

## Anonymous Referee #2

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This paper describes CO<sub>2</sub> and CH<sub>4</sub> concentration measurements made during the summer season on 101 farm reservoirs in an agricultural region of Saskatchewan, Canada. The authors then use a series of floating chamber measurements to infer diffusive fluxes of these two greenhouse gases at the pond surface via estimations of gas transfer. The authors also collect data on a number of abiotic and biotic landscape/waterbody characteristics that may help predict farm pond GHG concentrations. They then use general additive modeling to describe controls on waterbody concentration. While not currently emphasized, this paper follows up on a previous article that described novel N<sub>2</sub>O uptake dynamics in these same ponds. The authors emphasize a few findings: 1) more than half of farm ponds are net CO<sub>2</sub> sinks, 2) some (19%) farm ponds are net CO<sub>2</sub>-eq sinks when looking at diffusive emissions, 3) CO<sub>2</sub> concentrations are governed most by hydrology/landscape position, 4) CH<sub>4</sub> emissions are governed most by autochthonous production.

**Response:** We thank the reviewer for their critical analysis of our study and appreciate suggestions that further link this work to the broader literature. Detailed responses to comments are provided below.

The current framing of this paper is difficult for me to digest given the complete lack of any CH<sub>4</sub> ebullition measurements from these systems (and given that fluxes were estimated based on highly uncertain estimates of gas transfer). While the authors acknowledge that their estimates of CO<sub>2</sub>-eq emissions are likely low due to the lack of ebullition measurements, this is done at the very end of their paper. I think this point should be made sooner as it is an important detail that influences the interpretation of their findings. The relative contribution of ebullition to total methane flux can vary widely from system to system and the controls on the proportion of methane flux that is ebullitive are not well understood (Deemer et al. 2016 BioScience). It would be helpful to know if the authors observed any evidence of ebullition events during their floating chamber surveys? How much ebullition would have to be observed to push the net CO<sub>2</sub>-eq sink systems towards net-source? Also, what is the uncertainty in sink vs. source estimations due to uncertainty in system gas transfer velocity? To this same end, it is difficult to see the 19% of systems that are net CO<sub>2</sub>-eq sinks by looking at the authors' figures. Is this because the net CO<sub>2</sub>-eq sink is very small? For example, Figure 4 does not seem to show that over 50% of the systems in your study were net CO<sub>2</sub> sinks. I suggest adding a zero line to your figures and possibly creating an additional figure that shows fluxes site-by-site for the farm ponds in your study. The visual aids currently offered for showing the distribution of your own dataset are sort of overshadowed by a comparison with the broader literature.

**Response:** We agree that ebullition can be a major methane flux pathway and plan on investigating this in future field studies. Because the focus of the study was to assess the mechanistic drivers of CO<sub>2</sub> and CH<sub>4</sub> concentrations, the survey was designed to optimise data collection from a large number of sites and ebullition measurements were not carried out. Based on your suggestion, we now highlight this detail earlier in the Methods section:

*“To compare with the literature and assess the source/sink behaviour of the reservoirs, diffusive fluxes of carbon dioxide and methane fluxes were estimated for each water body. Given that the focus of the study was to investigate drivers of CO<sub>2</sub> and CH<sub>4</sub> concentrations across farm reservoirs, ebullition events were not measured during this survey and as such total CH<sub>4</sub> fluxes are likely underestimated. Diffusive fluxes were estimated using water column concentrations ( $C_{water}$ ) and average farm reservoir gas transfer velocity ( $k_c$ ) using the following equation:*

$$f_c = k_c(C_{water} - C_{air}), \quad (1)''$$

Line 112

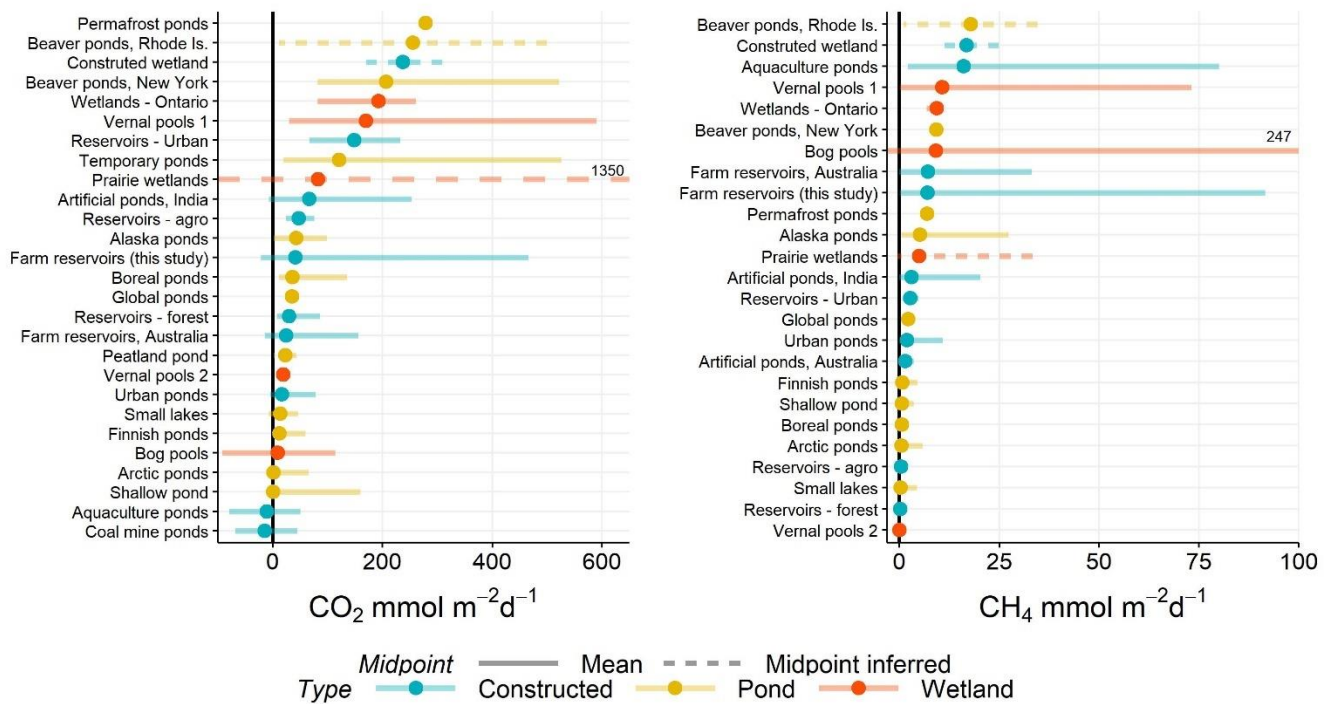
We agree that the highly variable nature of gas transfer velocities is the greatest source of uncertainty in flux calculations. As previously mentioned in the manuscript,  $k_{600}$  values for  $\text{CO}_2$  and  $\text{CH}_4$  were  $1.50 \pm 1.34 \text{ m d}^{-1}$  and  $1.64 \pm 1.14 \text{ m d}^{-1}$ , respectively. These data, along with the median, range, and calculated  $\text{CO}_2$  and  $\text{CH}_4$  fluxes, have now been added to Table 1 (highlighted in bold below) to provide more transparency to the reader. Please also note that flux and  $k_{600}$  data are provided in a GitHub repository (<https://github.com/JackieRWebb/Dugouts-CO2-CH4>) which will be publicly available upon publication. Finally, we respectfully note that application of uncertainty values for  $k_{600}$  to our fluxes will increase or decrease the sink or source capacity of the systems, but will not change the number of reservoirs that are  $\text{CO}_2$ -eq sinks/sources.

**Table 1: Farm reservoir and landscape physical, hydrological, and chemical characteristics of the study sites (n = 101)**

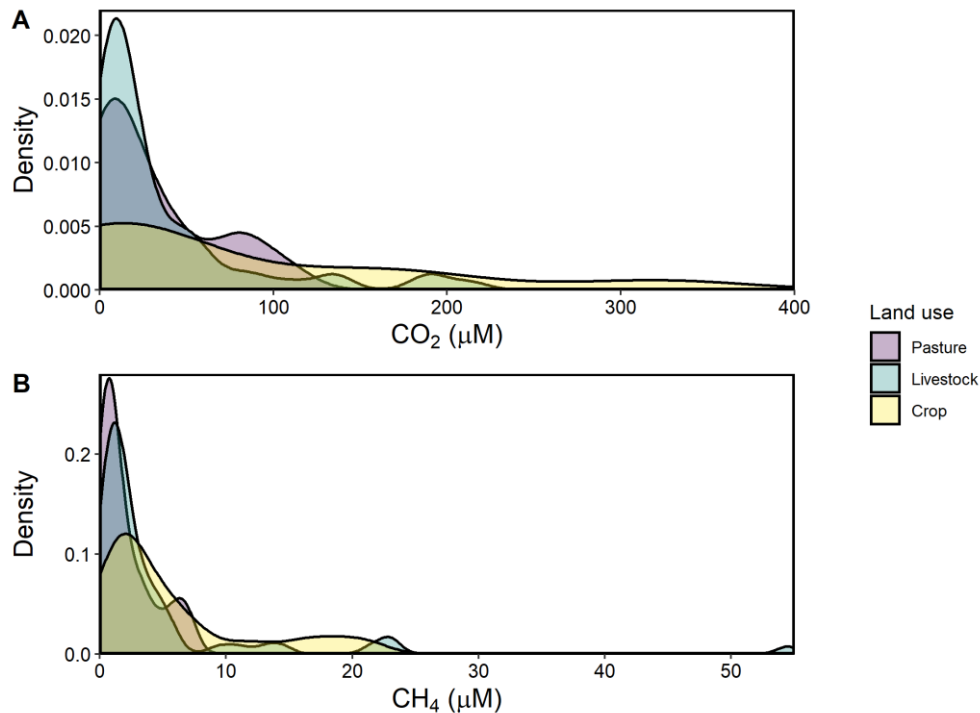
|   | <i>Units</i>                    | <i>N</i>   | <i>Mean</i> | <i>Median</i> | <i>Min</i>   | <i>Max</i>   |              |
|---|---------------------------------|--|-------------|---------------|--------------|--------------|--------------|
| Area  | $\text{m}^2$                    | 101  | 1,312       | 1,040         | 158          | 13,900       |              |
| Depth   | m                               | 101  | 2.08        | 2.10          | 0.18         | 5.10         |              |
| Buoyancy frequency                                    | $\text{s}^{-2}$                 | 99   | 0.01        | 0.005         | 0.00         | 0.03         |              |
| $\delta^{18}\text{O}$ inflow                          | ‰                               | 101  | -13.37      | -13.33        | -19.39       | -8.40        |              |
| Evaporation to inflow                                 |                                 | 101  | 0.46        | 0.43          | 0.04         | 1.58         |              |
| Water residence time                                  | Years                           | 100  | 0.76        | 0.66          | 0.08         | 2.51         |              |
| $\text{CO}_2$   | $\mu\text{M}$                   | 101  | 42.2        | 14.6          | 1.3          | 326.1        |              |
| $\text{CH}_4$   | $\mu\text{M}$                   | 101  | 4.3         | 1.9           | 0.1          | 54.5         |              |
| <b>Flux <math>\text{CO}_2</math></b>                  |                                 |  |             |               |              |              |              |
|   | <i>Positive</i>                 | <b>mmol <math>\text{m}^{-2} \text{d}^{-1}</math></b> | <b>47</b>   | <b>100.1</b>  | <b>58.1</b>  | <b>0.1</b>   | <b>466.2</b> |
|   | <i>Negative</i>                 | <b>mmol <math>\text{m}^{-2} \text{d}^{-1}</math></b> | <b>54</b>   | <b>-11.9</b>  | <b>-13.3</b> | <b>-21.3</b> | <b>-0.1</b>  |
| <b>Flux <math>\text{CH}_4</math></b>                  |                                 | <b>mmol <math>\text{m}^{-2} \text{d}^{-1}</math></b> | <b>101</b>  | <b>7.1</b>    | <b>3.2</b>   | <b>0.4</b>   | <b>91.5</b>  |
| <b><math>k_{600}</math>- <math>\text{CO}_2</math></b> |                                 | <b><math>\text{m d}^{-1}</math></b>                  | <b>15</b>   | <b>1.50</b>   | <b>0.98</b>  | <b>0.20</b>  | <b>4.12</b>  |
| <b><math>k_{600}</math>- <math>\text{CH}_4</math></b> |                                 | <b><math>\text{m d}^{-1}</math></b>                  | <b>23</b>   | <b>1.64</b>   | <b>1.25</b>  | <b>0.38</b>  | <b>4.14</b>  |
| Temperature   | $^{\circ}\text{C}$              | 101  | 20.1        | 19.9          | 15.7         | 29.5         |              |
| Dissolved $\text{O}_2$                                | %                               | 101  | 92.6        | 88.9          | 2.3          | 344.0        |              |
| Salinity  | ppt                             | 101  | 0.9         | 0.5           | 0.1          | 8.6          |              |
| pH  |                                 | 101  | 8.75        | 8.75          | 6.95         | 10.19        |              |
| Chlorophyll a   | $\mu\text{g L}^{-1}$            | 101  | 99.1        | 36.9          | 2.2          | 2,483        |              |
| $\text{NH}_3$   | $\mu\text{g N L}^{-1}$          | 100  | 354.7       | 100.0         | 10.0         | 5,930        |              |
| $\text{NO}_x$   | $\mu\text{g N L}^{-1}$          | 98   | 196.6       | 34.1          | 1.2          | 3,188        |              |
| TP  | $\mu\text{g P L}^{-1}$          | 98   | 285.2       | 80.0          | 8.7          | 6,480        |              |
| TN  | $\mu\text{g N L}^{-1}$          | 98   | 3,082       | 2,360         | 417.5        | 14,280       |              |
| DOC   | $\text{mg C L}^{-1}$            | 99   | 31.8        | 29.3          | 4.6          | 90.4         |              |
| Sediment organic carbon                               | %                               | 101  | 5.2         | 3.9           | 0.6          | 31.4         |              |
| Sediment organic nitrogen                             | %                               | 101  | 0.6         | 0.4           | 0.1          | 2.8          |              |
| Alkalinity  | $\text{mg L}^{-1}$              | 96   | 245.4       | 219.2         | 71.0         | 755.5        |              |
| Soil CEC  | $\text{M-eq } 100\text{g}^{-1}$ | 98   | 24          | 24            | 10           | 180          |              |
| $K_{\text{sat}}$                                      | $\text{cm hr}^{-1}$             | 101  | 9.9         | 5.0           | 0.0          | 39.7         |              |
| Elevation   | m                               | 101  | 627.6       | 598.0         | 484.0        | 997.0        |              |

As suggested a solid line indicating the threshold between positive and negative fluxes has been added to Figure 5 for better visualisation. The >50% reservoirs that were found to be sinks may be hard to distinguish because our data is highly skewed by some very high concentrations/fluxes. As per the

suggestion of Reviewer 1, this is demonstrated more clearly by the addition of a density plot (Figure 2).



**Figure 5: Range of CO<sub>2</sub> and CH<sub>4</sub> (diffusive) fluxes observed in natural and constructed small (<0.01 km<sup>2</sup>) waterbodies, including this study (farm reservoirs). Dots represent the mean reported in each study and error bars the range. If no mean value was reported, then the midpoint was inferred as the middle of range (dashed lines). Solid black line distinguished between positive and negative fluxes. All data is from the published literature and references can be found in the Table S6.**



**Figure 2: Kernel density estimates of CO<sub>2</sub> and CH<sub>4</sub> concentrations measured in 101 farm reservoirs grouped by land use.**

Also, while I am not very familiar with GAMs, I found this analysis a bit opaque and difficult to interpret as currently described. For example, were both N and P variables put into the model and NO<sub>x</sub>/DIN came out as more important? Also, how were the variables plotted in figures 2 and 3 selected? From what I can gather, you have plotted more than just the variables in the best model. For the sake of discussion, it would be nice to see a consistent set of variables and their relationship to both CH<sub>4</sub> and CO<sub>2</sub>.

**Response:** Variables for each model were selected based on previous knowledge from the literature on the potential mechanisms controlling CO<sub>2</sub> or CH<sub>4</sub> in freshwater bodies. The model is designed to test the hypothesis of selected environmental controls and included variables representing water chemistry and biology (Table S1), hydrology (Table S2), and external landscape factors (Table S3). As described in the methods, correlation analysis of covariate pairs was first carried out to guide variable selection in the final models as a) some variables represent the same mechanism and are highly correlated (e.g. total N and total P) and b) provided a first assessment of what variables correlated strongest with the response variable within each group of environmental factors. Results of these correlation analysis is provided in Supplementary materials (Table S1-S3). Finally, all variables plotted in Figs 3 and 4 represent those that were included in the GAM and therefore need to be presented, even if some variables came out as non-significant. It is from here that we learn what the most important mechanisms are for potentially controlling gas concentrations.

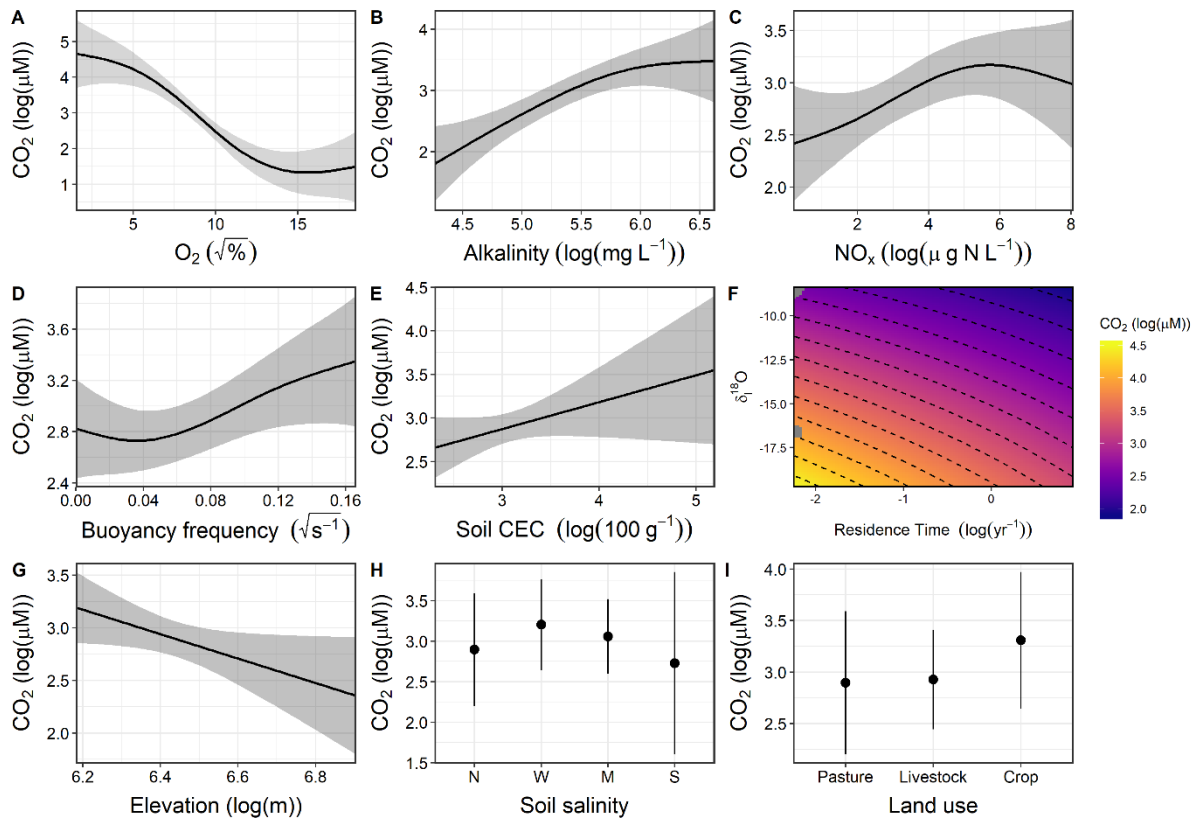
To me, the more novel part of this data set is the high fraction of ponds that are net CO<sub>2</sub> sinks. This is also a finding that is most strongly backed by the data that was collected since the conclusion doesn't rely as much on gas transfer estimates and since CO<sub>2</sub> ebullition is typically an extremely small fraction of total CO<sub>2</sub> emission. The extent of the CO<sub>2</sub> sink in these small agricultural ponds could be compared to the lesser extent reported in the global data set of artificial reservoir GHG dynamics (Deemer et al. 2016). It is also interesting that the CO<sub>2</sub> sink seems to scale more with landscape and hydrological factors than with ecosystem productivity. While multiple other studies have already emphasized the potential importance of nutrient management/eutrophication on lake, pond, and reservoir methane emissions (see Beaulieu et al. 2019 for a very recent global scale discussion), the findings you present in this paper suggest that landscape placement of farm reservoirs may help buffer GHG emissions independent of trophic status (via carbonate buffering and groundwater DIC chemistry dynamics). See paper by Pacheco et al 2013 in *Inland Waters* (which asks if eutrophication can reverse the aquatic C budget). To this end, it would also be nice to see plots comparing emission by land use for both CH<sub>4</sub> and CO<sub>2</sub> (right now the plot is only shown for CH<sub>4</sub>).

**Response:** We agree and have expanded the following paragraph in discussion to emphasize our findings on CO<sub>2</sub> uptake:

*“The negative fluxes observed in our farm dams represents one of the few studied small waterbodies that exhibit CO<sub>2</sub> sink behaviour, with most showing net heterotrophy (Fig. 5). Although other studies have noted CO<sub>2</sub> sink behaviour in artificial ponds and reservoirs (Peacock et al., 2019; Ollivier et al., 2019), this is the first study to capture such a high proportion (>52%) of CO<sub>2</sub> uptake in such systems, with negative fluxes estimated to range between -21 to -0.1 (mean -12) mmol m<sup>-2</sup> d<sup>-1</sup> for CO<sub>2</sub> (Table 1). These flux ranges compare to CO<sub>2</sub> uptake of -1 to -11 mmol m<sup>-2</sup> d<sup>-1</sup> in agricultural eutrophic lakes of North America (Finlay et al., 2010; Pacheco et al., 2013). Studies have shown the importance of eutrophication, leading to net autotrophy, in enhancing CO<sub>2</sub> uptake and reversing carbon budgets in lakes (Pacheco et al., 2013). However, a global analysis of GHG fluxes from lakes and reservoirs revealed that the consequence of increased CH<sub>4</sub> emissions with increasing trophic status often outweighs the impact of negative CO<sub>2</sub> fluxes (Deemer et al., 2016). Here, our model shows the potential importance of reservoir placement within the landscape as a way of reducing CO<sub>2</sub> emissions*

via hydrological and geochemical controls without the added consequence of increased CH<sub>4</sub> emissions.” Line 372

A suggested by yourself and Reviewer 1, land use is now included in Figure 3 for the CO<sub>2</sub> model. In addition, the new Figure 2 also shows the raw data distribution for CO<sub>2</sub> concentrations by land use.



**Figure 3: Response patterns farm reservoir CO<sub>2</sub> concentrations with abiotic, biotic, hydromorphological, and landscape variables based on GAMs. CO<sub>2</sub> was best estimated by a combination of a) DO saturation, b) alkalinity, c) NO<sub>x</sub>, d) buoyancy frequency, e) interaction between  $\delta^{18}\text{O}$  and WRT, f) soil CEC, g) and elevation, with soil salinity (h) and land use (I) not significant. Model deviance explained was 66.5%. The response patterns shown are the partial effect splines from the GAM (solid line) and shaded area indicated 95% credible intervals. See Table S4 and Figure S2 for summary of model statistics and model fit with observed data.**

The comparison between human-made and natural waterbodies is also interesting and novel. I think it would be good to more thoroughly introduce this question/concept (that the systems might fundamentally differ from each other) earlier in the paper and then come back to it in the discussion. A good reference for comparing human-made and natural waterbodies is Hayes et al. 2017 L&O Letters as well as Doubek & Carey 2017 Inland Waters.

**Response:** We agree that human-made and natural waterbodies function differently from each other on a range of ecological scales. However, our discussion of the literature review focuses on CO<sub>2</sub> and CH<sub>4</sub> fluxes only and to date have revealed few differences between constructed and natural systems, mainly because both systems have highly variable flux rates (Lines 382, 388). Given our focus on CO<sub>2</sub> and CH<sub>4</sub> fluxes here, we did not want to add overly speculative text on the potential impact of human-made and natural waterbodies.

Line by Line Edits

Line 18: add “surface” before “concentrations”

**Response:** Corrected

Lines 20-21: this is a little misleading since pH was actually a better predictor

**Response:** the term “best” has been removed.

Lines 23-24: state the timescale over which you are calculating CO<sub>2</sub>-equivalents

**Response:** “100-year radiative forcing” has been added.

Line 26: bringing up depth doesn’t seem appropriate here since depth didn’t come out as a significant predictor variable in your models

**Response:** Depth has been removed from this sentence and revised to more accurately reflect our model findings:

*“From our models, we show that the GHG impact of farm reservoirs can be greatly minimised with overall improvements in water quality and consideration to position and hydrology within the land scape.”* Line 25

Line 30-31: Holgerson and Raymond 2016 didn’t look at ebullition

**Response:** We have now clarified that this reference refers to diffusive fluxes only: *“Current assessments estimate that diffusive CO<sub>2</sub> and CH<sub>4</sub> emissions from small ponds (<0.001 km<sup>2</sup>) account for 15% and 40% of global emissions from lakes, respectfully (Holgerson and Raymond, 2016).”* Line 30

Line 45-46: Also check out Couto and Olden 2018. . . there aren’t really global papers that distinguish surface area of small farm reservoirs/ponds from small hydropower.

**Response:** We have added “artificial reservoirs” to this sentence to be clear that this global estimate does not just refer to farm reservoirs.

Lines 46-47: I suggest listing out numbers of reservoirs by country since the current phrasing is difficult to interpret. Either that or use a word like “collectively” to indicate that 8 million is the sum across multiple countries.

**Response:** “collectively” has been added.

Line 51: What does It mean to create reservoirs at a rate of up to 60% of standing stock? I’m a bit confused by this wording.

**Response:** “standing stock” has been replaced with “existing reservoirs”.

Lines 56-57: It is a bit awkward to suggest that eutrophication results in potent CO<sub>2</sub> release since autochthonous production actually works to fix CO<sub>2</sub> (see Pacheco et al. 2013).

**Response:** The mention to eutrophication has been removed from the sentence.

Lines 76-77: I suggest clarifying: you are identifying drivers of surface water concentration, not total flux. Although these are related, they are not the same thing.

**Response:** “fluxes” have been replaced with “concentrations”.

Lines 86-87: How did you select your sites? Randomly?

**Response:** Sites were selected from a database of farm reservoirs collected by a survey of regional landowners, as well as from sites on federal lands. Site selection was refined by ensuring a relatively even spatial distribution across the study area, while also considering ease of access.

Lines 197-202: What were N:P ratios like in these systems?

**Response:** Total N to P ratios (by mass) varied from 1.4 to 126. Readers will be able to refer to all raw data provided in a Github repository (<https://github.com/JackieRWebb/Dugouts-CO2-CH4>) which will be made public upon publication.

Results section: I suggest including a summary of the fluxes you estimate (and associated gas transfer rates from the floating chamber surveys). Can you estimate how variability in k might affect variability in your flux estimates? Are there cases where you have both a floating chamber and a concentration based estimate of flux? How much did these differ from each other?

**Response:** As suggested by the reviewer, we have added the summary statistics for both fluxes and measured gas transfer velocities to Table 1. In the results section, we have focused on describing gas concentrations and model results. Instead, description of fluxes are presented later in the paper to aid with comparison of literature values.

Line 227: change “by” to “with”

**Response:** Corrected

Line 246: Not a complete sentence.

**Response:** Sentence corrected to read “*Here, we see evidence for both linked and divergent processes (Fig. 3A).*” Line 261

Lines 261-262: This doesn’t seem like a very satisfying explanation to me. Is it also possible that differing hydrology leads to the more stratified systems also being the ones that are higher in CO<sub>2</sub>?

**Response:** We agree that this sentence is speculative and have removed it.

Line 269: add “of” between “effect” and “increased”

**Response:** Corrected

Line 270: Nitrification doesn’t produce CO<sub>2</sub>; it is an autotrophic process.

**Response:** “nitrification” has been removed.

Line 272: This is a pretty vague topic sentence. It would be helpful to be a little more specific.

**Response:** Sentence has been revised to read: “*Hydrological controls were found to be important regulators of CO<sub>2</sub> concentrations in these farm reservoirs.*” Line 286

Line 303: get rid of “by”

**Response:** Corrected

Lines 306-307: Deemer et al. 2016 and Beaulieu et al. 2019 are also good references here.

**Response:** References have been added

Lines 312-315: Higher CH<sub>4</sub> from higher C:N sediments suggests more (not less) important role for allochthonous C right?

**Response:** Our C/N ratios (8.5 to 13.4) were low enough to still be in the range of autochthonous C based on Liu et al., 2018. However, we have added a sentence to account for the input of allochthonous C contributing to higher C/N ratios: “*This suggests that in situ rather than terrestrial organic matter (OM) was likely the main source of C fuelling methanogenesis in these reservoirs, although increasing CH<sub>4</sub> concentrations with C/N may also represent a larger contribution of terrestrial OM.*” Line 328

Line 318-319: I would expect thermal stratification to influence bottom water CH<sub>4</sub> concentration more than surface water CH<sub>4</sub>, but you only have surface water concentrations in your model.

**Response:** Yes, this is most likely the case. We have clarified the sentence to read:

*“Thermal stratification of the water column did not significantly influence surface CH<sub>4</sub> concentrations in small farm reservoirs (Fig. 4E).”* Line 333

Line 331: Get rid of second “effect”

**Response:** Corrected

Line 334-335: Avoid using the word “clearly”. Also, it would be helpful to show the relationship between CH<sub>4</sub> and salinity in your Figure 3 to support this discussion.

**Response:** “Clearly” has been removed from the sentence which now reads: *“Evidently, the biological influence on CH<sub>4</sub> concentrations appears less pronounced in these larger, low-flow dams.”* Line 349. The inclusion of conductivity in the CH<sub>4</sub> model already represents a potential sulfate effect and supports this discussion.

Lines 365-366: State the actual factor that you used here too. Was it 34?

**Response:** At the suggestion of Reviewer 1 for additional information on the calculation of CO<sub>2</sub>-equivalent emissions, this has now been provided in the Methods:

*“For comparing CO<sub>2</sub>-equivalent fluxes, CH<sub>4</sub> fluxes were converted using the 100-year sustained-flux global warming potential (SGWP, Neubauer and Megonigal, 2015). This metric offers a more attainable measure of ecosystem climatic forcing, assuming gas flux persists over time instead of occurring as a single pulse as quantified using traditional global warming potentials (GWP, Myhre et al., 2013). Here, a SGWP multiplier of 45 was applied to all CH<sub>4</sub> fluxes in the literature comparison, which is slightly higher than the traditional GWP of 32 over a 100-year time frame (Myhre et al., 2013).”* Line 129

Lines 392-393: It seems like it would be nice to mention this parallel study earlier in your paper and give it a bit more discussion.

**Response:** We agree and now bring attention to this study in the Introduction:

*“This study builds on from our previous research farm reservoir GHG research which found an unexpected nitrous oxide (N<sub>2</sub>O) sink in 67% of reservoirs (Webb et al., 2019).”* Line 72

Lines 378-383: This all seems very speculative. As do lines 400-403.

**Response:** We agree that some of the mechanistic narrative is speculative; however, we also feel that our analysis is robust and that these statements provide promising avenues for further testing of tangible solutions for GHG reduction, both by ourselves and other researchers. Consequently, we have respectfully decided to retain this material, unless the editor feels strongly that it should be removed.

We now clarify the mention of building deeper reservoirs as a way to increase water residence time, which was a parameter in our model found to be related to lower CO<sub>2</sub> and CH<sub>4</sub> concentrations:

*“Increasing WRT by creating deeper reservoirs may promote primary production through increased water clarity (Dirnberger and Weinberger, 2005), facilitate CH<sub>4</sub> oxidation through the water column (Bastviken et al., 2008), and reduce the impact of watershed-derived solutes, terrestrial OM and benthic respiration.”* Line 407