed by fermentation and by homoacetogenesis (but not by syntrophic acetate oxidation) as defined in Xu et al. (2015) in their Appendix in Eq. A15 and A16 (Fig. 1b). Methylotrophic methanogenesis (Narrowe et al. 2019) is neglected in the model. The overall reaction rates are represented as:

$$\text{Reaction}_{rate_i} = \text{Biomass}_{func_i} \times \frac{\text{GrowR}_{func_i}}{\text{Efficiency}_{func_i}} \times \frac{[\text{Substrate}_{func_{1...n}}]}{[\text{Substrate}_{func_{1...n}}] + \text{KM}_{func_{1...n}}} \times f(T) \times f(pH) \qquad (1)$$

5

236 where $Reaction_{rate_i}$ (in nM cm^{-3} hr^{-1}) is rate of CH$_4$ production and/or consumption under variable substrate

237 concentrations. $Biomass_{func_i}$ (nM cm^{-3}) represents microbial functional groups: aceticlastic methanogens,

238 hydrogenotrophic methanogens, and aerobic methanotrophs, respectively. Growth rates and substrate use

239 efficiencies of microbial functional groups are represented as $GrowR_{func_i}$ (hr^{-1}) and $Efficiency_{func_i}$ (unitless),

240 respectively (Table 1). The substrate limitation on CH$_4$ production is imposed by assuming a Michaelis-Menten

241 relationship with the half-saturation constants for CH$_4$ production and oxidation being $KM_{func_{1...n}}$ (nM cm^{-3}).

242 Although minor contributions of iron dependent anaerobic CH$_4$ oxidation to net CH$_4$ emissions can be expected in

243 our study site (Ettwig et al., 2016), we did not represent this process here as anaerobic oxidation of CH$_4$ is still not

244 fully understood and it is generally low in most ecosystems.

245 The extent of change in $Biomass_{func_i}$ ($dBiomass_{func_i}$) is controlled by the balance between $Growth_{func_i}$ and

246 $Death_{func_i}$ following:

247 $\frac{dBiomass_{func_i}}{dt_{func_i}} = Growth_{func_i} - Death_{func_i}$ (2)

248 $Growth_{func_i} = Efficiency_{func_i} \times Reaction_{rate_i}$ (3)

249 where $Growth_{func_i}$ is calculated as a multiplicative function of $Efficiency_{func_i}$ and the $Reaction_{rate_i}$

250 $Death_{func_i} = DeadR_{func_i} \times Biomass_{func_i}$ (4)

251 and $Death_{func_i}$ is a function of $DeadR_{func_i}$ (death rate, Table 1) and $Biomass_{func_i}$ (microbial biomass).

252 All rate equations were modified by the scalers for temperature, f(T), and pH, f(pH) functions, described below. We

253 represented the temperature effect, f(T), using a classic Q$_{10}$ function:

254 $f(T) = Q_{10_i}^{\frac{Temperature_{soil} - Temperature_{reference}}{10}}$ (5)

255 We represented the pH effect, f(pH), based on Cao et al. (1995):

256 $f(pH) = \frac{(pH - pH_{minimum})*(pH - pH_{maximum})}{(pH - pH_{minimum})*(pH - pH_{maximum}) - (pH - pH_{optimum})^2}$ (6)

257 where we set the minimum, optimum, and maximum soil pH values to 4, 7, and 10, respectively. Following Xu et al.

258 (2015), we considered the contribution of acetate to pH as follows:

259 $pH = -1 * log_{10}10^{pH_{initial}} + 4.2E - 9 * Acetate$ (7)

260 Although other mechanisms to alter soil pH are present at the site, e.g., Fe reduction and oxidation (Teh et al., 2005;

261 Hall and Silver, 2013), these are not considered in the model at this time. Calibrated values of $GrowR_{func_i}$,

262 $DeadR_{func_i}$, $Efficiency_{func_i}$, KM_{func_i} and Q_{10_i} are presented in Table 1.

263 **2.4.2 Diffusion module for gaseous and solute transport in soil profile and across soil-air boundary**

264 In order to account for the diffusion of gases across the soil-air boundary and solutes (e.g. acetate) through soil water

265 films (Fig. 1), we added the diffusion module of the Dual Arrhenius and Michaelis Menten (DAMM) model

266 (Davidson et al., 2012; Sihi, 2020; Sihi et al., 2018, 2020a) to the existing microbial functional group model, which

267 we refer to as M3D-DAMM. We calculated initial concentration of gases like O$_2$, H$_2$, CO$_2$, and CH$_4$, $[Gas_{conc}]$, (unit:

6

290 V V^{-1}), as a function of a unitless diffusion coefficient of gas in air (D$_{gas}$), volume fraction of gas in air (V V^{-1}), and

291 gas diffusivity (a$^{4/3}$) as follows:

292 $$[Gas_{conc}] = D_{gas} \times \text{atmospheric concentration} \times a^{4/3} \tag{8}$$

293 where a$^{4/3}$ represents the tortuosity of diffusion pathway for gases as a function of soil water (SoilM) and

294 temperature (SoilT):

295 $$a^{4/3} = \left(\text{Porosity} - \frac{SoilM}{100}\right)^{4/3} \times \left(\frac{SoilT+273.15}{293.15}\right)^{1.75} \tag{9}$$

296 where the air-filled porosity (a) was calculated by subtracting the volume fraction of soil moisture (V V^{-1}) from total

297 porosity. Porosity was calculated as:

298 $$\left(1 - \frac{\text{Bulk density}}{\text{Particle density}}\right) \tag{10}$$

299 The exponent of 4/3 accounts for diffusivity of gases through porous media (Davidson and Trumbore, 1995). The

300 exponent of 1.75 represents the temperature response of gaseous diffusion (Massman, 1998; Davidson et al., 2006).

301 Following Davidson et al. (2012), the value used for gaseous diffusivity coefficient (D$_{gas}$) was calculated based on

302 an assumed boundary condition such that the concentration of gaseous substrates in the soil pore space would be

303 equivalent to the volume fraction of gases in air under completely dry conditions.

304 We assumed another boundary condition to determine the value of the aqueous diffusion coefficient, D$_{liq}$, such that

305 soluble substrates like acetate would be available at the enzymatic reaction site under conditions with saturating soil

306 water content (Davidson et al., 2012):

307 $$D_{liq} = \frac{1}{\text{Porosity}^3} \tag{11}$$

308 We represented soluble substrates (acetate) diffused through a soil water film as $\text{Aqueous} - \text{substrate}$ ($\mu M \, L^{-1}$),

309 which we calculated as follows:

310 $$\text{Aqueous} - \text{substrate}_{av} = \text{Aqueous} - \text{substrate} \times D_{liq} \times \left(\frac{SoilM}{100}\right)^3 \tag{12}$$

311 where the $\left(\frac{SoilM}{100}\right)^3$ term represents the diffusion rate of aqueous substrates to the enzymatic active site (Papendick

312 and Campbell, 1981). Concentrations of acetate in the aqueous phase ($\mu M \, L^{-1}$) were obtained from the

313 measurements across the catena averaged by depths (10 and 30 cm) of rhizon samplers.

314 We calculated CH$_4$ emissions, $CH_{4emission}$ (unit: μmole m^{-2} hr^{-1}), as a function of concentration ([CH_{4conc}]),

315 production (CH_{4prod}), and oxidation (CH_{4ox}) of CH$_4$, multiplied by the equivalent "depth" (set to 15 cm) (for cm^{-3}

316 volume to cm^{-2} area conversion) and 10^4 (for m^2 to cm^2 conversion) as follows:

317 $$CH_{4emission} = [CH_{4conc}] + (CH_{4prod} - CH_{4ox}) \times 10^4 \times depth \tag{13}$$

318 **2.4.3 Soil microsites**

319 The importance of diverse microsite conditions was inferred based on many previous observations in the field and

320 the lab of co-occurrences of oxic soil concentrations and reduced redox-active species (Silver et al., 1999; Teh et al.,

321 2005; Megonigal and Geunther 2008; Hall et al. 2013, 2016; Sihi et al., 2020a). The high clay content, abundant Fe

322 oxides, and visible redox mottling, particularly in the valley and slope soils facilitates a diversity of soil micro-

environments where O_2 and CH_4 can seemingly co-occur, albeit in different microsite locations (Silver et al., 1999; Teh and Silver, 2006). Microsite diversity was also invoked to help explain the rapid CH_4 emissions following drought at the field site (O'Connell et al., 2018). Techniques for accurately measuring in-situ microsite activities remain very limited to date, here or elsewhere. Therefore, we simulated production, consumption, and diffusion processes within soil microsites using a log-normal probability distribution function of soil moisture and available C based on these previously observed relationships (Fig. 1). The average values of individual processes across simulated microsites (represented by "i") represent the reaction in the bulk soil, which we constrained using the net measured CH_4 emissions.

$$\text{Bulk soil}_{average} = \frac{\sum \text{Frequency}_i \times [\text{microsite}]_i}{\text{Total microsites}} \qquad (14)$$

We directly adopted the probability distribution function of soil moisture and C from Sihi et al. (2020a), which constrained values of Frequency_i of soil microsites. We a priori assigned the size of the microsites to be at least an order magnitude smaller than the diameter used for bulk measurements of CH_4 fluxes. Thus, the mean diameter of microsites was assumed to be at the mm-scale (the size-class of small stable aggregates in these soils), as the diameter of soil chambers was 15.24 cm. Thus, the resultant number of total microsites below each soil flux chamber was 10,000.

2.4.4 Sensitivity Analysis

We evaluated the sensitivity of model parameters with a global variance-based sensitivity analysis using the *R-multisensi* package. This method uses a global sensitivity index ($0 < GSI < 1$) to determine the sensitivity of CH_4 emissions to model parameter values (Bidot et al., 2018). We conducted a multivariate technique to estimate GSI values in sequential steps. First, we implemented a factorial design on the uncertain model parameters, which is followed by a principal component analysis on model outputs. Then, we extracted GSI values by an ANOVA-based sensitivity analysis on the first principal component. To that end, parameters with high GSI values may explain high temporal variations of the observed CH_4 emissions and those with low GSI values are insignificant to reproduce the temporal dynamics of CH_4 emissions.

2.4.5 Statistical Analysis

We used R (version 3.5.1) for statistical analyses, modeling, and visualization purposes (R Core Team, 2018). Statistical analyses and figures were produced using *R-ggstatsplot* (Patil, 2018) and *R-ggplot2* (Wickham, 2016) packages. Differences in soil and porewater chemistry across the catena were compared using robust t-test. Correlograms for soil temperature, soil moisture, O_2, and soil CH_4 emissions were created using adjusted Holm correlation coefficients. All statistical analyses were conducted at the 5% significance level. We implemented the M3D-DAMM model using *R-FME* package (Soetaert, 2016).

3 Results

3.1 Observational dynamics of soil biogeochemistry

Soil and porewater chemistry varied along the catena (Fig. 2). Dissolved organic carbon (DOC) values followed the trend of ridge > slope > valley (p ≤ 0.001). Soil DOC concentrations (mean ± SE) were 0.55 ± 0.10, 0.30 ± 0.03, and 0.18 ± 0.03 mg g^{-1} in ridge, slope, and valley soils, respectively. Organic acid (acetate) concentrations were significantly higher in the ridge (6.57 ± 1.48 µM L^{-1}) and slope (6.42 ± 2.19 µM L^{-1}) than in the valley (1.80 ± 0.20 µM L^{-1}) (p = 0.003). Soil pH followed the trend of valley > slope > ridge (p < 0.001). Average soil pH ranged from 4.25 ± 0.11 in the ridge, to 4.49 ± 0.08 in the slope, and to 5.05 ± 0.09 in the valley.

Soil moisture and soil O_2 concentrations were distinctly different in the drought year (2015) compared to 2016. The drought in 2015 decreased soil moisture in the slope and ridge soils and increased O_2 concentrations in the valley soils (Fig. 3) (also see O'Connell et al., 2018). Generally, average soil moisture was higher in the valley (0.47 ± 0.05 in 2015 and 0.51 ± 0.01 v v^{-1} in 2016) as compared to the ridge (0.31 ± 0.12 in 2015 and 0.39 ± 0.03 v v^{-1} in 2016) and slope (0.30 ± 0.16 in 2015 and 0.41 ± 0.04 v v^{-1} in 2016). Average O_2 concentrations were generally lower in the valley (11.54 ± 5.94 in 2015 and 6.30 ± 2.96 % in 2016) as compared to the ridge (18.37 ± 0.72 in 2015 and 17.52 ± 0.42 % in 2016) and slope (18.09 ± 1.22 in 2015 and 16.89 ± 0.58 % in 2016). After the drought ended, the recovery of soil moisture in the ridge and slope soils proceeded more quickly than the recovery of O_2 concentrations in the valley soils (Fig. 3). Soil temperature ranges were averaged across the topographic gradient and were similar in both years (average was 21.58 ± 1.88 in 2015 and 22.97 ± 1.04 °C in 2016).

In 2016, net CH_4 emissions were generally positive in the valley and were marginally negative in the ridge and slope (Fig. 4). The dynamics of CH_4 were very different following the 2015 drought, resulting in net positive CH_4 emissions in the post-drought period for all topographic positions (Fig. 3) (as described in more detail in O'Connell et al. 2018). The magnitude of CH_4 emissions was greater in the valley, followed by the slope and then the ridge. The strength of the relationships between net CH_4 emissions and soil temperature, moisture, and O_2 concentrations were contingent on both topographic position and year (2015 vs 2016) (Fig. 5). For example, the relation between CH_4 emissions and soil moisture was stronger in 2016 (normal year) than in 2015 (drought year). The correlation between CH_4 emissions and O_2 concentrations was stronger and more negative in 2015 than 2016. Correlations between soil moisture and O_2 concentrations were negative and stronger in 2016 than in 2015. Correlation coefficients between soil O_2 concentrations and CH_4 emissions were negative and strongest for valley soils and lowest for ridge soils in 2015, but were uncorrelated in 2016 for ridge and slope soils (Fig. S2).

3.2 Model simulations of methanogenesis and methanotrophy

In general, there was little bias in the relationships between the observed and simulated CH_4 emissions (Fig. 6). The model explained 72% and 67% of the variation in soil CH_4 emissions for 2015 and 2016, respectively, although the model performance varied across the catena (Figs. 6, S3, S4). Overall, simulated CH_4 emissions captured the trend of valley > slope > ridge for 2016. The model also captured the dramatically different dynamics of field CH_4

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484 emissions as a function of topography during and after the 2015 drought. Net positive CH_4 emissions were simulated

485 in the drought recovery and post-drought periods in the ridge and slope in 2015, while net negative emissions were

486 simulated in the other times for these landscape positions. Additionally, simulated net CH_4 emissions were

487 decreased during the drought and drought recovery in the valley soils, as well as the strong net CH_4 emissions in the

488 valley soils in the post-drought period.

489 The ridge and slope positions were more similar to each other than to the valley soils. Simulated decreased

490 production of acetate and hydrogen during the 2015 drought in the ridge and slope positions resulted in decreased

491 biomass of aceticlastic methanogens and hydrogenotrophic methanogens (Figs. S5, S6). Gross CH_4 production

492 therefore decreased during these time periods (Fig. S7). Simultaneously, as soil moisture decreased, simulated

493 methanotrophic biomass increased during the drought (Fig. S5). The simulated biomass of both aceticlastic

494 methanogens and hydrogenotrophic methanogens increased dramatically in the ridge and slope soils during drought

495 recovery (aceticlastic methanogens: 3.3 and 5.3 times higher than drought period for ridge and slope, respectively;

496 hydrogenotrophic methanogens: 6.1 and 12 times higher than drought period for ridge and slope, respectively) and

497 post-drought (aceticlastic methanogens: 5.2 and 8.8 times higher than drought period for ridge and slope,

498 respectively; hydrogenotrophic methanogens: 12 and 24 times higher than drought period for ridge and slope,

499 respectively) period. Concomitantly, production of acetate and H_2 was much higher in the ridge and slope soils

500 during the drought recovery (acetate: 1.8 and 2.4 times higher than the drought period for ridge and slope soils,

501 respectively; H_2: 3.5 and 6.0 times higher than the drought period for ridge and slope soils, respectively) and the

502 post-drought (acetate: 2.3 and 3.2 times higher than the drought period for ridge and slope, respectively; H_2: 5.6 and

503 10 times higher than the drought period for ridge and slope, respectively) period. Together, gross CH_4 production in

504 the ridge and slope soils was significantly higher during the drought recovery (1.9 and 2.5 times higher than the

505 drought period for ridge and slope, respectively) and post-drought periods (3.4 and 4.6 times higher than the drought

506 period for ridge and slope, respectively) compared to the drought (Fig. S7). Simulated production of acetate was

507 increased that also lowered soil pH values during drought recovery (Fig. S6), with a more pronounced effect in the

508 ridge and slope soils. Additionally, simulated methanotrophic biomass and CH_4 oxidation decreased during the post-

509 drought period (Figs. S5, S7), which is the same time period during which net CH_4 production increased strongly.

510 For the valley soils, simulated values of aceticlastic methanogens and concomitant acetate production increased

511 during the 2015 drought (Figs. S5, S6). During the drought recovery and post-drought period, both aceticlastic

512 methanogens and acetate production decreased in the valley, while hydrogenotrophic methanogens and H_2

513 production were stable. Gross CH_4 production, however, remained relatively flat during the drought event in the

514 valley, and only increased during the post-drought period (Fig. S7). Simulated CH_4 oxidation and methanotrophic

515 biomass, on the other hand, increased dramatically during the drought and drought recovery period (Figs. S5, S7),

516 and then decreased strongly during the post-drought period. However, simulated methanotrophic biomass was

517 smaller in the valley soils compared to the ridge and slope soils. Methane oxidation by methanotrophs exerted strong

518 controls on simulated net CH_4 emissions, not only in the valley but in all the topographic positions.

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3.3 The influence of microsites on net methane emissions

Concomitant with decreased soil moisture, the simulated diffusion of gases (O_2, H_2) was enhanced during the drought event in 2015, while diffusion of the solute (acetate) was dramatically decreased, particularly for the ridge and slope soils (Fig. S8). However, reduction in soil moisture and increase in O_2 can inhibit fermentative hydrogen production (Cabrol et al., 2017). Consequently, simulated gross CH_4 production through hydrogenotrophic and aceticlastic pathways both decreased during the drought event for the ridge and slope positions (Figs. S7, S9). As soil moisture increased during the drought recovery and post-drought periods, the diffusion of gases decreased, and diffusion of acetate increased in the ridge and slope soils (Fig. S8). Consequently, simulated values of gross CH_4 production increased and gross CH_4 oxidation decreased during drought recovery and the post-drought period (Fig. S7). These factors likely contribute to the large pulses of net CH_4 emissions during the post-drought period for ridge and slope positions (Fig. 3).

Overall, the valley soils were relatively insensitive to changes in the diffusion rate of either gases or solutes (Fig. S8), most likely because soil moisture remained relatively stable, regardless of drought conditions (Fig. 3). The lower sand and higher clay contents in the valley soils (Brenner et al., 2019), as well as the lower topographic position, likely caused the valley soils to remain wetter than the slope and ridge soils. Therefore, simulated values of gross CH_4 production were fairly stable in the valley soils (Fig. S7) during the drought and drought recovery period. Simulated production, oxidation, and net flux of CH_4 was further modified by reactions occurring within soil microsites. For example, during the drought (~DOY 200 in 2015), gross CH_4 production was more frequent in soil microsites in the valley compared to the slope and ridge (Fig. 7). Simulated values of CH_4 oxidation were much greater in microsites in the slope and ridge positions, so the net CH_4 emissions were positive in the valley soils and negative in the ridge and slope positions. During the 2015 post-drought period (DOY 345), the frequency of CH_4 production was much greater in all topographic positions compared to the drought period (DOY 200), and it was also more enhanced in the valley soils compared to the slope and ridge. Thus, net positive CH_4 emissions were observed in all topographic positions in the post-drought period (Fig. 3). Methane oxidation at DOY 345 was much greater in the ridge and slope compared to the valley, similar to predictions at DOY 200. Therefore, the prominent CH_4 emissions from all three topographic positions were primarily due to increased production (CH_4 production on DOY 345 was 150, 248, and 80 % higher than DOY 200 in ridge, slope, and valley, respectively) rather than decreased oxidation (CH_4 oxidation was 32, 31, and 43 % lower on DOY 345 than DOY 200 in ridge, slope, and valley, respectively), which agrees with previous studies in our site (Teh et al., 2005, 2008; von Fischer and Hedin, 2002).

Diffusion into microsites strongly affected the concentrations of gases and solutes experienced by microbes, and differences as a function of topographic position were again predicted. Acetate production and diffusion were enhanced in valley soils during the drought, when compared to the slope and ridge soils (Fig. S10). The H_2 production was also enhanced in the valley soils during the drought, but the wetter valley soils experienced lower rates of H_2 diffusion compared to the ridge and slope soils. Increases in O_2 diffusion were also apparent in the ridge and slope soils during the drought, and those increases were greater than in the valley soils. During the post-drought

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571 period, however, the frequency of H_2 and O_2 diffusion was much greater for the ridge soils compared to the valley

572 soils (Fig. S10).

573 Of all parameters, the most sensitive ones were those that controlled CH_4 production through the aceticlastic

574 pathway, followed by the parameters related to CH_4 oxidation (Fig. 8). The GSI values for parameters related to

575 aceticlastic methanogenesis and methanotrophy ranged between 0.25 - 0.75, whereas the corresponding GSI values

576 for hydrogenotrophic methanogenesis were always < 0.1.

4 Discussion

578 **4.1 Mechanisms governing net methane emissions**

579 Although the initial concentrations of available C for fermentation (i.e. DOC) and substrate for aceticlastic

580 methanogenesis (i.e. acetate) in the bulk soil followed the trend of ridge > slope > valley (Fig. 2), the pattern of net

581 CH_4 emissions across the catena was opposite (valley > slope ≥ ridge), especially in 2016 (Fig. 4). The seemingly

582 counterintuitive relations of substrate concentrations in the bulk soil versus net CH_4 emissions can be explained by

583 modeling the differing redox conditions across soil microsites. Diffusion promoted the availability of the acetate

584 substrate through more connected soil water films in the wetter valley soils and caused higher gross CH_4 production

585 in 2016, as compared to the relatively drier slope and ridge soils (Figs. S7, S8). In contrast, diffusion of gaseous

586 methanotrophic substrates (CH_4 and O_2) was promoted in the air-filled pore spaces in the drier ridge and slope soils

587 (Fig. S8), resulting in reduced net CH_4 emissions for these two topographic positions in 2016 (Fig. 4). Further,

588 reduced diffusion of O_2 in the wetter valley soils decreased gross methanotrophy compared to the slope and ridge

589 soils (Figs. S7, S8). Consequently, in 2016, net CH_4 emissions dominated the valley soils but were minimal in the

590 ridge and slope soils.

591 On the other hand, the drought event in 2015 decreased the simulated CH_4 emission in the slope and ridge soils by

592 decreasing H_2 production, and both production (Fig. S6) and diffusion of acetate (Fig. S8). The drought increased

593 the CH_4 sink strength of both ridge and slope soils as the observed net CH_4 emissions became more negative during

594 the drought compared to the pre-drought period (Fig. 3). Contributing factors predicted by the model include

595 enhanced O_2 diffusion into the drier ridge and valley soils (Fig. S8), as well as enhanced methanotrophic biomass

596 (Fig. S5). In the valley, the primary impact of the drought appeared to be due to increased methanotrophy (Fig. S7),

597 since acetate, H_2, and gross CH_4 production were predicted to continue unabated (Fig. S6, S7). This suggests that

598 drought enhanced consumption of atmospheric CH_4 in our site, which is consistent with findings from natural

599 droughts and throughfall exclusion experiments in other wet tropical forest soils (Aronson et al., 2019; Davidson et

600 al., 2004, 2008; Wood and Silver, 2012).

601 However, simulation of observed CH_4 emission during drought recovery in 2015 required explicit representations of

602 the complex interaction of the diffusive supply of solute and gases, dynamics of the microbial functional groups, and

603 the associated acetate-pH feedback loop across the distribution of soil microsites (Fig. 3). The drought recovery

604 increased soil moisture which likely prompted anaerobiosis across all topographic locations by significantly

605 reducing gas diffusivity in a fraction of the simulated microsites (11, 17, and 21 % in ridge, slope, and valley,

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611 respectively) (McNicol and Silver, 2014; Sihi et al., 2020a; Teh et al., 2005). The return to dominantly reducing

612 conditions also was predicted to stimulate fermentation and the production of acetate through homoacetogenesis

613 (Fig. S6). Enhanced production and diffusion of acetate during recovery (Fig. S8) triggered growth in the predicted

614 biomass of aceticlastic methanogens (Fig. S5), which in turn, increased rates of aceticlastic methanogenesis (Fig.

615 S9).

616 Simulated rates of hydrogenotrophic methanogenesis also increased in anaerobic microsites (Figs. S9, S10),

617 mediated by increased production of H_2 and subsequent stimulation of the biomass of hydrogenotrophic

618 methanogens during the drought recovery in 2015 (Fig. S5). Overall, the absolute values of simulated gross CH_4

619 production through hydrogenotrophic and aceticlastic pathways (Fig. S9) outweighed the simulated gross CH_4

620 oxidation rates (Fig. S7), resulting in net soil CH_4 emissions across the catena during the post-drought period (Fig.

621 3).

622 Acetate-driven CH_4 increases, decreases in methanotrophy due to decreasing O_2, and increasing hydrogenotrophic

623 methanogenesis all contributed to the post-drought pulses of CH_4 (Fig. 8). Both kinds of methanogens increase

624 during drought recovery and post-drought, but aceticlastic methanogens were two orders of magnitude more

625 abundant than hydrogenotrophic methanogens. Additionally, acetate may accumulate in microsites during drought,

626 and then become more available with drought recovery due to enhanced solute diffusion (Fig. S8). The model

627 simulations suggest that hydrogen diffusion was lessened under the drought recovery, which is consistent with

628 decreasing rates of gas diffusion through saturated soils (Fig. S8). Further, H_2 has a faster turnover rate compared to

629 acetate (Xu et al. 2015) and therefore accumulation in soils, especially shallow soils which are the subject of this

630 study, is minimized. So, acetate versus hydrogen substrate availability, in microsites better, explains the observations

631 of higher CH_4 production under the post-drought conditions.

632 Additionally, acetate is a source of proton and should reduce soil pH (Amaral et al., 1998; Conrad and Klose, 1999;

633 Jones et al., 2003). Previous studies (Xu et al., 2015; Xu et al., 2010) demonstrated that acetate-driven soil pH

634 reduction can reduce net CH_4 production by as much as 30%, especially in systems with low initial soil pH like our

635 study site. Given that optimal pH for biological activities peaks near neutral pH, the relatively higher soil pH in the

636 valley versus ridge and slope soil further enhanced the topographic patterns of CH_4 emissions (Conrad, 1996; also

637 see Figs. 2, 3, and 4). Note that the initial soil pH across the landscape was already in the acidic range (Fig. 2),

638 consequently, the simulated acetate production and concomitant decrease in soil pH during the 2015 drought

639 recovery further suppressed gross CH_4 production in ridge soils in comparison to the valley soils (Figs. S6 and S7).

640 Iron reducing bacteria can also suppress CH_4 production either by competing with aceticlastic methanogens for

641 acetate substrate or controlling the flow of acetate to both hydrogenotrophic and aceticlastic methanogens by

642 dissimilatory iron reduction (Teh et al., 2008). Additionally, Fe reduction can increase soil pH either by proton

643 consumption and colloid dispersion, while Fe oxidation can lead to more acidic conditions (Hall and Silver, 2013;

644 Thompson et al., 2006). None of the Fe-associated mechanisms are currently represented in the M3D-DAMM

645 model.

646 Hence, high temporal resolution field-scale measurements of CH_4 emissions and soil and porewater chemistry

647 facilitated evaluation of the combined effects of soil redox conditions (moisture and O_2 concentrations) and

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718 associated pH feedbacks on underlying processes occurring across soil microsites, while accounting for variation
719 along the catena as a result of changing climatic drivers over time. The M3D-DAMM model captured the Birch-type
720 effect by quantifying the pulses in soil CH$_4$ emissions as a function of increases in soil moisture following a strong
721 drought (Birch, 1958). Specifically, the model coupled with microsite diffusivity explained CH$_4$ emissions common
722 to wet valley soils and rare in comparatively drier ridge and slope soils and predicted the net release of CH$_4$
723 emissions from all topographic positions following a strong drought.

724 **4.2 Sensitivity analysis**

725 The variance-based sensitivity analysis confirmed the importance of microbial functional groups and their complex
726 interactions with the surrounding biophysical and chemical environments in controlling CH$_4$ production and
727 oxidation. For example, the growth and death of aceticlastic methanogens and the relative efficiency of aceticlastic
728 methanogenesis were the most sensitive parameters (Fig. 8), which is consistent with another modeling effort on
729 CH$_4$ fluxes across the Arctic landscape (Wang et al., 2019). Although from completely different ecosystem types,
730 Wang et al. (2019) and the present study confirmed the importance of simulating soil topographies and microbial
731 mechanisms when evaluating the heterogeneities in CH$_4$ fluxes. Representations of both direct (methanogenic
732 substrate) and indirect (soil pH feedback) effects of acetate may have contributed to higher GSI values for
733 parameters representing aceticlastic methanogenesis, which is similar to a previous study (Xu et al., 2015). The
734 sensitivity of CH$_4$ emissions to the parameters representing methanotrophy were secondary to those representing
735 aceticlastic methanogenesis, which is consistent with the increase in methanotrophic biomass during the drought.
736 Our predicted changes in microbial biomass might be unacceptably large for the entire soil microbial community,
737 which may only double or perhaps quadruple in response to changes in conditions, but individuals can grow
738 exponentially (Goberna et al. 2010; Pavlov and Ehrenberg 2013; Roussel et al. 2015; Buan 2018).

739 **4.3 Other processes**

740 We did not completely reproduce the net emissions of soil CH$_4$ during the 2015 post-drought period across the
741 catena with the M3D-DAMM model. To capture the full potential of net emissions of CH$_4$ (white shading in Fig. 3)
742 from sesquioxide-rich soils, future modeling efforts may need to explicitly include the dynamics of redox-sensitive
743 elements such as Fe and associated pH feedback under contrasting redox conditions (Barcellos et al., 2018;
744 Bhattacharyya et al., 2018; Hall and Silver, 2013, 2015, 2016; O'Connell et al., 2018; Parfitt et al., 1975; and Silver
745 et al., 1999). Wetting events can lower soil redox potential and reduce electron acceptors like Fe(III) to Fe(II). This
746 concomitant reduction of Fe may increase soil pH, especially in anaerobic microsites, which could further increase
747 net emissions of soil CH$_4$ (Tang et al., 2016; Zheng et al., 2019). Accounting for these effects may allow model
748 simulations to better match the highest observed net CH$_4$ emissions in the post-drought period (Fig. 3).
749 Additionally, the reduction of Fe(III) to Fe(II) has supported anaerobic CH$_4$ oxidation in other ecosystems (Ettwig et
750 al., 2016). Within this context, a measurable amount of anaerobic oxidation of CH$_4$ has previously been reported at
751 our study site (Blazewicz et al., 2012). Additionally, Fe-reducing microorganisms can utilize acetate as a substrate
752 and thereby compete with methanogens and reduce net methane emissions (Teh et al., 2008). Given the gradient of

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757 Fe in our study site, it is likely that biogeochemical cycling of Fe and CH_4 are coupled (O'Connell et al., 2018)
758 which should be accounted for in future modeling efforts. For example, a modeling study supported the importance
759 of Fe in simulating CH_4 cycling in an Arctic soil (Tang et al., 2016). To that end, building a comprehensive
760 framework that also includes Fe biogeochemistry will afford greater confidence in projected CH_4 emissions from
761 wet tropical forests under future climatic conditions (Bonan et al., 2008; Pachauri et al., 2014; Xu et al., 2016).

762 **5 Conclusions**

763 High-frequency CH_4 emission measurements coupled with real-time soil chemical measurements identified spatial
764 and temporal variations affecting CH_4 production and oxidation in wet tropical forest soils of Puerto Rico. Overall,
765 contrasting patterns of soil moisture between ridge and valley soils played an instrumental role in governing net CH_4
766 emissions. For example, consistently greater soil moisture likely favored methanogenesis by lowering the
767 availability of O_2 in valley soils compared to ridgetop soils, especially in microsites with high soil moisture and soil
768 C content. However, soil porewater chemistry, particularly the concentrations of acetate and associated soil pH
769 influenced the pattern of net emissions of CH_4 across the catena (valley > slope > ridge) during wetting after the
770 2015 drought. Thus, our results provide compelling evidence of the importance of both hot spots and hot moments
771 in generating and mediating CH_4 emissions in wet tropical forest soils. A microbial functional group-based model
772 coupled with a diffusivity module and consideration of soil microsites adequately reproduced both the spatial and
773 temporal dynamics of soil CH_4 emissions, although mechanisms involving Fe biogeochemistry were neglected.
774 This study suggests that representing the microbial mechanisms and the interactions of microbial functional groups
775 with the soil biophysical and chemical environment across soil microsites is critical for modeling CH_4 production
776 and consumption. To that end, explicit consideration of these underlying mechanisms improved predictions of CH_4
777 dynamics in response to regional climatic events and provided insig ht into differential dynamics of solute and gas
778 diffusion, different microbial functions, and gross CH_4 production and oxidation as a function of topography. Hence,
779 we contribute to the ongoing development and improvements of Earth system and process models to better simulate
780 microbial roles in CH_4 cycling at regional and global scales. However, observational data concerning the activities
781 of different soil microbial functional groups is still needed to confirm the mechanisms proposed here. Future studies
782 should integrate geochemical and microbiological information relevant for oscillatory redox conditions in wet
783 tropical forests, especially those related to the redox-sensitive elements to build a comprehensive framework for
784 modeling tropical soil CH_4 emissions.

785 **Code and data availability**

786 Meteorological data (http://criticalzone.org/luquillo/data/dataset/4723/) are available from the Luquillo CZO
787 repository. 2015 greenhouse gas fluxes (DOI: 10.6073/pasta/316b68dd254e353e1acfb16d92bac2dc) are available
788 from the Luquillo LTER repository. The 2016 greenhouse gas fluxes (DOI: 10.15485/1632882), soil chemistry
789 (DOI: 10.15485/1618870), and rhizon lysimeter data (DOI: 10.15485/1618869) are available from ESS-DIVE
790 repository. R scripts used for this modeling exercise are archived at the following Zenodo repository (DOI:
791 10.5281/zenodo.3890562).

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Author contributions

DS performed the data curation of 2016 flux data and the soil and lysimeter data, collated diffusion and microsite processes into the model presented herein, interpreted and validated the model application, developed the visualization, and wrote the original draft. XX provided the model code used in the investigation and assisted with its modification and application. MSO collected the 2016 field flux data. CSO and WLS provided the 2015 flux data and the 2015-2016 field soil measurements for temperature, oxygen, and moisture. CSO developed workflow for field flux data management, cleaning and analysis. WLS acquired the funding, administered the project, and supervised the research team involved with collection of the 2015 data. CLL collected the rhizon water samples and soil samples from the field site, with assistance from MAM. JMB analyzed the rhizon water samples in the lab. JRP, RKQ, and JMB completed the laboratory soil analyses. BDN supplied, installed, and maintained the rhizon water samplers. MAM acquired the funding and administered the project that collected the 2016 data, conceptualized the paper and proposed the methods, supervised the research team, and contributed to the writing, interpretation, and visualization of subsequent drafts. All authors contributed to the manuscript through reviewing and editing subsequent drafts.

Competing interests

The authors declare that they have no conflicts of interest.

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1046 **Table 1: Fitted values of M3D-DAMM model parameters.**

Parameters	Fitted values	Description	Unit	Source
$GrowR_{H2Methanogens}$	0.31		1/day	Servais et al., 1985
$GrowR_{AceMethanogens}$	1.59	Growth rates	1/day	Servais et al., 1985
$GrowR_{Methanotrophs}$	0.12		1/day	Servais et al., 1985
$DeadR_{H2Methanogens}$	0.03		1/day	Servais et al., 1985
$DeadR_{AceMethanogens}$	0.54	Death rates	1/day	Servais et al., 1985
$DeadR_{Methanotrophs}$	0.008		1/day	Servais et al., 1985
$Efficiency_{H2Methanogens}$	0.2	Substrate	unitless	Grant, 1998
$Efficiency_{AceMethanogens}$	0.04	use	unitless	Kettunen et al., 2003
$Efficiency_{Methanotrophs}$	0.4	efficiencies	unitless	Kettunen et al., 2003
KM_{Ace}	16		mmol/m3	Grant, 1998; McGill et al., 1981
$KM_{H2ProdAce}$	11		µmol/m3	Conrad, 1989
$KM_{H2ProdCH4}$	$2.14*10^{-5}$	Half-saturation	mmol/m3	Fennell and Gossett, 1998
$KM_{CO2ProdCH4}$	$9.08*10^{-9}$	constants	mmol/m3	Stoichiometry theory
$KM_{CH4ProdAce}$	13		mmol/m3	Kettunen et al., 2003
$KM_{CH4ProdO2}$	0.03		mmol/m3	Kettunen et al., 2003
$KM_{CH4OxidCH4}$	0.06		mmol/l	Kettunen et al., 2003
$KM_{CH4OxidO2}$	0.74		mmol/l	Kettunen et al., 2003
$ACmax_{AceProd}$	0.52	Maximum	mmol/m3/h	Smith and Mah, 1966
$Acemax_{H2Prod}$	1.31	reaction rates	mmol acetate/g/h	Conrad, 1989
$rCH4Prod$	0.84	Rate	mol CH$_4$/mol acetate	Kettunen et al., 2003
$rCH4Oxid$	3.06	constants	mol O$_2$/mol CH$_4$	Kettunen et al., 2003
$Q_{10ACMin}$	1.16		unitless	Segers, 1998
$Q_{10AceProd}$	1.21		unitless	Atlas and Bartha, 1987; Kettunen, 2003; Van Hulzen et al., 1999
$Q_{10H2CH4Prod}$	1.27	Temperature	unitless	Segers, 1998
$Q_{10CH4Prod}$	1.13	sensitivities	unitless	Kettunen et al., 2003
$Q_{10CH4Oxid}$	1.18		unitless	Kettunen et al., 2003

1047

1048 Initial values of model parameters were collected from literature ("Source"). Also see Xu et al. (2015) for detailed information
1049 on model parameters.

050

(a)

Microsite frequency

$[S_i]$, $[G_i]$, $SoilM_i$, $Diff_i$, $Prod_i$, Ox_i

Increasing concentrations or rates

(b)

SOM/Litter — CO₂ / DOC
Acetate
H⁺
CO₂
Acetate
H⁺
H₂
CO₂
CH₄
CH₄

(1) Acetoclastic methanogenesis
(2) Hydrogenotrophic methanogenesis
(3) Methanotrophy

051
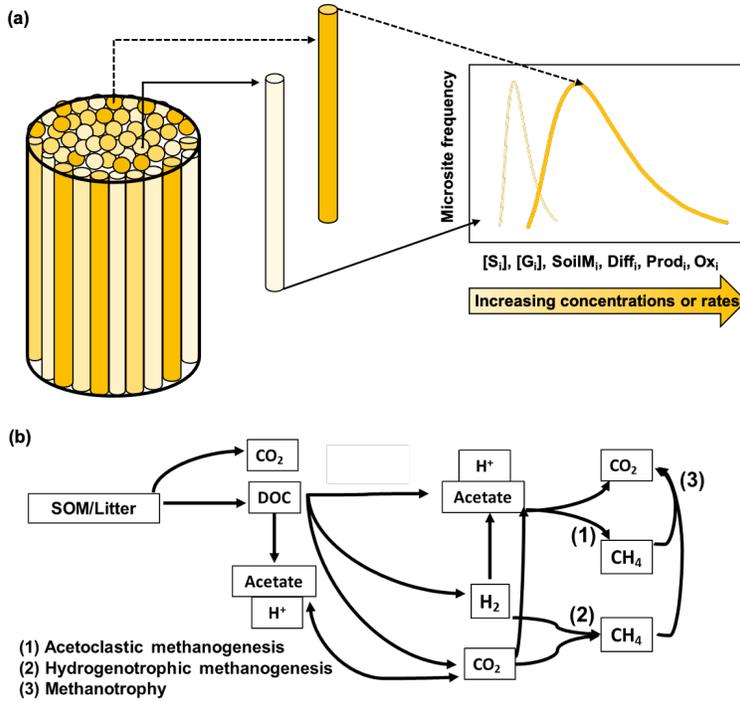
Figure 1: Conceptual figure of the modelling approach. Top panel (a) Top panel (a) shows the model representation of soil microsite distribution (modified from Sihi et al., 2020a, also see Eq. 14). The cylinder refers to the volume beneath the soil chambers. The intensity of different cylinder colors figure refers to rate of a process or the intensity of a concentration inside microsites in each theoretical cylinder, e.g., a dark color means a higher rate/intensity, and a light color means a lower rate/intensity for a given process. The 2D graph on the right refers to the probability density function of the rate of the process or intensity of the concentration in the bulk soil. A wide distribution skewed to the right (dark line) implies higher bulk rates of the process or higher concentrations, and a narrow distribution skewed to the left (light line) implies lower bulk rates of the process or lower concentrations, of any of the following: solute concentration $[S_i]$, gas concentration $[G_i]$, soil moisture $(SoilM_i)$, gas and solute diffusion $(Diff_i)$, methane production $(Prod_i)$, and methane oxidation (Ox_i). Bottom panel (b) is the schematic of the microbial functional group-based model for simulating soil methane (CH_4) dynamics in field soils (modified from Xu et al., 2015). The schematic represents the decomposition of soil organic matter (SOM) and plant litter into carbon dioxide (CO_2) and dissolved organic matter (DOC); the production of acetate and hydronium ion (H^+) from decomposition and fermentation of DOC which also decreases pH, the production of acetate and hydronium ion (H^+) from homoacetogenesis which decreases pH; and the production of dihydrogen ion (H_2) and CO_2 from decomposition of DOC. The intermediary products then have three possible non-mutually exclusive pathways (1) aceticlastic methanogenesis, which is the production of methane from aqueous acetate found in soil solutions, (2) hydrogenotrophic methanogenesis, which is the production of methane from hydrogen, and (3) methanotrophy, which is the oxidation of methane into carbon dioxide.

22

(a)

(b)

Air
Soil
H₂   O₂

SOM/Litter — CO₂ / DOC
Acetate
H⁺

(1) Acetoclastic methanogenesis
(2) Hydrogenotrophic methanogenesis
(3) Methanotrophy

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Figure 2: Soil and porewater chemistry (dissolved organic carbon [DOC] (a), acetate (b), and pH (c)) along the ridge-slope-valley topographic gradient.

Figure 3: Temporal dynamics of observed meteorological drivers (soil temperature (a-c), soil moisture (d-f), soil oxygen (g-i)) and net methane emissions (j-l) for 2015 (Data are taken from O'Connell et al., 2018). For methane emissions, symbols represent observed data and lines represent model simulations. Dark gray, medium gray, light gray, and white shading represent pre-drought, drought, drought recovery, and post drought events (O'Connell et al., 2018).

24
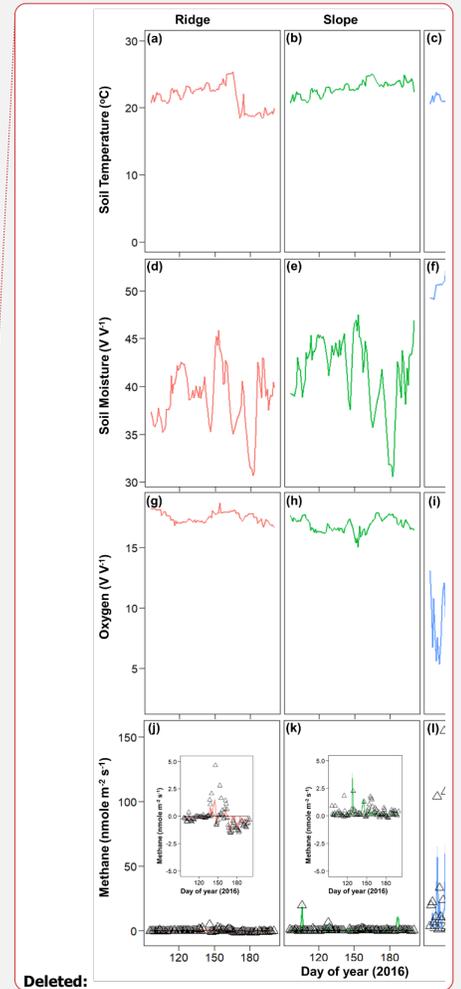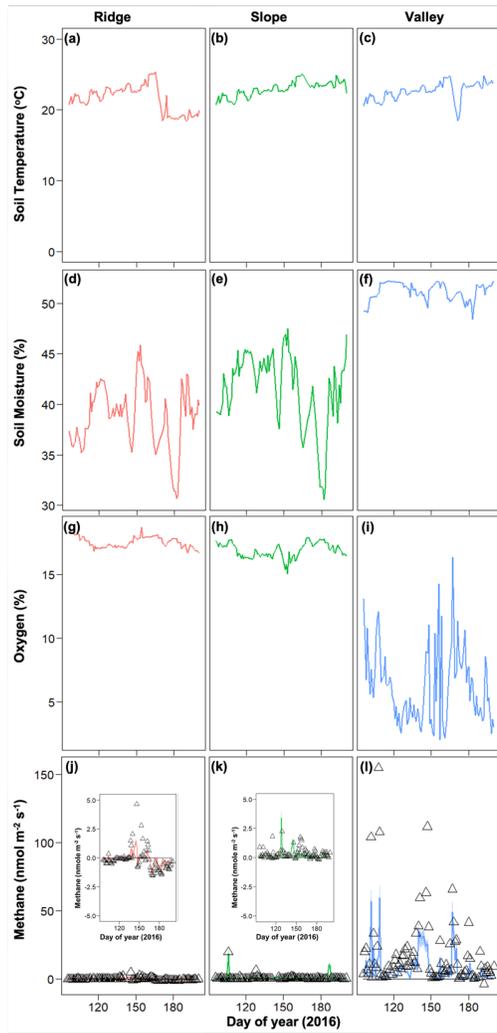
Figure 4: Temporal dynamics of observed meteorological drivers (soil temperature (a-c), soil moisture (d-f), soil oxygen (g-i)) and net methane emissions (j-l) for 2016. For methane emissions, symbols represent observed data and lines represent model simulations.

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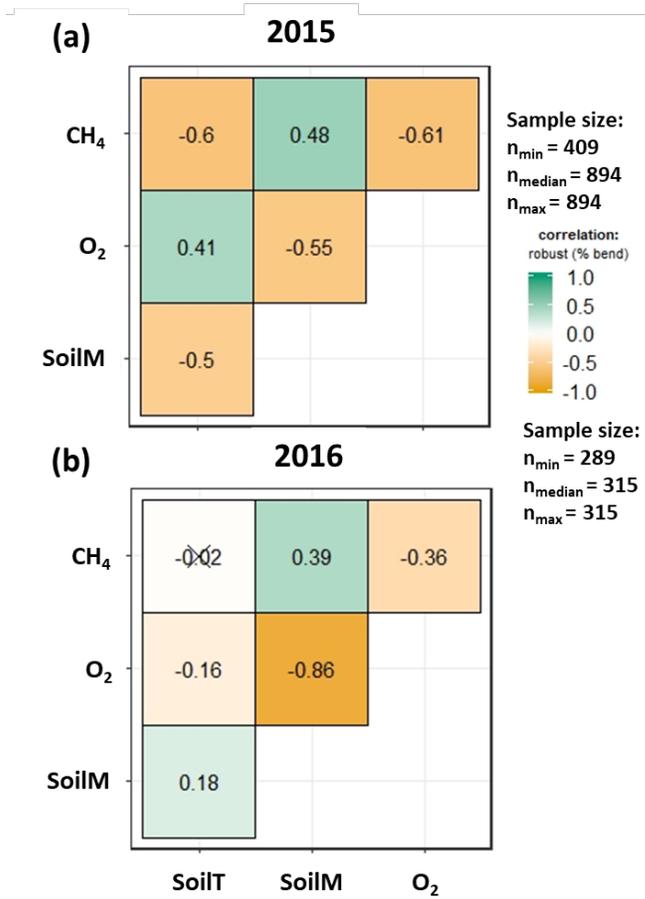
Figure 5: Relation between soil meteorology and methane emissions for 2015 (a) and 2016 (b). SoilM, SoilT, O₂, CH₄ represent soil moisture, soil temperature, oxygen, and methane, respectively. Numbers represent adjusted Holm correlation coefficients, and numbers with "X" indicate a non-significant correlation at $p < 0.05$.

26

For 2015

(a) y = 0.58x + 0.928
R² = 0.72

(b)

For 2016

(c) y = 1.13x + 1.09
R² = 0.67

(d)
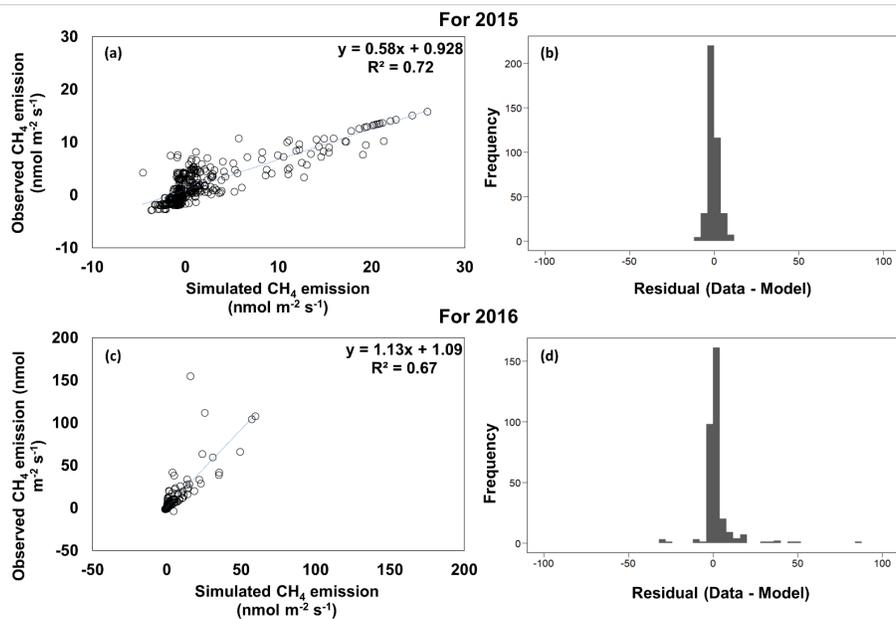
Figure 6: Observed versus simulated methane (CH₄) emissions and model residuals for 2015 (a, b) and 2016 (c, d).

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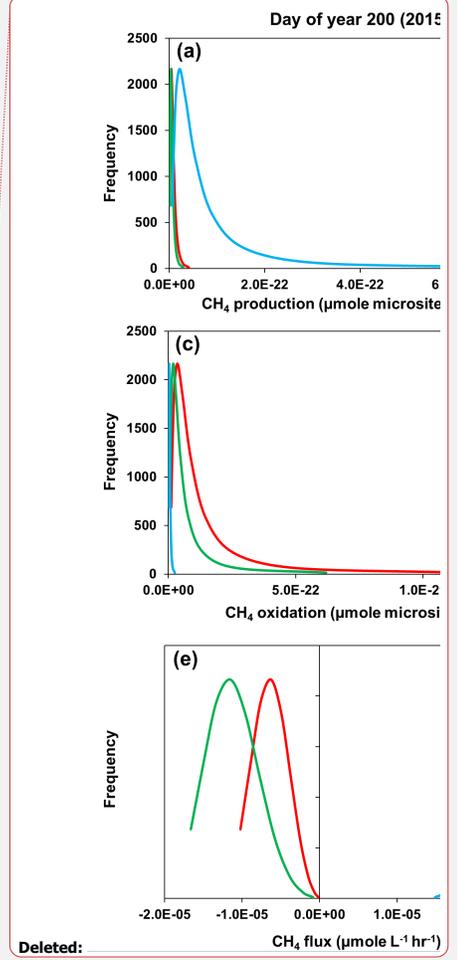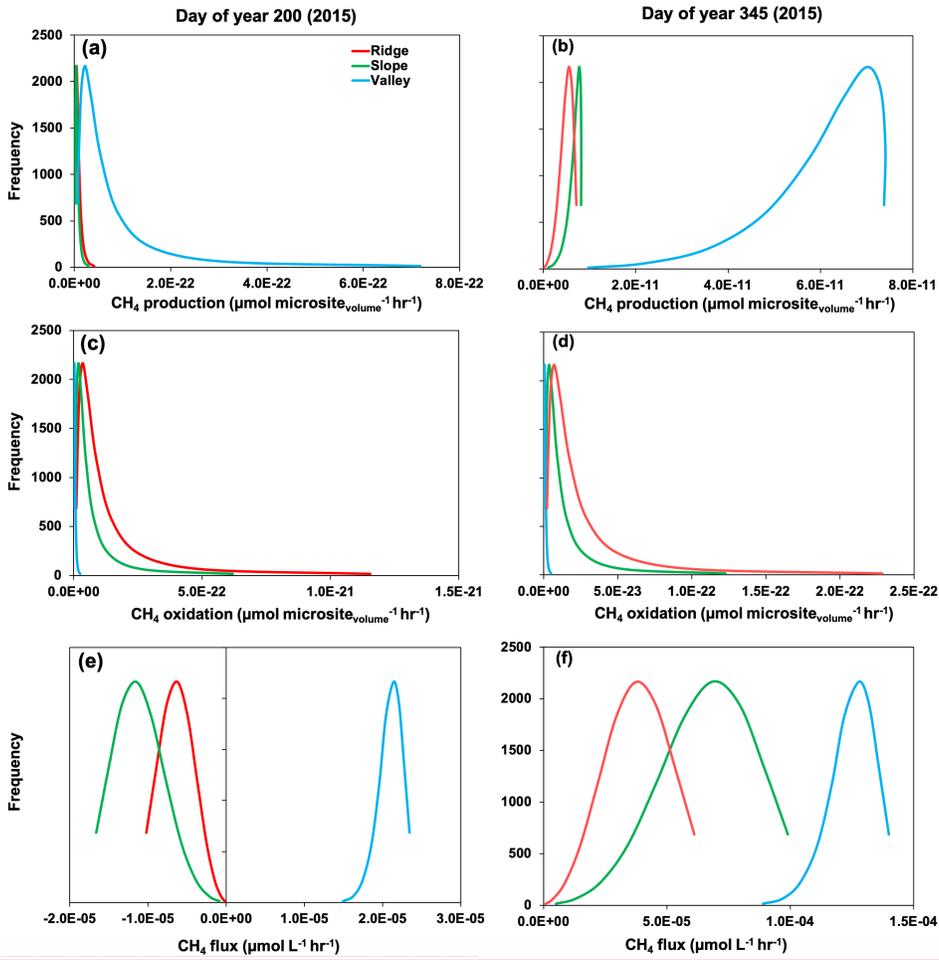
Figure 7: Rates of gross methane (CH$_4$) production (a, b), oxidation (c, d), and net flux (e, f) across simulated soil microsites. Day of year 200 and 345 represent drought and post-drought recovery, respectively (see medium gray and white shading in Fig. 3).

28
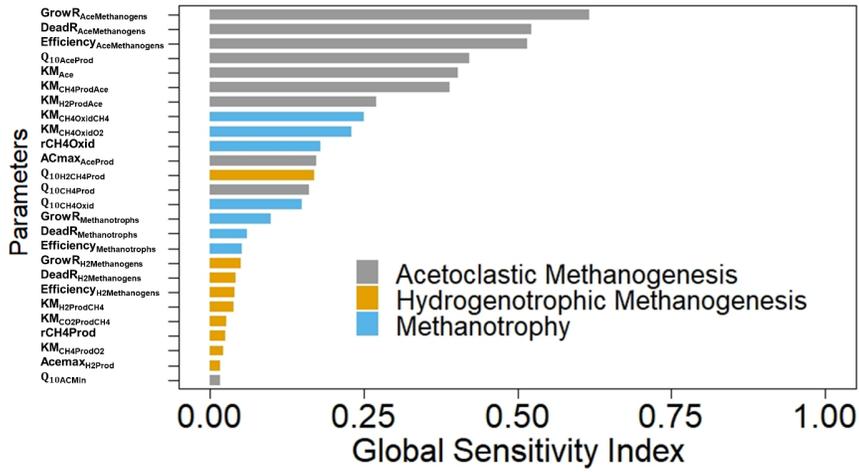
Figure 8: Global sensitivity indices of M3D-DAMM model parameters (defined in Table 1). Gray, yellow, and blue colors represent parameters for aceticlastic methanogenesis, hydrogenotrophic methanogenesis, and methanotrophy, respectively.

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