Anonymous Referee #1

Received and published: 14 February 2019

Review of manuscript bg-2019-11

This study address multiple types of CH4 emissions in wetlands (ebullition, diffusion and plant-mediated flux), their temporal variability (diurnal cycles and seasonal differences), the spatial variability among four wetland vegetation communities in both permanent och seasonal wetlands, and links to wetland soil properties. Hence, it standsout as a potentially valuable study for improved understanding of wetland CH4 emissions. However, I have some concerns and questions below that I think should be addressed

We thank reviewer 1 for their constructive comments and suggestions, we have responded to each of these comments in blue font below.

General comments:

It would be good to early on clarify that the word wetland is here used in a broad sense including both wet vegetated environments and open waters/lakes.

We agree, this now reads (lines 52-54):

"Wetlands are considered one of the most valuable ecosystems on Earth (Costanza et al., 2014) and may be classified as both permanently inundated (i.e lakes and shallow waters) and seasonally inundated (i.e. vegetated) biomes."

L 160 and elsewhere: In warm environments, bubbling can sometimes happen rather continuously leading to very high R2 values (I have experience this myself several times in the tropics). Given the short measurement periods and the very high flux rates sometimes found from the floating chambers, I wonder if they did not received considerable bubbling in such a continuous way leading to linear increase in the headspace.

We agree this can occur. However, we are also confident that we were able to detect discrete ebullition. For example, our companion paper now published (*Jeffrey, L. C., Maher, D. T., Johnston, S. G., Kelaher, B. P., Steven, A. and Tait, D. R. (2019), Wetland methane emissions dominated by plant-mediated fluxes: Contrasting emissions pathways and seasons within a shallow freshwater subtropical wetland. Limnol Oceanogr. doi:10.1002/lno.11158*) focuses solely on aquatic emissions and provides examples (Fig. S3 – see below) of disregarded floating chambers featuring ebullition bubbles.

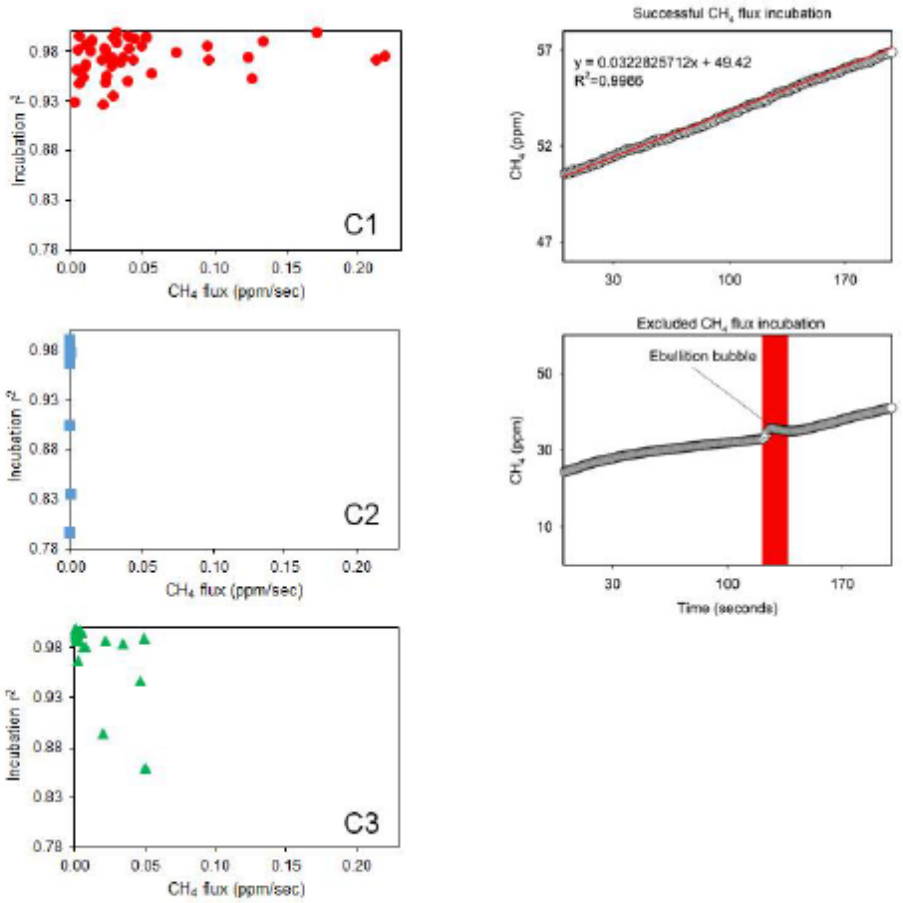

Figure S3. Examples of CH_4 flux linear regression r^2 vs flux rate (ppm/sec) for each campaign (left column) and samples of floating chamber CH_4 fluxes showing increasing CH_4 concentration (ppm) vs time (per second) indicating a successful incubation (top right panel) and an excluded incubation (bottom right panel) due to ebullition bubble release.

To identify this in the manuscript we have added the following:

"One chamber measurement was removed as an outlier (as it was more than three times the standard deviation of the mean) and any chambers capturing ebullition bubbles (determined by a nonlinear increase in concentration) were also disregarded, see example in Jeffrey et al. (2019)."

The high variability in the diffusive flux in Fig 3 also seem to support this guess. Are there any data on surface water concentrations of CH4 that could be used together with modelled piston velocities to estimate diffusive flux, or are there any other independent data to verify the high fluxes found as diffusion fluxes? If not, I would hesitate to report the very high fluxes (up to 10 mmol m-2 d-1) as diffusion and I would instead report values from flux chambers as total open water flux including both diffusion and ebullition. This would be a minor loss for the manuscript, compared to the risk of considerably overestimating diffusive fluxes.

We have recently published a companion paper focused on diffusion, ebullition and plant mediated fluxes from the same site using the same techniques (Jeffrey et al. 2019). In this companion paper we assessed water column concentrations, chamber-derived diffusive fluxes, and calculated convection-driven fluxes. That study highlighted that there was both temporal variability in water column CH4 concentrations (CH_4 ranging from ~60 uM to 250 uM over a diurnal cycle), and also spatial variability with water column CH_4 ranging from 7 to 254 uM throughout the wetland. We also found that convection (occurring only during night) could enhance the piston velocity by up to 17%.

It is likely that this spatial and temporal variability in water column concentrations is the main driver of the observed variability on our current chamber flux estimates. We do not have water column CH4 concentrations from the field campaigns in this present study - however, considering the extremely high water column CH_4 concentrations observed in our companion paper (averaging ~ 80 uM), a diffusive flux rate estimate of 10 mmol/m2/d is not extreme and would only require a piston velocity of ~ 0.5 cm/hr. This is piston velocity is similar to the diffusive transfer velocities in wetland measured by deliberate gas tracer experiments (e.g. Ho et al., 2018).

I think that it is difficult to claim that this study cover seasonal differences for the CH_4 emissions, which are known to have a high day-to-day variability, because there seems to have been on measurement day per season only.

We agree. We accounted for high resolution measurements however these were snapshots in time. We have removed reference to our fluxes representing 'seasonal' differences from the following lines:

Abstract (lines 32-34): "*We account for aquatic CH_4 diffusion and ebullition rates, and plant-mediated CH_4 fluxes from three distinct vegetation communities, thereby examining diurnal and intra-habitat variability"*

Lines 346-351: ***"Figure 5.*** *Fluxes of CH_4 from diel sampling and ebullition over two campaigns from the permanent wetland and adjacent 24 h time series of the seasonal wetland vegetation types. Note: Diffusive fluxes during C2 include chambers featuring lilies, dashed line represents the average, solid line represents the median and dots represent 5^{th} and 95^{th} percentiles. Letters show groups that did not differ significantly ($p>0.05$) using ANOVA on ranks and Dunn's pairwise comparisons within each campaign."*

Lines 369-370: ***"Figure 6.*** *Correlations of CH_4 with temperature (ºC) and photo-synthetically active radiation (PAR) (lum ft^{-2}) for the three wetland vegetation sites of Cattai Wetland during two field campaigns."*

Lines 408-409: *"This was associated with the lowest fluxes of CH_4 for both sampling periods (Fig. 5, Table 1)."*

Lines 467-469: *"These were similar to our findings with highest CH_4 fluxes of each campaign time series occurring near midday (10:50 am during C1; 4.88 mmol m^{-2} d^{-2} and 12:15 pm during C2; 2.06 mmol m^{-2} d^{-2}) (Fig. 3)."*

Lines 554-556: *"Our CH_4 emissions rates were at the low end of the scale of measurements made in southern hemisphere subtropical systems but within range of northern hemisphere subtropical systems of similar latitudes (Fig. 9)."*

Lines 593-597: Conclusion: *"Results reveal distinct differences between the areal CH_4 fluxes of four different eco-types located within a remediated subtropical Australian wetland and indicate high*

variability between campaigns. By combining novel and well established techniques we delineated several CH_4 pathways of both seasonal and permanent wetland sources (ebullition, diffusion and plant-mediated pathways) and linked these to hydrological drivers."

Specific comments:

Abstract: Please define "AVS".

Amended.

L84-86: Tiny language thing: Two "now" in same sentence.

Amended.

P156-158. How many replicate floating chamber measurements were performed during each measurement time at each location, and how many measurements times during each campaign?

We have added details as follows (Lines 175-177):

"A total of 39 CH_4 floating chamber incubations averaging ~8 minutes in duration were recorded over the two campaigns, with 19 during C1 (nine at night) and 30 during C2 (12 at night)."

L185: 10 minute intervals in the daytime sampling would return in the order of 4-6 measurements per hour, but Figure 4 does not show that many points. Were fluxes really measured at 10 min intervals as said here?

We agree this was potentially confusing, this was the approximate intervals between incubation start times. The manuscript stated incubation times '*Vegetation incubation times ranged from 6 to 15 minutes*'. To clarify the number of vegetation incubations measured each day and night, per campaign, we have re-worded this paragraph as follows (lines 205-212):

"*During the first time-series (C1), an average of 16.7 ± 2.9 daytime flux measurements (i.e. after sunrise) and 7.3 ± 1.6 night time (i.e. after sunset) were recorded within each habitat. During the second campaign (C2) an average of 27.7 ± 2.9 (day time) and 10.3 ± 1.5 (night time) flux measurements were recorded within each habitat. In addition, CH_4 fluxes from the adjacent exposed sediments or shallow overlying water at each site were also measured at ~4 hourly intervals to determine the influence and role of plant-mediated CH_4 fluxes compared to non-vegetated CH_4 fluxes…."*

L226-230: Please show unit and value of R, as there are several versions to choose from. Should there not be a conversion from ppm to partial pressure in the equation, e.g. s*(1/1000000)*Total_Pressure?

R is in the units of $m^3.atm.K^{-1}.mol^{-1}$, which has a value of $8.205*10^{-5}$ in this case. Text has been added to clarify this point. We assume atmospheric pressure is 1 atm in our calculations, this has been added to the methods section (Lines 251-256):

" $F = (s(V/RT_{air}A))t$ *(1)*

where s is the regression slope for each chamber incubation deployments (ppm sec^{-1}), V is the chamber volume (m^3), R is the universal gas constant (8.205×10^{-5} $m^3.atm.K^{-1}.mol^{-1}$), T_{air} is the air temperature inside the chamber (K), A is the surface area of the chamber (m^2) and t is the conversion factor from seconds to day, and to mmol. We assume that atmospheric pressure is 1 atm."

Given the variability, was there really a significant difference between day and night?

We have performed statistical analysis to assess differences between day and night fluxes and have added the following to the manuscript methods (Lines 262-266):

"2.6 Statistical analysis

As the CH_4 flux data was non-parametric we used a Kruskal-Wallis one way analysis of variance (ANOVA) on ranks to test for significant differences between each campaign, between flux pathways and between diel variability, where $p<0.001$. Dunn's multiple pairwise comparisons were then used to analyse specific sample pairs ($p<0.05$)."

And abstract (lines 39-39):

…"Significantly higher CH_4 emissions ($p<0.001$) of the seasonal wetland were measured during flooded conditions…"

And to our results (lines 334-351):

"CH_4 fluxes from the three vegetation types were significantly higher during C1 than during C2 ($p<0.001$). During C1, the CH_4 fluxes from the Juncus and Phragmites were not significantly different from each other but were both significantly higher ($p<0.001$) than Juncus/Forest however, during C2 the CH_4 fluxes of each seasonal wetland habitat were significantly different between all habitats ($p<0.05$) (Fig. 5). The highest average CH_4 fluxes in each of the vegetation types always occurred during the daytime but were not significantly different to night time fluxes (Fig. 5, Table 1). Phragmites consistently emitted the highest CH_4 fluxes (2.27 ± 1.42 mmol m^{-2} d^{-1} during C1 and 0.77 ± 0.46 mmol m^{-2} d^{-1} during C2). The Juncus/ Forest ecotype within the seasonal wetland consistently produced the lowest CH_4 fluxes of all sites, with a negligible flux that was not significantly different from zero occurring during C2 (-0.01 ± 0.08 mmol m^{-2} d^{-1})."

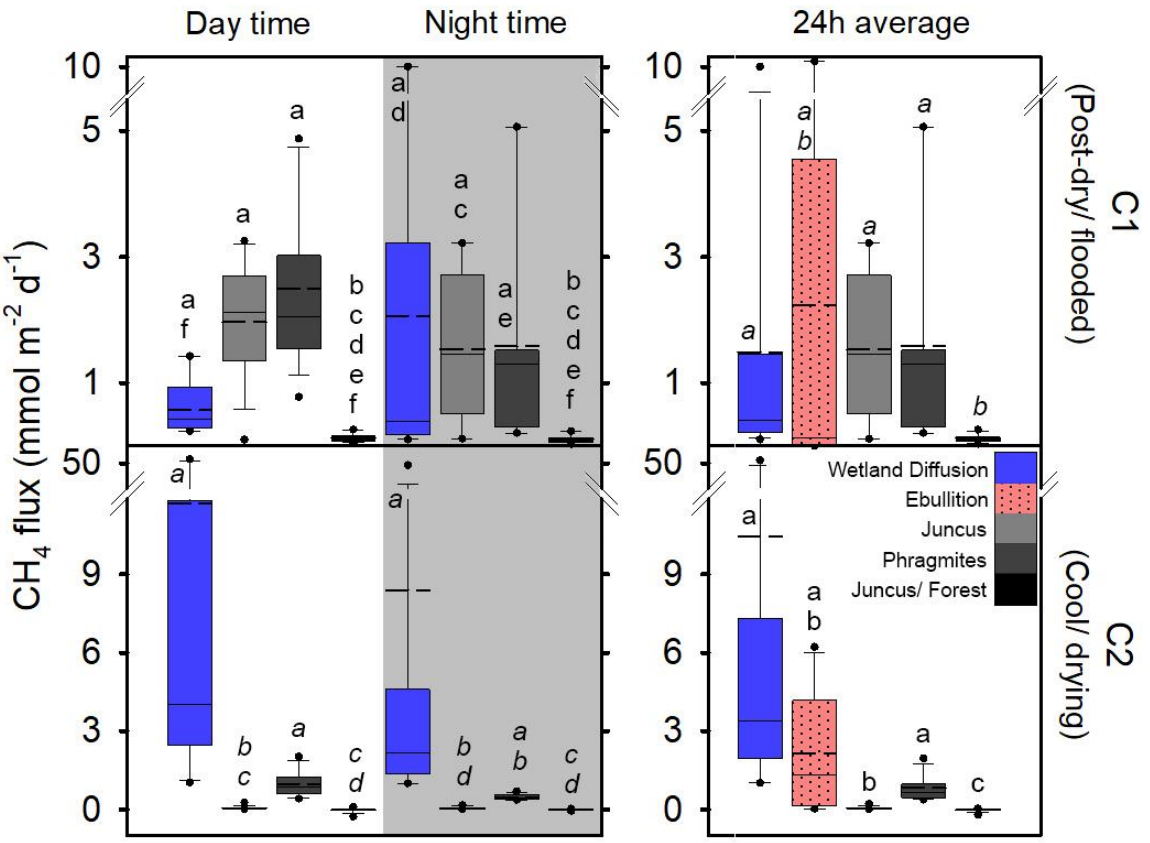

Figure 5. *Fluxes of CH_4 from diel sampling and ebullition over two campaigns from the permanent wetland and adjacent 24 h time series of the seasonal wetland vegetation types. Note: Diffusive fluxes during C2 include chambers featuring lilies, dashed line represents the average, solid line represents the median and dots represent 5th and 95th percentiles. Letters show groups that did not differ significantly ($p>0.05$) using ANOVA on ranks and Dunn's pairwise comparisons within each campaign.*

L264-265: This statement does not seem to hold for Veg C right?

After statistical analysis, this now reads (Lines 338-340):

"The highest average CH_4 fluxes in each of the vegetation types always occurred during the daytime but were not significantly different to night time fluxes (Fig. 5, Table 1)."

L265-266: See above: Was there a significant diel variability?

As address above this now reads (lines 338-341):

"The highest average CH_4 fluxes in each of the vegetation types always occurred during the daytime but were not significantly different to night time fluxes (Fig. 5, Table 1). Phragmites consistently emitted the highest CH_4 fluxes (2.27 ± 1.42 mmol m^{-2} d^{-1} during C1 and 0.77 ± 0.46 mmol m^{-2} d^{-1} during C2)…."

Line 267-268: Is the Veg C flux really negative or rather not significantly different from zero, ie Veg C flux is to be seen as zero?

As the flux is nominal we have re-worded as (lines 341-344):

"…The Juncus/ Forest ecotype within the seasonal wetland consistently produced the lowest CH_4 fluxes of all sites, with a negligible flux that was not significantly different from zero occurring during C2 (-0.01 ± 0.08 mmol m^{-2} d^{-1})."

L269-271: See above comment. I think data and its variability indicate the floating chambers received lots of ebullition in spite of the gas accumulation being linear. Please provide independent evidence supporting that numbers represent diffusive flux only, or consider reporting fluxes as total flux.

In addition to our earlier response addressing this point and our evidence supporting that the reported data represent diffusive flux only (see response to General comment no. 2), we note that the rates are within those reported in previously published studies of diffusive fluxes from similar latitudes, and thus are representative of both open water and lilies.

The higher fluxes during C2 are also likely due to the re-emergence of lily species (Nymphaea sp.) during C2 which are included in some chamber measurements (but were not present not C1). These were mentioned in the manuscript, but we have now added further details to the following areas to clarify for the reader (lines 346-351):

"Figure 5. *Fluxes of CH_4 from diel sampling and ebullition over two campaigns from the permanent wetland and adjacent 24 h time series of the seasonal wetland vegetation types. Note: Diffusive fluxes during C2 include chambers featuring lilies, dashed line represents the average, solid line represents the median and dots represent 5^{th} and 95^{th} percentiles. Letters show groups that did not differ significantly (p>0.05) using ANOVA on ranks and Dunn's pairwise comparisons within each campaign."*

lines 353-357:

…" The permanent wetland showed an inverse trend with seven-fold and significantly higher (p<0.001) diffusive fluxes during the cool/drying C2 when lilies were present (10.46 ± 15.81 mmol m^{-2} d^{-1}) compared to the post-dry/flooded C1 when no lilies were present (1.49 ± 2.75 mmol m^{-2} d^{-1}), while the ebullition rates were similar during both campaigns (Fig. 5, Table 1)….."

lines 326-335:

"…A lag time (ranging from weeks to months) for recovery of the CH_4 pool post-drought has been observed in other systems (Boon et al., 1997) and also during lab-based experiments (Knorr et al., 2008; Freeman et al., 1992). Further, during C2 the return of macrophyte species Nymphaea caspensis most likely enhanced CH_4 gas transport from the rhizosphere to the floating chambers, as discussed in detail in Jeffrey et al. (2019). Therefore this combination of drivers most likely explain the higher CH_4 fluxes during C2 when the system (and lilies) had sufficient time to recover, despite lower water column temperatures that would normally reduce microbial metabolism rates. This hypothesis is also supported by the shift of net positive redox potential…"

Lines 171-175:

"To account for spatial and temporal variability, measurements were conducted during both day-time and night-time, and sampling within vegetated areas featuring lilies (Nymphaea capensis); that

were only present during the second campaign, forested areas (Melaleuca sp.) and in areas where no aquatic vegetation was present (i.e. open water).”

L275: I do not follow the end of this sentence and do not see how Figure 4 can support this statement.

We agree. We have amended this sentence, incorporated new results from the ANOVA as follows (lines 357-360):

“Overall, the diffusive fluxes of the permanent wetland were within range of CH_4 fluxes from the three seasonal wetland habitats but were significantly higher than Juncus/Forest during both campaigns, and Juncus during C2 (Fig. 5). Diel diffusive flux variability was not significant between day time and night time (Table. 1, Fig. 5).”

L330 and elsewhere: Is re-flooding the only possible explanation of the differences found in the redox between the seasonal and the permanent wetland? Could not the difference also represent a difference between areas with emergent aquatic plants having O2 leaking out from the roots and maintaining oxidized conditions, and on the other hand areas without this type of root zone aeration in the permanent wetland? This root zone aeration is mentioned below in another context. Should it not also be highlighted here when discussion the sediment redox depth profiles?

Although we agree this is another plausible explanation, especially for the seasonal wetland sites, it is unlikely to apply for the permanent wetland, as the *opposite trend* occurred due to the absence of lilies during C1; where the positive redox potentials were observed. During C2 when the lilies returned, lower redox was observed. To clarify this point, in the permanent wetland discussion we have added: (lines 537-540)

“…Further, although aquatic vegetation can facilitate root zone aeration therefore increasing sedimentary redox potential, as no aquatic vegetation was present in the permanent wetland during C1, this further suggests water level drawdown of the was the main driver of redox conditions.”

And to the seasonal wetland discussion we have added the following text (lines 510-514):

“The differences are therefore likely explained by the higher positive redox potentials (Table 1) that may be partially attributable to rhizome aeration by the nearby trees, and more abundant thermodynamically favourable terminal electron acceptors (i.e. Fe(III) and SO_4^{2-}) (Fig. 5) all of which can inhibit methane production within the sediments (Burdige, 2012).”

L 387-389 and elsewhere: Some studies have highlighted different patterns. See e.g. Milberg et al. 2017 AoB Plants. doi.org/10.1093/aobpla/plx029

We have added this paper to the discussion as follows (lines 463-467):

“…Milberg et al. (2017) found no apparent diel patterns of CH_4 fluxes from Phragmites australis during seven campaigns within the Swedish growing season. Kim et al. (1998) showed that CH_4 emissions peaked around midday and that daytime emissions were about 3-fold higher than night time emissions, positively correlating with temperature and PAR…”

L410-411 and elsewhere: Is the difference between passive and pressurised gas transfer the only possibility? The sediment redox potentials reported correlate with CH_4 fluxes. Could the sediment conditions not also be influenced also by root depth or root density varying between plant species? If there are no clear explanations, and speculations are necessary, it would be good to highlight not

only one alternative (that are frequently discussed in the literature) but also other possible alternatives.

We agree on the need to canvas a wider range of possible explanations and have now discussed potential alternatives as follows (lines 490-499):

"In comparison, in Phragmites these day:night ratios were almost triple this (67% and 94% higher) during the same periods. This may potentially be due to the more efficient daytime conductive gas transfer pathway of CH_4 through Phragmites australis compared to the more passive diffusive CH_4 gas transfer pathway of Juncus kraussii and/or the effectiveness of these different species to alter sedimentary redox conditions. This suggests that non-pressurized pathways may result in lower net rhizosphere-atmosphere gas exchange of CH_4 from seasonal wetland vegetation. Alternatively, root depth and root density differ between these two species (Moore et al., 2012, De La Cruz et al., 1977), therefore further influencing redox dynamics in the rhizosphere, and the potential extent of net gas exchange."

L412-413 and elsewhere: See above. Another perspective could be that that no significant CH4 fluxes were found from the Veg C site. I suggest letting the statistics decide the perspective.

As now addressed in the results, we have added 'significant' to this as follows (lines 500-501):

"The Juncus/ Forest habitat emitted significantly lower fluxes of CH_4 during both time series campaigns and was a net sink for CH_4 during C2 (Table 1, Fig. 8)..."

L419-425: Why is not possibly more extensive root zone aeration by the additional tree roots mentioned as one hypothesis?

As mentioned above, we have added to this hypothesis as follows (lines 507-514):

"Shading by the overhanging trees may inhibit the daytime diffusive CH_4 gas transport through Juncus/ Forest habitat assumable to lower rates of photosynthesis, however PAR was only lower during C2 (Fig. 7) and so does not appear to explain the CH_4 flux differences observed during C1. The differences are therefore likely explained by the higher positive redox potentials (Table 1) that may be partially attributable to rhizome aeration by the nearby trees, and more abundant thermodynamically favourable terminal electron acceptors (i.e. Fe(III) and SO_4^{2-}) (Fig. 5) all of which can inhibit methane production within the sediments (Burdige, 2012)."

L428-429: See above. (a) Consider the possibility that the floating chambers reflect total flux and not diffusion only. (b) I am not convinced this study can make claims about seasonal differences based on one measurement day per season only as day-to-day fluxes can be highly variable. Therefore, parts of the discussion about reasons for the seasonal difference seem obsolete.

(a) As per previous comments, we are confident that reported diffusion values are accurate and likely due to the presence of lilies enhancing the flux as mentioned in detail above. (b) As per previous suggestions and reviewer #2 comments also, we have removed all claims to quantifying 'seasonal fluxes' from the manuscript and stick to the changes in drivers in our discussion.

L451: I suggest removing "Permanent" here, because many large non-permanent wetland areas are also important (most tropical wetlands vary greatly in size over a year).

Removed and this now reads (lines 546-548):

"Within the global wetland CH_4 budget both subtropical systems and southern hemisphere systems are poorly represented (Bartlett and Harriss, 1993;Bastviken et al., 2011) (Fig. 9)."

Fig 1 and elsewhere: Why were not all measurements and core collections taking place nearby each other? How comparable are the results if data were collected far apart?

At the seasonal wetland sites (Veg A, B and C) cores were taken nearby, but not directly at the site of the flux measurements to ensure minimal disturbance of the site. As the permanent wetland was fairly homogenous (as found during previous study of the wetland i.e. Jeffrey et al., 2019), the cores were extracted from a location to avoid trampling disturbance to fragile sediments and lily habitat, and to avoid artificial ebullition release prior to deployment. We have added the following to our methods explaining this (lines 222-224):

"The cores were sampled in close proximity to the time series habitats (5 to 15 m) in December 2016, but within the permanent wetland the cores were taken from elsewhere to avoid disturbance of the shallow water column and sediments."

Figure 4 and elsewhere: (a) Does Fig 4 really show seasonal fluxes? Can at all seasonal fluxes be claimed from two measurement days as shown here? How to know that these two days were representative of whole seasons? (b) Please inform readers how many replicate measurements were made at each time point for the fluxes?

We have removed all terms referring our study to 'seasonal fluxes' and replaced with 'campaigns' and as above have referenced our companion study and included the number of chamber measurements featured in this study in our methods (lines 171-178):

"To account for spatial and temporal variability, measurements were conducted during both day-time and night-time, and sampling within vegetated areas featuring lilies (Nymphaea capensis); that were only present during the second campaign, forested areas (Melaleuca sp.) and in areas where no aquatic vegetation was present (i.e. open water). A total of 39 CH_4 floating chamber incubations averaging ~8 minutes in duration were recorded over the two campaigns, with 19 during C1 (nine at night) and 30 during C2 (12 at night). The average r^2 value of linear regressions of CH_4 concentrations versus time during chamber incubations was 0.97 ± 0.05."

End of Referee #1 response file

Anonymous Referee #2

Received and published: 5 March 2019

I apologize for the delay in getting my review in. Overall I think this study is interesting and the paper is mostly well written. It is unfortunate that it is just 2 seasonal sampling events. It is unclear if the sampling occurred over more than one day each season? Please clarify. The authors do a good job of limiting their results to what they can say with the data at hand (assuming that they sampled more than one day per season). I do think that some things need to be clarified. Below I provide comments and suggestions of issues that need to be clarified.

We thank referee #2 for their constructive feedback and suggestions. We have attended to all of these in details below in blue font.

Lines 35 and 36- negative relationships between Fe, and SO4, and CH4? Or Fe and CH4, and SO4 and CH4? The wording is unclear.

Amended as follows (Lines 35-38):

"For example, distinct negative relationships between CH_4 fluxes and both Fe(III) and SO_4^{2-} were observed. Where sediment Fe(III) and SO_4^{2-} were depleted distinct positive trends occurred between CH_4 emissions and Fe(II) / acid volatile sulphur (AVS).

Line 46- what do you mean by early system recovery periods? Recovery from what? Was this wetland recovering from something? This was a remediated wetland?

We meant recovery from anthropogenic drainage. To clarify this for the reader, the abstract now reads as follows (lines 45-47):

"…We suggest that wetland remediation strategies should consider geochemical profiles to help to mitigate excessive and unwanted methane emissions, especially during early system remediation periods."

Line 59- how are drivers and effects of seasonal weather oscillations different?

We have added (lines 64-70):

"Resolving the drivers, pathways and effects of seasonal weather oscillations on wetland CH_4 sink or source behaviours is important to enable more accurate climate model projections and to reduce uncertainties in the global wetland CH_4 budget (Saunois et al., 2016; Kirschke et al., 2013). Weather oscillations affect the total wetland areal extent and inundation periods, with wet conditions facilitating anaerobic conditions favouring methanogenesis, while the opposite is seen during dry periods which potentially mitigates CH_4 emissions (Whiting and Chanton, 2001;Wang et al., 1996)."

Line 62- See problems with Mitsch et al 2013 calculations from Bridgham et al 2014 and Neubauer 2014 papers. I see you cite those papers.

We agree and have acknowledged Bridgham et al., (2014)'s response paper as follows (lines 70-75):

"Mitsch et al. (2013) estimated that the average ratio of freshwater wetland CO_2 sequestration to CH_4 emissions was 25.5:1, though was later refuted by Bridgham et al. (2014). As CH_4 is 34 times more potent than carbon dioxide (CO_2) over a 100 year time scale (Stocker et al., 2013), this suggests that many freshwater wetlands may have a net positive radiative forcing effect on climate (Petrescu et al., 2015;Hernes et al., 2018)."

Line 68- “lack of spatially resolved wetland CH4 emission data”? There are many studies that have measured this. Some of which you already cited.

Agree, by ‘spatial’ we meant latitudinal as discussed with figure 9. This now reads (lines 77-82):

“*The lack of latitudinally-resolved wetland CH_4 emission data, as well as the limited number of studies constraining the multiple wetland CH_4 flux pathways (i.e. ebullition, diffusion and plant-mediated) coupled with ongoing anthropogenic conversion of wetland systems (Saunois et al., 2016;Neubauer and Megonigal, 2015;Bartlett and Harriss, 1993) further contribute to the uncertainties around CH_4 regional to global scale budgets.*”

Line 84- Is Lal 2008 an appropriate citation for this sentence?

Removed.

Line 92-how was that 1.2 Pg C estimated?

We have now provided an explanation as follows (lines 99-104):

“Within Australia, it has been estimated that more than 50% of natural wetlands have been lost to land use change, drainage and degradation since European settlement (Finlayson and Rea, 1999;ANCA, 1995). By comparing and reviewing pristine Australian wetland carbon stocks to drained sites, and GHG dynamics, Page and Dalal (2011) estimated that through biomass loss, enhanced soil respiration, N_2O production and a reduction in CH_4 emissions, that Australian wetland loss equated to ~1.2 Pg CO_2 equivalents emitted to the atmosphere.”

Line 112- why do you expect the fluxes going to differ across the wetland communities?

We have added (lines 122-128):

“…We hypothesize that wetland CH_4 emissions will differ significantly between the campaigns and between the four wetland communities due to differences in soil chemistry, hydrology and plant physiology. We account for three atmospheric flux pathways for methane; ebullition, diffusion and plant-mediated fluxes, over diurnal cycles and within different hydrological conditions. CH_4 fluxes were also assessed in relation to the underlying soil properties, including sulphate, reactive iron III and iron II, acid volatile sulphur, chloride and organic carbon.”

Line 162-163- Why were those fluxes reported elsewhere? Is that paper available?

This is a companion study that is now published. This passage is now updated as (lines 181-183):

“…Examples of these, in addition to the ebullition and diffusive CH_4 flux methods and measurements from the permanent wetland have previously been reported elsewhere (Jeffrey et al., 2019).”

Line 164- how many chambers did you have in each vegetation type? How many days did you measure fluxes? Was it only one day each season?

We sampled in triplicate within each vegetation type (three sites), so n=9 in total. We measured at least a complete diel cycle each season. Each campaign covered five days with ebullition deployments, diel diffusion rates and redox etc. To more clearly clarify this in the manuscript we have added the following lines 186-191:

"Simultaneous time series chamber experiments were conducted over a minimum of 24 hours to measure diel CH_4 fluxes during each season from the three different wetland vegetation ecotypes. These ecotypes were Juncus kraussii, Phragmites australis and Juncus kraussii amongst Casuarina sp. forest (Fig. 1). In each ecotype, three acrylic bases (65 x 65 x 30 cm) were installed four months before the first time series experiment, to minimise disturbance to the sediment profile and vegetative rhizosphere.

And as per referee #1 suggestions we have also included more details about the number of chamber measurements taken during each campaign as follows at lines 204-212:

"Vegetation incubation times ranged from 6 to 15 minutes depending on the flux rate and were taken from triplicate chambers to account for heterogeneity within each ecotype. During the first time-series (C1), an average of 16.7 ± 2.9 daytime flux measurements (i.e. after sunrise) and 7.3 ± 1.6 night time (i.e. after sunset) were recorded within each habitat. During the second campaign (C2) an average of 27.7 ± 2.9 (day time) and 10.3 ± 1.5 (night time) flux measurements were recorded within each habitat. In addition, CH_4 fluxes from the adjacent exposed soils or shallow overlying water at each site were also measured at ~4 hourly intervals to determine the influence and role of plant-mediated CH_4 fluxes compared to non-vegetated CH_4 fluxes."

And diffusive chamber measurements (lines 175-177):

"…A total of 39 CH_4 floating chamber incubations averaging ~8 minutes in duration were recorded over the two campaigns, with 19 during C1 (nine at night) and 30 during C2 (12 at night)."

Lines 279-281- This sentence is more Discussion.

We agree and have moved to discussion as follows at line 375-379:

"Sediment profiles provide insights to the historical geochemical changes that have occurred across the CASS landscapes of the four Cattai Wetland sites (Fig. 5). We base our results and discussion on the upper rhizosphere depth zone (20 cm) as this featured the highest organic carbon concentrations is therefore assumed to be an active area of carbon metabolism, and CH_4 production and consumption (Nedwell and Watson, 1995)…."

Line 302- Structuring the Discussion in the same order as the Results makes it easier for the reader. I suggest you Discuss your results in the same order they were presented in the Results section.

We agree and have aligned our results to be the same order as our discussion.

Line 326-CASS wetland restoration the same as remediation?

Now amended to 'remediation' to be consistent.

Lines 345 and 346- It gets hard to keep track of C1, C2, Veg A, Veg B. Could there be more straightforward ways of talking about these?

As per previous suggestions we have renamed our three vegetation sites with more intuitive titles: 'Juncus', 'Phragmites' and 'Juncus/Forest' but will keep C1 and C2 to represent the two campaigns.

Line 352-354- This is more of a results sentence and I am not sure I understand what you are saying. Please clarify.

We agree and have removed as this sentence was redundant and have now combined with the previous paragraph as (lines 422-428):

"…Further, as iron reduction yields more free energy than SO_4^{2-} reduction (Burdige, 2012), then Fe reduction at the Juncus site may outcompete CH_4 production ahead of SO_4^{2-} reduction at Phragmites, which may help explain some of the differences in CH_4 production between the two sites. The positive significant trends between Fe(II), AVS and the Cl:SO_4^{2-} ratios with CH_4 flux rates (r_s=0.88, p<0.01) further support our hypothesis that reducing conditions and a smaller pool of sediment Fe(III) and SO_4^{2-} facilitate higher CH_4 production rates (Fig. 7)…."

Line 409 and 410- this Veg A and B is getting tiring. Why not just talk about the species?

As mentioned above, we have amended throughout the manuscript and adjusted all figures. This are now introduced first by scientific name and then shortened as follows at lines 156-159:

"The seasonal wetland to the south is dominated by the sedge; Juncus kraussii ('Juncus' from herein) and features scattered stands of Phragmites australis ('Phragmites' from herein) with areas of slightly higher elevation dominated by Juncus kraussii below Casuarina sp. ('Juncus/ Forest' from herein) (Fig. 1)."

Line 433- it is hard for readers to access submitted papers. Please do not cite papers that are not already published in some form.

These are now published and the reference list has been updated.

Line 467- Again see Bridgham et al. 2014 about the problems with Mitsch et al use of radiative forcing vs balance.

As these numbers have been refuted, we have removed Mitch and provided a more suitable reference to this uncertainty at lines 565-569:

"Although remediating degraded wetlands through re-flooding is a common technique to improve biodiversity, increase C sequestration and improve downstream water quality issues (Johnston et al., 2014;Johnston et al., 2004), our results propose a nuanced dilemma for land use managers, as wetland remediation can potentially have net positive radiative forcing effects on the Earth's climate due to high rates of CH_4 production (Petrescu et al., 2015)."

Line 452, comma between budget and however.

Amended.

Figure 6- those are really low r2 values! Are these significant relationships? If they are not significant, it is better not to report the value. And r2 of 0.0005 is better to just say there was no relationship.

Amended.

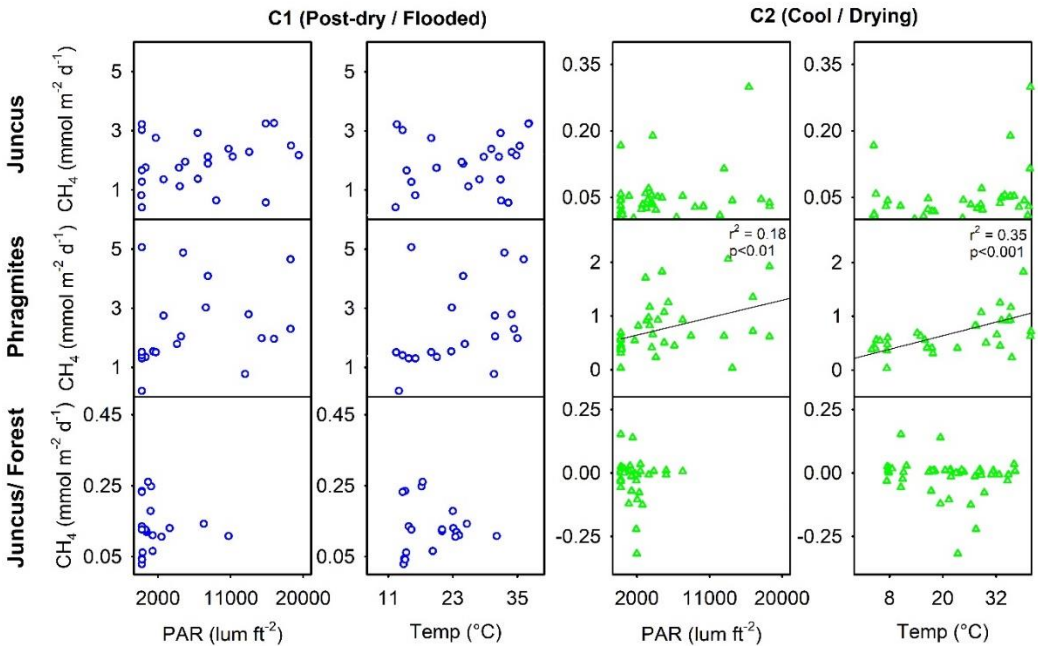

Figure 6. Correlations of CH_4 with temperature (ºC) and photo-synthetically active radiation (PAR) (lum ft^{-2}) for the three seasonal wetland vegetation sites of Cattai Wetland during two field campaigns.

Figure 8- I really like this figure. Is Fe(III) in Veg C above the axis break? It is a little hard to tell.

We have added a dashed line to show the axis break more clearly as follows:

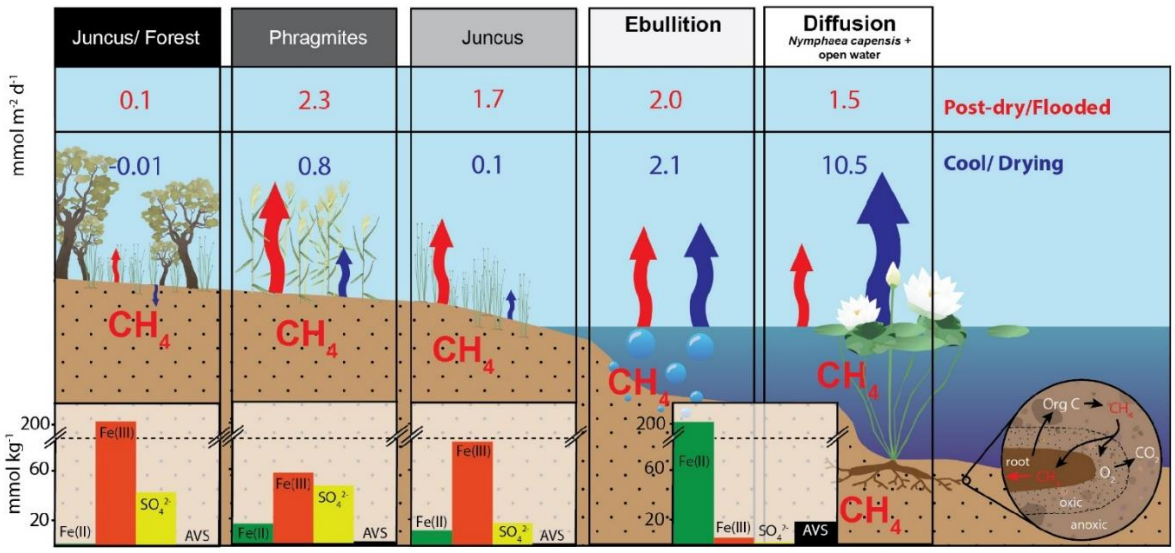

Figure 8. Conceptual model summarising the terrestrial and aquatic CH_4 fluxes (mmol m^{-2} d^{-1}) and sediment core profile parameters (mmol kg^{-1}) of the permanent and seasonal wetlands during C1 (post-dry/flooded conditions) and C2 (cool/drying conditions) of Cattai Wetland. Conceptual diagram expanded from Jeffrey et al. (2019) and rhizome process insert adapted from (Conrad, 1993). Note: Dashed line highlights y-axis break.

End of Referee #2 response file

Rhizosphere to the atmosphere: contrasting methane pathways, fluxes and geochemical drivers across the terrestrial-aquatic wetland boundary

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Key Words:

Diffusion

Ebullition

Sediment redox

Coastal acid sulphate soils

Sulphate reduction

Iron reduction

Abstract

Although wetlands represent the largest natural source of atmospheric CH_4, large uncertainties remain regarding the global wetland CH_4 flux. Wetland hydrological oscillations contribute to this uncertainty, dramatically altering wetland area, water table height, soil redox potentials and CH_4 emissions. This study compares both terrestrial and aquatic CH_4 fluxes ~~over two distinct seasons~~ in ~~both~~ permanent and seasonal remediated freshwater wetlands in subtropical Australia over two field campaigns representing differing hydrological and climatic conditions. We account for aquatic CH_4 diffusion and ebullition rates, and plant-mediated CH_4 fluxes from three distinct vegetation communities, thereby examining ~~seasonal,~~ diel~~urnal~~ and intra-habitat variability. CH_4 emission rates were related to underlying sediment geochemistry. For example, distinct negative relationships between CH_4 fluxes and both Fe(III) and SO_4^{2-} ~~and CH_4 fluxes~~ were observed. Where sediment Fe(III) and SO_4^{2-} were depleted~~,~~ ~~whereas~~ distinct positive trends occurred between CH_4 emissions and Fe(II) / ~~A~~acid ~~V~~volatile ~~S~~sulphur (AVS~~, where sediment Fe(III) and SO_4^{2-} were depleted~~. ~~The highest~~Significantly higher CH_4 emissions ($p<0.01$) of the seasonal wetland were measured during flooded conditions and always during daylight hours, which is consistent with soil redox potential and temperature being important co-drivers of CH_4 flux. The highest CH_4 fluxes were consistently emitted from the permanent wetland (1.5 to 10.5 mmol m^{-2} d^{-1}), followed by the Phragmites australis community within the seasonal wetland (0.8 to 2.3 mmol m^{-2} d^{-1}), whilst the lowest CH_4 fluxes came from a region of forested Juncus sp. (-0.01 to 0.1 mmol m^{-2} d^{-1}) which also corresponded with the highest sedimentary Fe(III) and SO_4^{2-}. We suggest that wetland remediation strategies should consider geochemical profiles to help to mitigate excessive and unwanted methane emissions, especially during early system remediation periods.

1.0 Introduction

Wetlands are considered one of the most valuable ecosystems on Earth (Costanza et al., 2014) and may be classified as both permanently innndated (i.e lakes and shallow waters) and seasonally inundated (i.e. vegetated) biomes. They are biodiversity hotspots that provide ecosystem services such as water filtration, sediment trapping, floodwater retention and carbon (C) storage (Bianchi, 2007). Wetlands account for ~5.5% of terrestrial surfaces (Melton et al., 2013) and have been estimated to store from ~4% (Bridgham et al., 2014) to ~30% (Mitsch et al., 2013) of Earth's estimated 2500 Pg soil C pool (Lal, 2008). Pristine wetlands have long been considered net C sinks due to their high rates of productivity and low rates of decomposition (Petrescu et al., 2015) ~~(Mitsch et al., 2013)~~; however due to their waterlogged nature and anaerobic soils, wetlands are ideal environments for the production of methane (CH_4), a potent greenhouse gas. As such, wetlands are recognised as Earth's largest natural source of CH_4 to the atmosphere (185 ± 21 Tg C yr^{-1}) (Saunois et al., 2016).

Resolving the drivers, pathways and effects of seasonal weather oscillations on wetland CH_4 sink or source behaviours is important to enable more accurate climate model projections and to reduce uncertainties in the global wetland CH_4 budget (Saunois et al., 2016;Kirschke et al., 2013). Weather oscillations affect the total wetland areal extent and inundation periods, with wet conditions facilitating anaerobic conditions favouring methanogenesis, while the opposite is seen during dry periods which potentially mitigates CH_4 emissions (Whiting and Chanton, 2001;Wang et al., 1996). Mitsch et al. (2013) estimated that the average ratio of freshwater wetland CO_2 sequestration to CH_4 emissions was 19.5:1, though this was later refuted by Bridgham et al. (2014). As CH_4 is 34 times more potent than carbon dioxide (CO_2) over a 100 year time scale (Stocker et al., 2013), this suggests that many freshwater wetlands may have a net positive radiative forcing effect on climate (Petrescu et al., 2015;Hernes et al., 2018). However, variability in geomorphology, wetland maturity, salinity and underlying geochemical composition all contribute to variable CH_4 dynamics (Bastviken et al., 2011;Mitsch and Gosselink, 2007;Poffenbarger et al., 2011;Whiting and Chanton, 2001). The lack of ~~spatially~~latitudinally-resolved wetland CH_4 emission data, ~~as well as~~ the limited number of studies constraining the multiple wetland CH_4 flux pathways (i.e. ebullition, diffusion and plant-mediated) ~~coupled with~~and the ongoing anthropogenic conversion of wetland systems (Saunois et al., 2016;Neubauer and Megonigal, 2015;Bartlett and Harriss, 1993) further contribute to the uncertainties around CH_4 regional to global scale budgets.

Extensive clearing and drainage of many coastal wetlands has occurred over the previous two centuries in order to accomodate agriculture, aquaculture and urban development (White et al., 1997;Armentano and Menges, 1986;Villa and Bernal, 2018). Drained wetlands can lead to rapid soil organic matter oxidation, and transform systems to net CO_2 sources (Deverel et al., 2016;Pereyra and Mitsch, 2018). Drainage systems can also reduce wetland inundation periods and alter sediment redox-dependant geochemistry and microbially-mediated reactions (Johnston et al., 2014), particularly those involving bioavailable iron (Fe(III)), sulphate (SO_4^{2-}) and nitrate (NO_3^-). Importantly, anaerobic carbon metabolism employing these terminal electron acceptors (Fe(III), SO_4^{2-}, NO_3^-) competes thermodynamically with methanogenic bacteria and archaea and thereby can inhibit CH_4 production (Burdige, 2012;Lal, 2008;Karimian et al., 2018;á Norði and Thamdrup, 2014). With increasing value ~~now~~ placed on the ecosystems services provided by wetlands, many degraded systems are now undergoing remediation and re-flooding (Johnston et al., 2014). However, the ecosystem benefits, such as enhanced biodiversity and water quality, may come at a price in the form of high initial CH_4 flux rates, and predicted net radiative forcing for several centuries post-remediation - thus posing a 'biogeochemical compromise' (Hemes et al., 2018~~;Lal, 2008~~).

Within Australia, it has been estimated that more than 50% of natural wetlands have been lost to land use change, drainage and degradation since European settlement (Finlayson and Rea, 1999~~;) (~~ANCA, 1995). By comparing and reviewing pristine Australian wetland carbon stocks to drained sites, and GHG dynamics, Page and Dalal (2011) estimated that through biomass loss, enhanced soil respiration, N_2O production and a reduction in CH_4 emissions, that ~~T~~this ~~equates~~ equated to ~~an estimated~~ ~1.2 Pg CO_2 equivalents emitted to the atmosphere ~~through oxidation of soil organic carbon (Page and Dalal, 2011)~~. Much of eastern Australia's freshwater coastal wetlands are underlain by Holocene derived sulphidic sediments (i.e pyrite – Fe_2S, known as coastal acid sulphate soils; CASS) formed during periods of higher sea levels (White et al., 1997;Walker, 1972). When CASS are drained, pyrite is oxidised, producing sulphuric acid (H_2SO_4). This results in highly acidic soils with pH levels as low as 3 (Sammut et al., 1996;Johnston et al., 2014). After rainfall events, groundwater transports H_2SO_4 from the CASS landscapes into nearby creeks and estuaries (Sammut et al., 1996). The low pH groundwater discharge also mobilises iron and aluminium, fuels aquatic deoxygenation, and can lead to large fish kills and degradation of infrastructure (White et al., 1997;Johnston et al., 2003;Jeffrey et al., 2016;Wong et al., 2010). Drained CASS wetlands typically contain abundant reactive Fe(III) and exhibit complex sulphur and Fe cycling (Burton

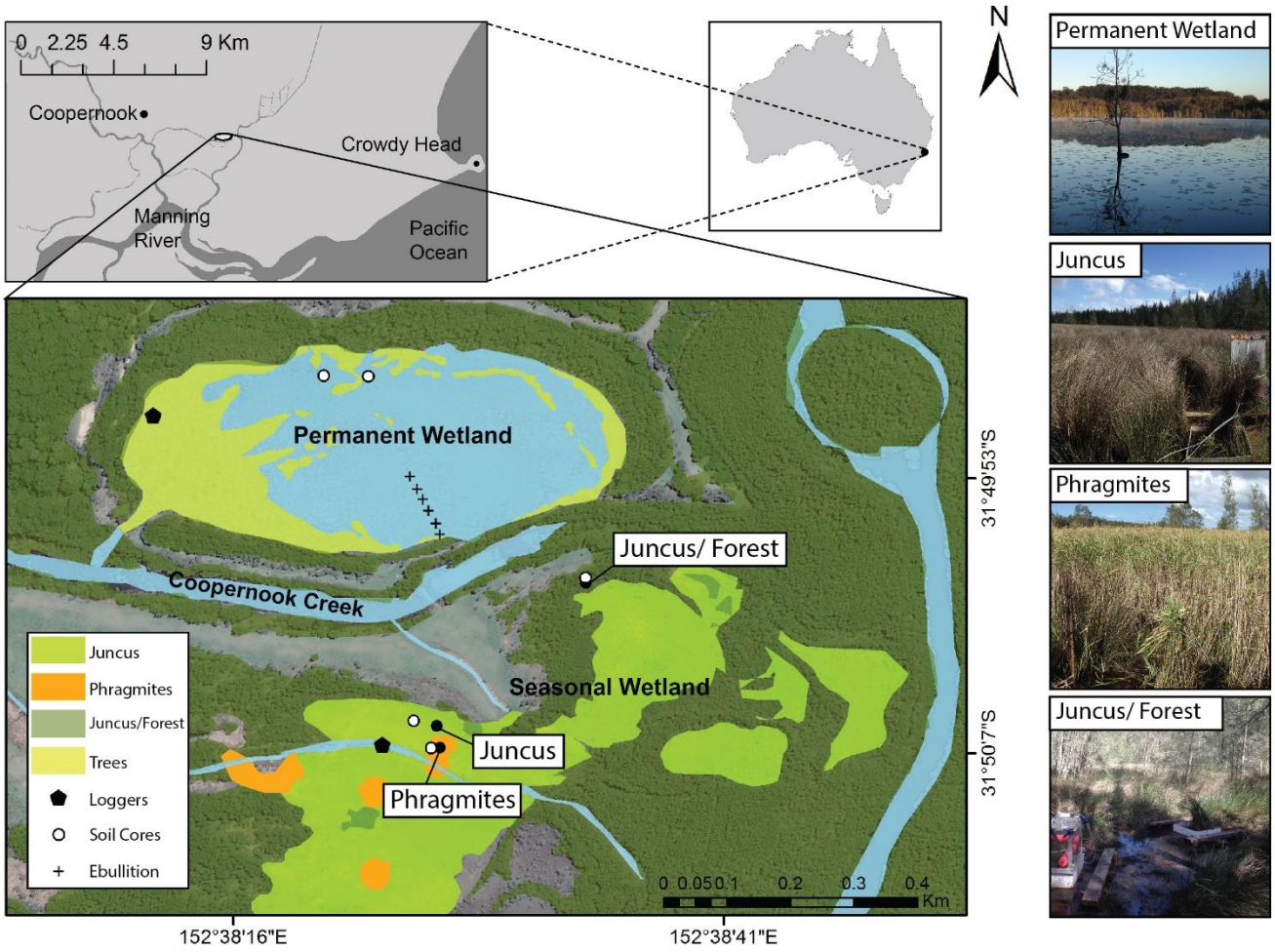
et al., 2006;Boman et al., 2008;Burton et al., 2011). Wetland iron and sulfur cycling can profoundly influence CH_4 production and consumption via a series of complex redox reactions coupled with organic matter mineralisation (Holmkvist et al., 2011;Sivan et al., 2014). As such, terminal electron acceptor availability is critical when considering wetland remediation and the biogeochemical compromise paradigm.

Here we assess CH_4 emissions rates from a remediated freshwater CASS wetland in subtropical eastern Australia, and compare fluxes from the permanent wetland and the adjacent seasonal wetland ecotypes. We hypothesize that wetland CH_4 emissions will differ significantly between the ~~seasons~~ campaigns and between the four wetland communities due to differences in soil chemistry, hydrology and plant physiology. We account for three atmospheric flux pathways for methane; ebullition, diffusion and plant-mediated fluxes, over ~~diurnal~~ diel cycles and within different ~~seasons~~hydrological conditions. CH_4 fluxes were also assessed in relation to the underlying soil properties, including sulphate, reactive iron III and iron II, acid volatile sulphur, chloride and organic carbon.

2.0 Methods

2.1 Study site

Cattai Wetland is located on the mid-coast of New South Wales, Australia. The reserve covers 500 hectares, featuring a shallow permanent wetland covering an area of approximately 16 hectares that is adjacent to a seasonal wetland and floodplain located to the south (Fig. 1). Both sites discharge into the nearby Coopernook Creek, a tributary of the larger Manning River estuary. The site was extensively cleared and low-lying areas drained during the early 1900's in order to aid agriculture and development in the region. As a result of this anthropogenic drainage, the oxidation of CASS produced sulphuric acid and episodic acidic discharge to adjacent creeks for many years (Tulau, 1999). To ameliorate acidic discharge, the natural hydrology of the site was restored in 2003 through the decommissioning of agricultural drains and removal of floodgates. Re-flooding of the CASS landscape has reduced the production of sulphuric acid, acid discharge and aluminium and iron mobilisation, hence improving the downstream water quality (GTCC, 2014).



148

149 **Fig. 1** The seasonal wetland study sites consisting of ~~Veg A~~Juncus (*Juncus kraussii*), ~~Veg~~
150 ~~B~~Phragmites (*Phragmites australis*), ~~Veg C~~Juncus/ Forest (*Juncus kraussii* below *Casuarina*
151 *sp.*) and the permanent wetland indicating sediment coring sites, ebullition replicate transect,
152 24 h vegetation time series sites and imagery of vegetation ecotypes.

153 The region receives a mean annual rainfall of 1180 mm with the majority falling during
154 early autumn with an average maximal monthly rainfall occurring in March (152 mm). The
155 lowest rainfall generally occurs during the winter months with average minimal rainfall during
156 September (60 mm). Average minimum and maximum summer temperatures range from 17.6
157 °C to 29 °C (January) and in winter range from 5.9 °C to 18.5 °C (July) (BOM, 2018). The
158 dominant vegetation type within the permanent wetland is an introduced waterlily species
159 (*Nymphaea capensis*), while the fringes of the wetland consist of wetland tree species;
160 *Casuarina* sp. and *Melaleuca quinquenervia*. The seasonal wetland to the south is dominated
161 by the sedge; *Juncus kraussii* ~~(Veg A)~~ ('Juncus' from herein) and features scattered stands of
162 *Phragmites australis* ('Phragmites' from herein)~~(Veg B)~~ with areas of slightly higher elevation

dominated by *Juncus kraussii* below *Casuarina sp.* (‘Juncus/ Forest’ from herein) ~~(Veg C)~~ (Fig. 1).

2.2 The aquatic CH_4 flux of the permanent wetland

To quantify CH_4 ebullition rates, up to 12 ebullition domes were deployed during two ~~distinct~~ different ~~seasons~~ hydrological conditions (detailed below) at ~20 m intervals along a longitudinal transect, from the edge of the permanent wetland towards the centre. Each dome was carefully suspended below the water level by flotation rings, ensuring minimal disturbance of sediment and the water column. Gas samples were extracted from the headspace of each dome using a 300 mL gas tight syringe at periods of ~48 h. The volume was recorded and each sample then diluted using ambient air (1:729 ratio) and analysed in situ using a using a manufacturer calibrated cavity ring-down spectrometer (Picarro G2201-*i*) to determine CH_4 concentrations (ppm). Diffusive CH_4 fluxes from the permanent wetland were measured using a floating chamber with a portable greenhouse gas analyser (UGGA, Los Gatos Research). To account for spatial and temporal variability, measurements were conducted during both day-time and night-time, and sampling within vegetated ~~–~~areas featuring lilies (*Nymphaea capensis*); that were only present during the second campaign, forested areas (*Melaleuca* sp.) and in areas where no aquatic vegetation was present (i.e. open water). A total of 39 CH_4 floating chamber incubations averaging ~8 minutes in duration were recorded over the two campaigns, with 19 during C1 (nine at night) and 30 during C2 (12 at night). The average r^2 value of linear regressions of CH_4 concentrations versus time during chamber incubations was 0.97 ± 0.05. One chamber measurement was disregarded as an outlier (as it was more than three times the standard deviation of the mean) and any chambers capturing ebullition bubbles (determined by a nonlinear increase in concentration) were also disregarded. Examples of these, ~~T~~in addition to the ~~seasonal~~ ebullition and diffusive CH_4 flux methods and measurements from the permanent wetland have previously been reported elsewhere (Jeffrey et al., 2019).

2.3 Plant-mediated CH_4 fluxes

Simultaneous time series chamber experiments were conducted over a minimum of ~~~~24 hours to measure diel CH_4 fluxes during each ~~season~~ campaign from the three different wetland vegetation ecotypes. These ecotypes were *Juncus kraussii* ~~(Veg A)~~, *Phragmites australis* ~~(Veg B)~~ and *Juncus kraussii* amongst *Casuarina sp.* forest ~~(Veg C)~~ (Fig. 1). In each ecotype, three ~~65 x 65 x 30 cm~~ acrylic bases (65 x 65 x 30 cm) were installed four months before the first

time series experiment, to minimise disturbance to the sediment profile and vegetative rhizosphere. Vegetative flux chambers were constructed of an aluminium frame with clear Perspex walls and roof that matched the areal footprint of the pre-inserted acrylic bases. The chambers were 100 cm, 150 cm and 50 cm high for at ~~Veg A, B and C~~Juncus, Phragmites and Juncus/Forest sites respectively. The custom sizes were tailored for the different vegetation heights, whilst minimising chamber volume as much as possible. Each chamber was leak-tested under laboratory conditions prior to fieldwork.

Before each field incubation, chambers were flushed with atmospheric air then carefully lowered over the vegetation and onto the acrylic base ensuring an air tight seal. A small fan circulated internal air within each chamber. Air within the chamber was pumped through a closed loop from the top of the chamber using gas tubing (Bevaline), passing through a drying agent (Drierite desiccant) and then analysed in situ using a calibrated cavity ring-down spectrometers (Picarro G2201-*i* or LosGatos), recording the flux rate of CH_4 (ppm/sec). The gas flow was returned near the base inside each vegetation chamber closing the loop. Vegetation incubation times ranged from 6 to 15 minutes depending on the flux rate and were taken from triplicate ~~sites~~ chambers to account for heterogeneity within each ecotype. During the first time-series (C1), an average of 16.7 ± 2.9 daytime flux measurements (i.e. after sunrise) and 7.3 ± 1.6 night time (i.e. after sunset) were recorded within each habitat. During the second campaign (C2) an average of 27.7 ± 2.9 (day time) and 10.3 ± 1.5 (night time) flux measurements were recorded within each habitat. In addition, CH_4 fluxes from the adjacent exposed ~~sediments~~ soils or shallow overlying water at each site were also measured at ~4 hourly intervals to determine the influence and role of plant-mediated CH_4 fluxes compared to non-vegetated CH_4 fluxes. Light and temperature loggers (Onset Hobo) measured the changes in diel~~urnal~~ air temperature (°C) and photosynthetically active radiation (PAR) at each site.

2.4 Soil geochemistry and redox conditions

A water logger (Minidiver) was deployed in the permanent wetland before the first campaign to monitor changes in water depth (cm) and temperature (°C). Field pH (pH_F) and the redox potential (Eh_F; reported against standard hydrogen electrode) were determined in situ, by directly inserting the electrode into the soils (5 cm depth, 8 replicates) at each site. A composite sampling approach (3 cores) was used to collect sediment samples from each site, to determine organic C content, $Fe(III)_{HCl}$, $Fe(II)_{HCl}$, Cl, SO_4^{2-} and acid volatile sulphur (AVS).

The cores were sampled in ~~cores were extracted in December 2016,~~ close proximity to the time series habitats (5 to 15 m) in December 2016, but from the permanent wetland cores were taken from elsewhere to avoid disturbance of the shallow water column and sediments. The cores were extracted by inserting a 4.0 cm diameter acrylic tube into the sediment to a depth of up to 50 cm. Cores were immediately sectioned into 2 cm increments to a depth of 20 cm, and 5 cm increments thereafter, ensuring higher vertical resolution in the organic rich near-surface sediments. Samples were immediately placed into air-tight bags, then frozen within 12 hr of collection at -16°C in a portable freezer and transferred to -80°C freezer in the laboratory. Frozen samples were thawed in an oxygen-free anaerobic chamber (1-5% H_2 in N_2), using an oxygen consuming palladium (Pd) catalyst. The defrosted samples were homogenised using a plastic spatula.

AVS content was determined by adding 1-2 g of wet sediment with 6 M HCl:1 M L-ascorbic acid. The liberated H_2S was captured in 5 ml of 3% Zn acetate in 2 M NaOH and then quantified using iodometric titration. The reactive Fe fractions were determined using a sequential extraction procedure optimised for acid sulphate soils based on Claff et al. (2010). Poorly crystalline solid-phase Fe (II) and Fe (III) were determined by extracting 2 g wet sub-samples with cold N_2-purged 1 M HCl for four hours. Aliquots of 0.45 µm-filtered extract were analysed for Fe (II) [$Fe(II)_{HCl}$] and total Fe [Fe_{HCl}] using the 1,10-phenanthroline method with the addition of hydroxylammonium chloride for total Fe (APHA, 2005). The Fe(III) [$Fe(III)_{HCl}$] was determined by the difference of [Fe_{HCl}] – [$Fe(II)_{HCl}$]. Total organic carbon (TOC) and total S (S_{Tot}) were determined via a LECO CNS-2000 carbon and sulfur analyser. Chloride and sulfate concentrations were measured using filtered (0.45 µm) aliquot from a 1:5 water extract of freshly defrosted wet soil, as per Rayment and Higginson (1992) via ion chromatography using a Metrosep A Supp4-250 column, an RP2 guard column and eluent containing 2 mM $NaHCO_3$, 2.4 mM Na_2CO_3 and 5% acetone, in conjunction with a Metrohm MSM module for background suppression.

2.5 Calculations

Both the air-water and vegetative CH_4 fluxes were calculated for the chamber deployments in the permanent wetland and seasonal wetland using the equation:

$$F = (s(V/RT_{air}A))t \quad (1)$$

where s is the regression slope for each chamber incubation deployments (ppm sec^{-1}), V is the chamber volume (m^3), R is the universal gas constant (8.205 x 10^{-5} m^3.atm.K^{-1}.mol^{-1}), T_{air} is the air temperature inside the chamber (K), A is the surface area of the chamber (m^2) and t is the conversion factor from seconds to day, and to mmol. We assume that atmospheric pressure is 1 atm.

Ebullition rates (E_b) (mmol m^{-2} d^{-1}) were calculated using the equation:

$$E_b = ([CH_4].CH_{4Vol.})/ A.V_m.Td \quad (2)$$

where [CH_4] is the CH_4 concentration in the collected gas (%), $CH_{4Vol.}$ is the gas volume sampled (L), A is the funnel area (m^2), V_m is the molar volume of CH_4 at in situ temperature (L) and Td is deployment time (days).

2.6 Statistical analysis

As the data was non-parametric we used a Kruskal-Wallis one way analysis of variance (ANOVA) on ranks, to test hypothesis about differences in campaigns, CH_4 flux pathways and diel variability, where a statistically significant difference is where $p<0.001$. The Dunns method was then used to analyse the multiple pairwise comparisons ($p<0.05$).

3.0 Results

Prior to the first campaign in April 2017 (C1), an extreme hot/drying summer period occurred ~~during early 2017~~ (Fig. 2). This resulted in an average wetland water column temperature of 23.3 ± 0.7 ºC and a water depth in the permanent wetland as low as ~7.3 cm, with exposed sediments along the wetland perimeter during the preceding month. There was a high rainfall event prior to C1 with ~~Total rainfall for the two weeks prior to C1 was~~ 342 mm of rainfall recorded over the preceding two weeks and~~, with~~ an additional 35 mm of rain occurring during C1 fieldwork (Fig. 2) thus raising the water column depth in the permanent wetland to 77.2 cm in less than four weeks. This C1 deployment was therefore categorized as the 'post-dry/flooded' period, where air temperatures ranged from 13.3 to 22.8 ºC and the average water column temperature in the permanent wetland was 20.4 ± 0.5 ºC. The second fieldwork campaign was conducted in September 2017 (C2) under cool/drying conditions, where air temperatures ranged from as low as 3.4 ºC to 34.9 ºC (Fig. 2), with cooler average water temperatures 12.6 ± 0.4 ºC in the permanent wetland (Fig. 2). The depth of the permanent wetland at this time had dropped slightly to ~33 cm (Fig. 2).

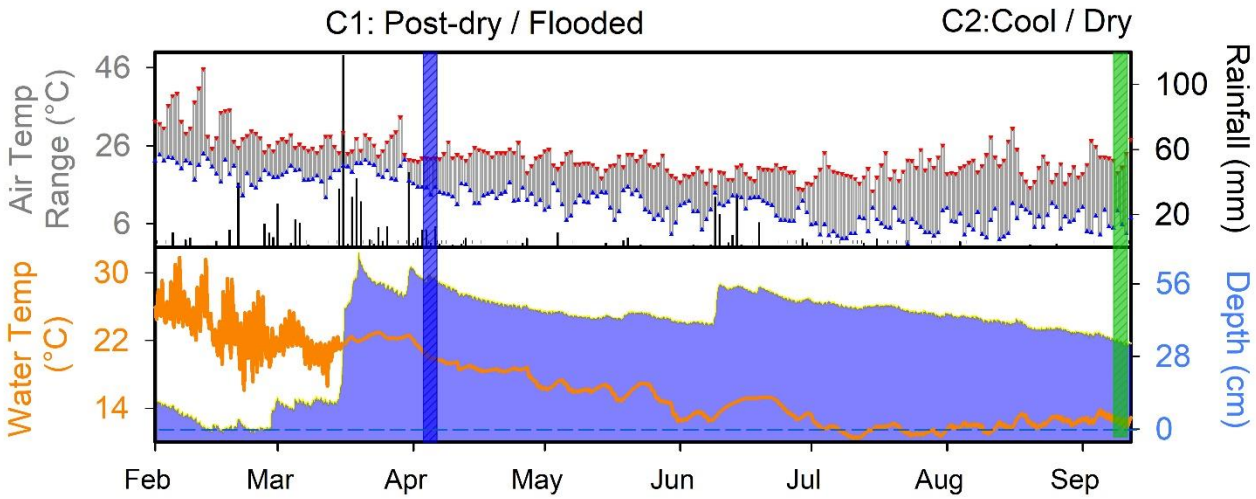


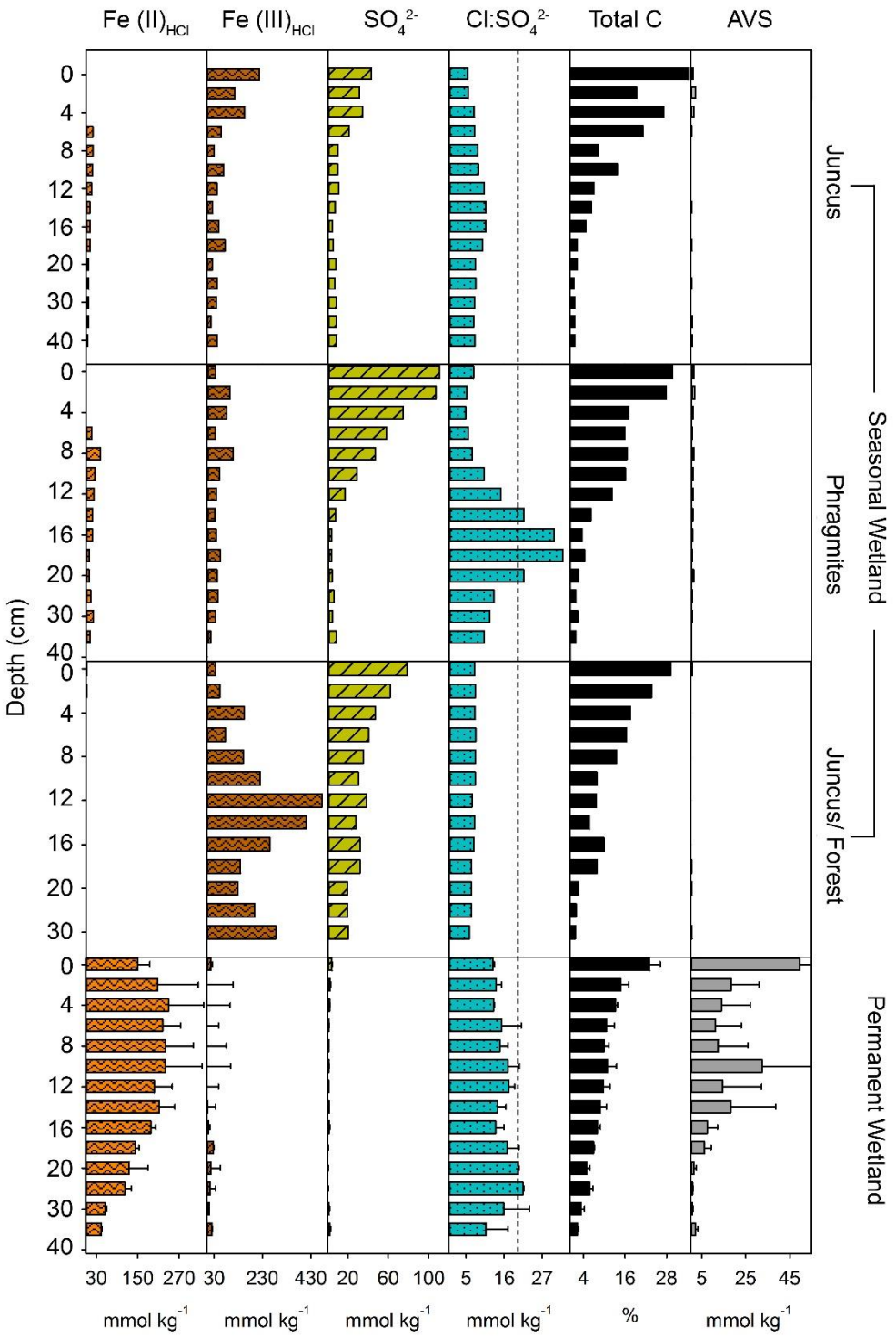
Figure 2. Hydrograph for the seven months of 2017 indicating daily rainfall, maximum/ minimum air temperature, water temperature and antecedent hydrology. Vertical coloured bands represent the two fieldwork campaigns.

3.1 Sediment core profiles and soil redox potentials

Average concentrations from soil cores (Table 1, Fig. 3) were based upon the top 20 cm of the profile, where the highest organic carbon concentrations were found. The $Fe(III)_{HCl}$ concentrations were greater than $Fe(II)_{HCl}$ at all three seasonal wetland sites, however the permanent wetland showed an opposite trend with low concentrations of both Fe(III) (5.6 ± 10.7 mmol kg^{-1}) and SO_4^{2-} (1.5 ± 1.0 mmol kg^{-1}) (Fig. 3, Table 1). The highest average concentrations of $Fe(III)_{HCl}$ were found at the Juncus/ Forest site (204.0 ± 51.6 mmol kg^{-1}) and highest and similar concentrations of SO_4^{2-} were in Phragmites and Juncus/ Forest sediments (45.4 ± 41.0 mmol kg^{-1} and 43.3 ± 16.7 mmol kg^{-1}) (Fig. 3, Table 1). Net positive redox potential was found at all four sites during C1 (under post-dry/ flooded conditions) indicating a lag time between recent flooding and the onset of reducing conditions. In contrast, a negative redox potential was found within the permanent wetland and Phragmites during C2, indicating reduced conditions under cool drying conditions (Table 1). The TOC concentrations (%) were highest in the upper profiles and similar across all sites (Fig. 3, Table 1) averaging 13.4 ± 7.6%.

Table 1. Summary of plant-mediated CH_4 fluxes from the seasonal wetland time series and diel CH_4 fluxes and ebullition from the permanent wetland during C1 (post-dry/ flooded) and C2 (cool/ drying). The corresponding sediment core data are average concentrations from 0 to 20 cm below ground level.

	Permanent Wetland		Seasonal Wetland Sites		
CH_4 flux (mmol m^{-2} d^{-1})	Ebullition	Diffusion	Juncus	Phragmites	Juncus/ Forest
C1 - Post-dry/ Flooded					
Sediment flux			0.06	0.04	0.10
Day time		0.57	1.79	2.64	0.13
Night time		2.07	1.50	1.59	0.10
Daily average	2.02	1.49	1.70	2.27	0.12
C2 - Cool / Drying					
Sediment flux			0.0004	0.20	0.0003
Day time		11.72	0.06	0.94	0.13
Night time		8.39	0.04	0.48	0.10
Daily average	2.10	10.46	0.05	0.77	-0.01
Sediment core average (0-20cm)					
Fe_{HCl} (II) (mmol kg^{-1})		202.3	11.6	15.4	1.5
Fe_{HCl} (III) (mmol kg^{-1})		5.6	83.3	56.1	204.0
SO_4^{2-} (mmol kg^{-1})		1.5	17.6	45.4	43.3
$Cl:SO_4^{2-}$		14.8	8.4	13.9	7.4
AVS (µmol g^{-1})		18.5	0.7	0.9	0.3
TOC (% C)		11.6	14.3	14.8	14.6
C1 - Redox Eh (mV)		71.7	46.5	9.6	54.4
C2 - Redox Eh (mV)		-216	12	-89	424



312

313 **Figure 3.** Soil profiles of the permanent and seasonal wetland sites indicating $Fe(II)_{HCl}$,
314 $Fe(III)_{HCl}$, SO_4^{2-}, $Cl:SO_4^{2-}$ (a proxy for depletion of marine-derived sulphate, where >20 is
315 broadly indicative of SO_4^{2-} reduction and <8 CASS pyrite oxidation (Mulvey, 1993)), total C

and acid volatile sulphur (AVS). Note: The permanent wetland profiles are averages from two adjacent sites with error bars representing the standard deviation.

3.2 Permanent and Seasonal Wetland CH_4 fluxes

The vegetation time series revealed ~~diurnal~~ diel variability of plant-mediated CH_4 emissions occurred at most ecotypes, with the highest CH_4 fluxes occurring during daytime around mid-day and the lowest CH_4 fluxes during the night time (~~Fig. 3~~Fig. 4, Table 1). The lowest CH_4 fluxes were found ~~at~~ in Juncus/ Forest~~Veg C~~ habitat with a net negative CH_4 flux observed during C2 time series. The CH_4 sediment fluxes measured amongst each vegetation time series were consistently much lower than the plant-mediated CH_4 fluxes indicating that the vegetation was indeed the main conduit for CH_4 to the atmosphere (~~Fig. 3~~Fig. 4, Table 1). The CH_4 fluxes were highly variable between the replicates at each site. Temperature and PAR followed similar ~~diurnal~~diel trends to each other and had positive correlations to CH_4 emissions (~~Fig. 3~~Fig. 4).

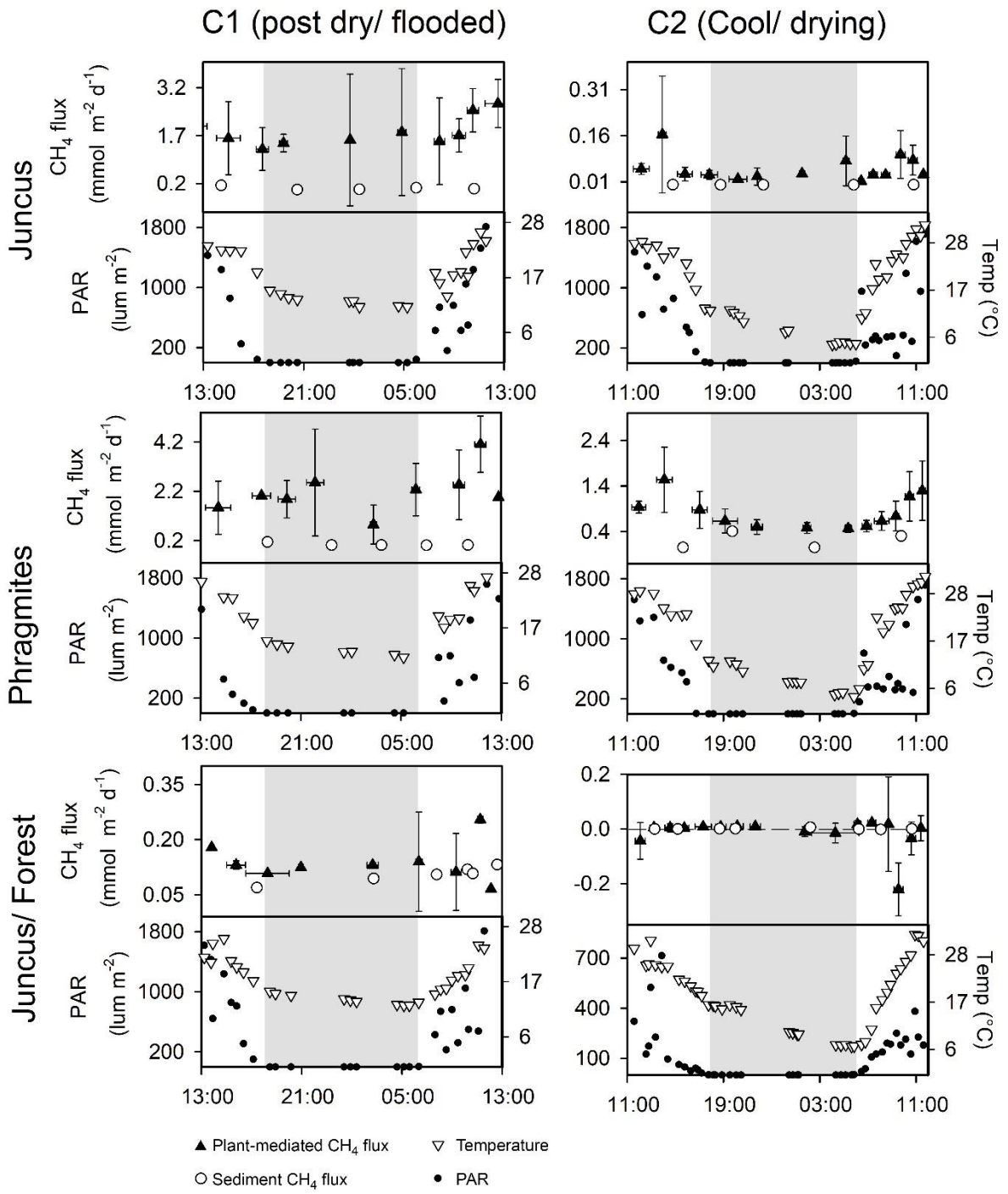


Figure 34. Simultaneous 24 h time series of vegetative CH_4 fluxes from the seasonal wetland ecotypes at Cattai Wetland during C1: post-dry/flooded (Apr 2017) and C2: cool/drying conditions (Sep 2017). The vertical error bars of the plant-mediated CH_4 flux (mmol m^{-2} d^{-1}) represent standard deviation of the triplicate time series measurements taken from each site and horizontal bars represent the total aggregated time period represented by replicate chambers.

The grey shading indicates night-time. Note: Different y-axis scales for CH_4 to highlight ~~diurnal~~diel trends.

CH_4 fluxes from the three vegetation types were significantly higher ~~i~~during~~n~~ C1 than during C2 (~~Fig. 4~~$p<0.001$; Fig. 5, Table 1). During C1, the CH_4 fluxes from the Juncus and Phragmites were not significantly different from each other but were both significantly higher ($p<0.001$) than Juncus/Forest however, during C2 the CH_4 fluxes of each seasonal wetland habitat were significantly different between all habitats ($p<0.01$) (Fig. 5). The highest average CH_4 fluxes in each of the vegetation types always occurred during the daytime but were not significantly different to night time fluxes (~~Fig. 4~~Fig. 5, Table 1). Phragmites habitat~~*Phragmites sp.* (Veg B)~~ consistently emitted the highest CH_4 fluxes (2.27 ± 1.42 mmol m^{-2} d^{-2} during C1 and 0.77 ± 0.46 mmol m^{-2} d^{-1} during C2). The Juncus/ Forest~~Veg C~~ ecotype within the seasonal wetland consistently produced the lowest CH_4 fluxes of all sites, with a ~~net negative~~negligible flux that was not significantly different from zero occurring during C2 (-0.01 ± 0.08 mmol m^{-2} d^{-1}).

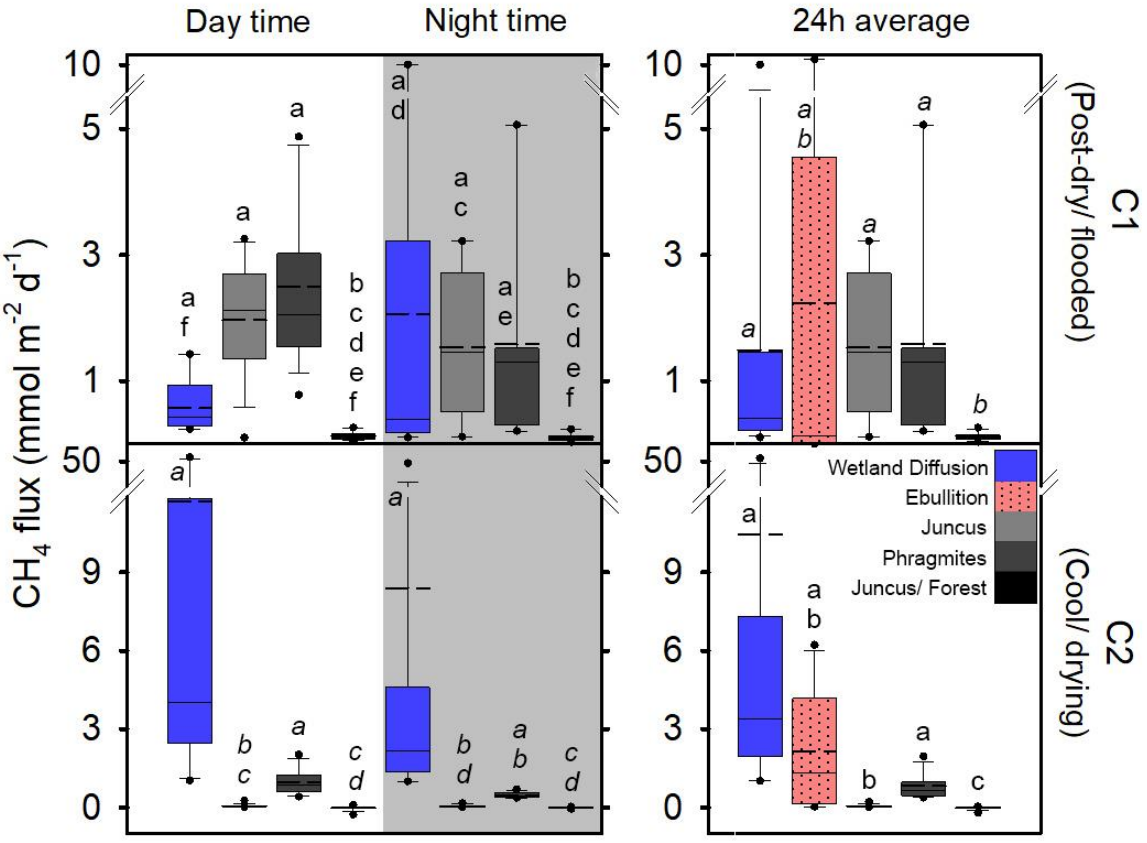


Figure 45. ~~Seasonal f~~Fluxes of CH_4 from ~~diurnal~~diel sampling and ebullition over two campaigns from the permanent wetland and adjacent 24 h time series of the seasonal wetland vegetation types ~~A, B and C~~. Note: Diffusive fluxes during C2 include chambers featuring lilies, ~~D~~dashed line represents the average, solid line represents the median and dots represent 5th and 95th percentiles. Letters show groups that did not differ significantly ($p>0.05$) using ANOVA on ranks and Dunn's pairwise comparisons.

The permanent wetland showed an inverse trend with seven-fold and significantly higher higher ($p<0.01$) diffusive fluxes during the cool/drying C2 when lilies were present (10.46 ± 15.81 mmol m^{-2} d^{-1}) compared to the post-dry/flooded C1 when no lilies were present (1.49 ± 2.75 mmol m^{-2} d^{-1}), while the ebullition rates were similar during both ~~seasons~~ campaigns (~~Fig. 4~~Fig. 5, Table 1). Overall, the diffusive fluxes of the permanent wetland were within range of CH_4 fluxes from the three seasonal wetland habitats, with diffusive fluxes significantly different to the Juncus/Forest during both campaigns, and with Juncus during C2 (Fig. 5). Diel diffusive flux variability was not significant.~~Overall, the plant-mediated CH_4 fluxes from the three seasonal wetland vegetation ecotypes (Veg A, B and C) were within the range of aquatic fluxes measured from the permanent wetland for the post-dry/flooded C1 time series, but not for the cool/drying C2 time series, when the permanent wetland CH_4 fluxes were much higher (Fig. 4Fig. 5)~~.

Table 1. Summary of plant-mediated CH_4 fluxes from the seasonal wetland time series and ~~diurnal~~diel CH_4 fluxes and ebullition from the permanent wetland during C1 (post-dry/ flooded) and C2 (cool/ drying). The corresponding sediment core data are average concentrations from 0 to 20 cm below ground level.

	Permanent Wetland		Seasonal Wetland Sites		
CH_4 flux (mmol m^{-2} d^{-1})	Ebullition	Diffusion	Juncus	Phragmites	Juncus/ Forest
C1 - Post-dry/ Flooded					
Sediment flux			0.06	0.04	0.10
Day time		0.57	1.79	2.64	0.13
Night time		2.07	1.50	1.59	0.10
Daily average	2.02	1.49	1.70	2.27	0.12
C2 - Cool / Drying					
Sediment flux			0.0004	0.20	0.0003
Day time		11.72	0.06	0.94	0.13
Night time		8.39	0.04	0.48	0.10
Daily average	2.10	10.46	0.05	0.77	-0.01
Sediment core average (0-20cm)					
Fe_{HCl} (II) (mmol kg^{-1})		202.3	11.6	15.4	1.5
Fe_{HCl} (III) (mmol kg^{-1})		5.6	83.3	56.1	204.0
SO_4^{2-} (mmol kg^{-1})		1.5	17.6	45.4	43.3
$Cl:SO_4^{2-}$		14.8	8.4	13.9	7.4
AVS (µmol g^{-1})		18.5	0.7	0.9	0.3
TOC (% C)		11.6	14.3	14.8	14.6
C1 - Redox Eh (mV)		71.7	46.5	9.6	54.4
C2 - Redox Eh (mV)		-216	12	-89	424

~~3.3 Sediment core profiles and soil redox potentials~~

~~Average concentrations from soil cores (Table 1, Fig. 5~~Fig. 3~~) were based upon the top 20 cm of the profile, where the highest organic carbon concentrations were found. This upper rhizosphere depth zone is assumed to be an active area of carbon metabolism and CH_4 production and consumption (Nedwell and Watson, 1995). The $Fe(III)_{HCl}$ concentrations were greater than $Fe(II)_{HCl}$ at all three seasonal wetland sites, however the permanent wetland showed an opposite trend with low concentrations of both Fe(III) (5.6 ± 10.7 mmol kg^{-1}) and SO_4^{2-} (1.5 ± 1.0 mmol kg^{-1}) (Fig. 5~~Fig. 3~~, Table 1). The highest average concentrations of $Fe(III)_{HCl}$ were found at the Veg C site (204.0 mmol kg^{-1}) and highest and similar concentrations of SO_4^{2-} were in Veg B and Veg C sediments (45.4 ± 41.0 mmol kg^{-1} and 43.3 ± 16.7 mmol kg^{-1}) (Fig. 5~~Fig. 3~~, Table 1). Net positive redox potential was found at all four sites during C1 (under post-dry/ flooded conditions) indicating a lag time between recent flooding and the onset of reducing conditions. In contrast, a negative redox potential was found within the permanent wetland and Veg B during C2, indicating reduced conditions under cool

drying conditions (Table 1). The TOC concentrations (%) were highest in the upper profiles and similar across all sites (Fig. 5Fig. 3, Table 1) averaging 13.4 ± 7.6%.

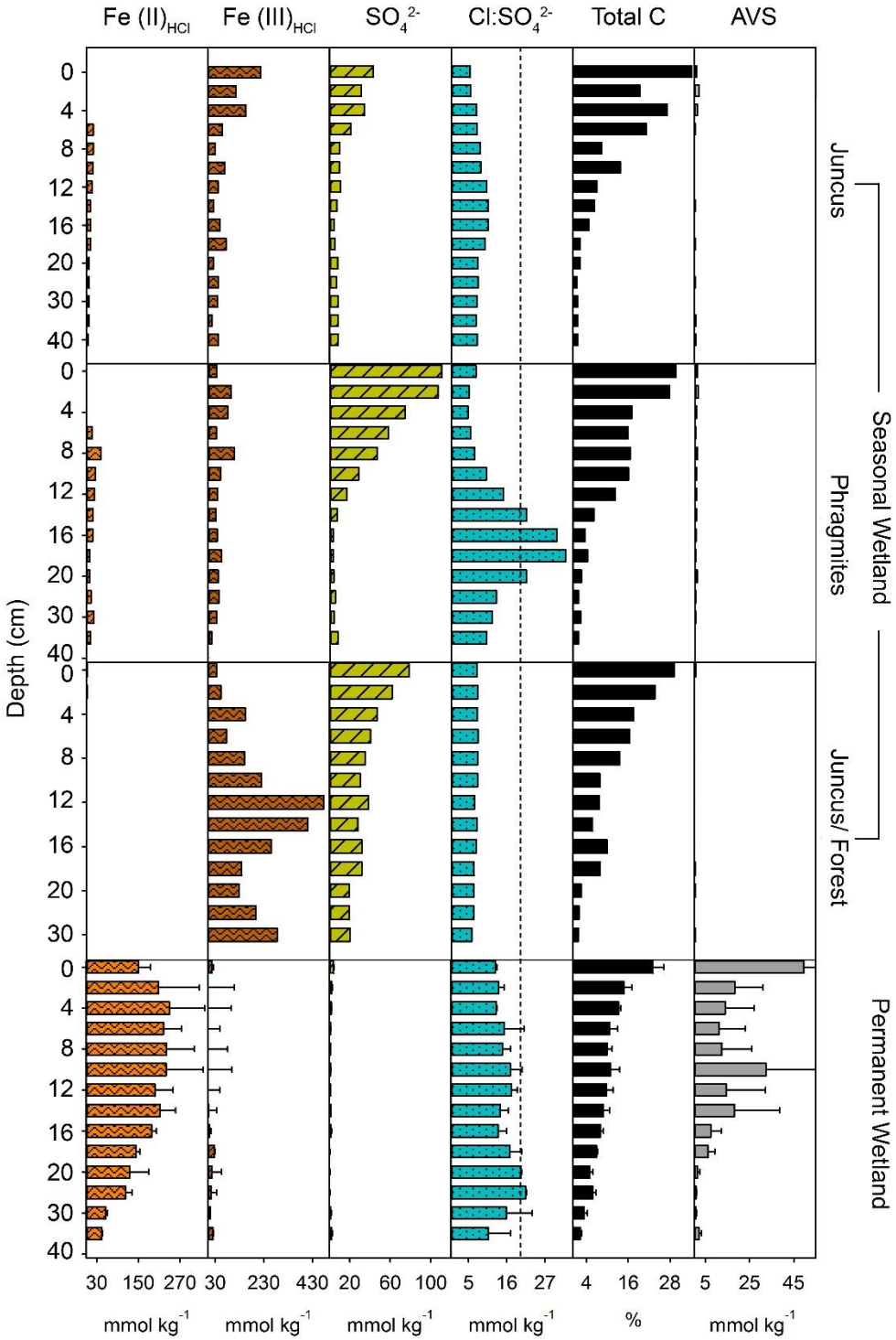


Figure 5. Soil profiles of the permanent and seasonal wetland sites indicating $Fe(II)_{HCl}$, $Fe(III)_{HCl}$, SO_4^{2-}, $Cl:SO_4^{2-}$ (a proxy for depletion of marine-derived sulphate, where >20 is

~~broadly indicative of SO_4^{2-} reduction and <8 CASS pyrite oxidation (Mulvey, 1993)), total C and acid volatile sulphur (AVS). Note: The permanent wetland profiles are averages from two adjacent sites with error bars representing the standard deviation.~~

3.~~4~~ 3 Temperature and PAR

Correlation plots for both temperature (ºC) and sunlight (PAR) versus CH_4 emissions from the three vegetation ecotypes showed no distinct relationships with the exception of Phragmites~~Veg B~~ during C2 for PAR (r^2=0.18, p<0.01) and temperature (ºC) (r^2=0.35, p<0.001). No clearer trends were observed by combining all site measurements, nor separating daytime fluxes and drivers from night time fluxes and drivers.

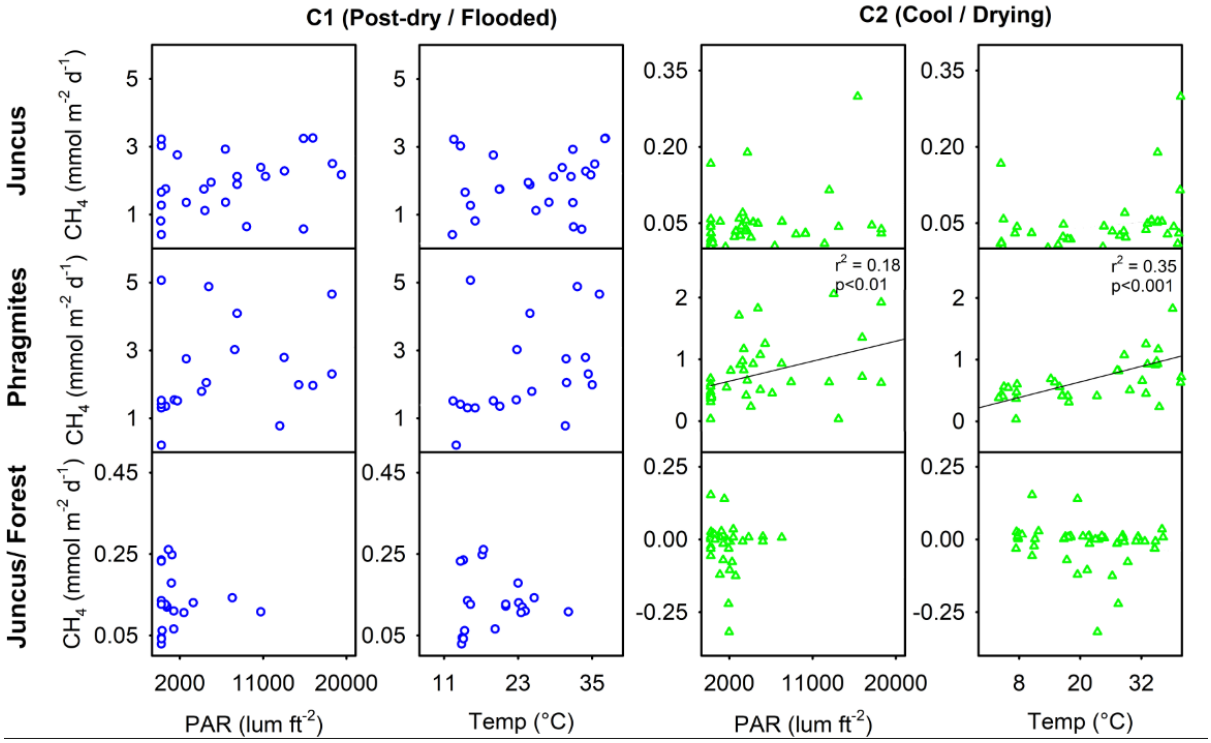


Figure 6. Correlations of CH_4 with temperature (ºC) and photo-synthetically active radiation (PAR) (lum ft^{-2}) for the three ~~seasonal~~ wetland vegetation sites of Cattai Wetland during two ~~seasonal~~ field campaigns.

4.0 Discussion

4.1 Geochemistry of the CASS landscape

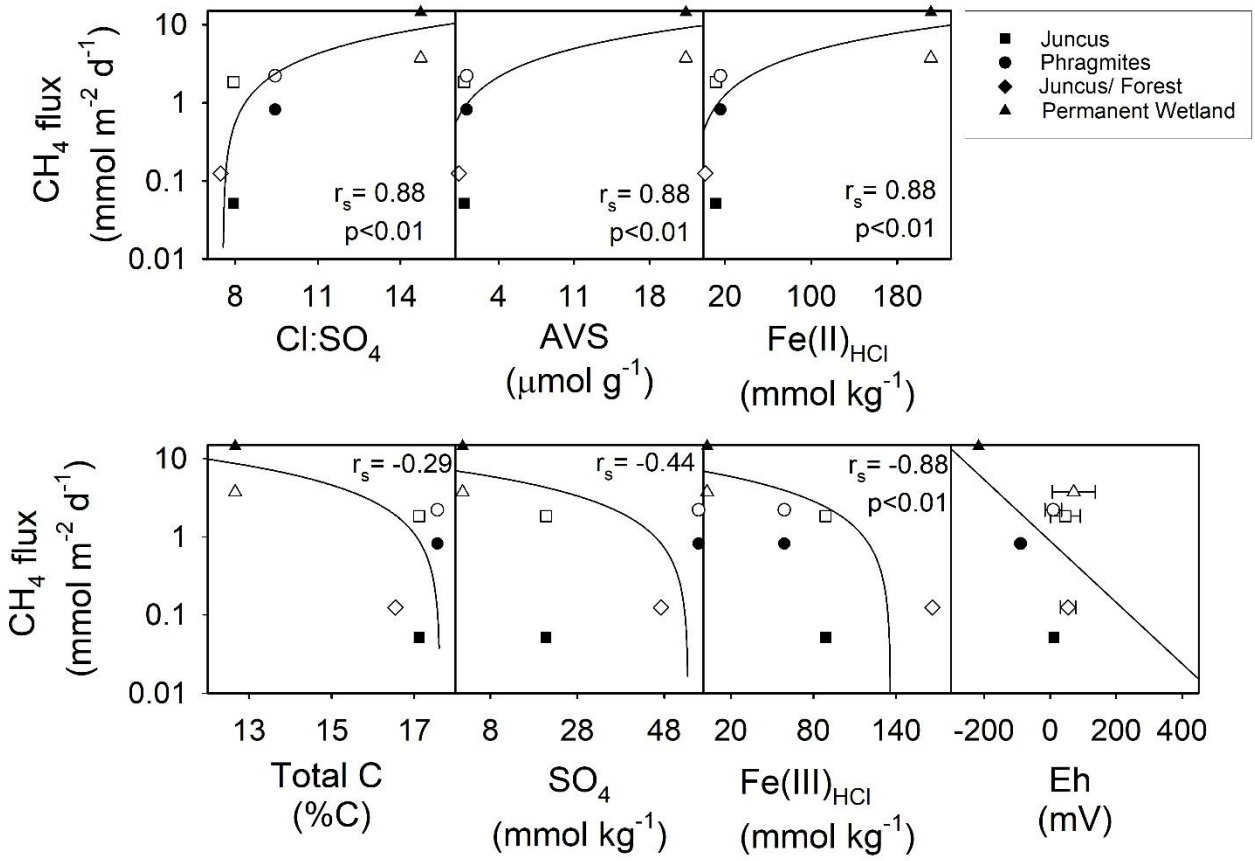
Sediment profiles provide insights to the historical geochemical changes that have occurred across the CASS landscapes of the four Cattai Wetland sites (~~Fig. 5~~Fig. 3). We base our results and discussion on ~~This~~the upper rhizosphere depth zone (20 cm) as this featured the highest organic carbon concentrations and is therefore assumed to be an active area of carbon metabolism, -and CH_4 production and consumption (Nedwell and Watson, 1995). If we assume that relatively uniform deposition of late Holocene materials occurred, the differences between present day profiles are related to historical changes in hydrology and land use, topographic elevation, geochemical trajectories and vegetative carbon inputs. For example, the permanent wetland shows distinct differences to the adjacent seasonal wetland sites, with divergent geochemical signatures of both iron and sulphate that reflect the sustained inundation (Table 1, Fig 5). The permanent wetland had significantly lower Fe(III) ($p<0.001$) and 11 to 30 fold lower SO_4^{2-} concentrations within the upper soil profile compared to the seasonal wetland. The ratio of $Fe(III)_{HCl}$ to $Fe(II)_{HCl}$ from the flooded soils of the permanent wetland was 0.03, indicating the sediments were almost completely depleted of Fe(III). Under reducing conditions where there is low SO_4^{2-} and little to no Fe(III) to competitively exclude methanogenesis, CH_4 production becomes more favourable. Indeed, CH_4 production was on average highest from the permanent wetland, especially when considering the duel CH_4 pathways of ebullition and air-water diffusion (Table 1).

In addition to sulphate reduction, some depletion of the sulphur pool from the permanent wetland may have occurred due to drainage exports of sulphuric acid (H_2SO_4) discharging from the CASS landscape throughout the last century. Alternatively, reducing conditions induced by re-flooding freshwater wetlands is known to encourage the re-formation of AVS and pyrite (FeS_2) and produce alkalinity, thereby attenuating acid production and discharge (Burton et al., 2007;Johnston et al., 2012;Johnston et al., 2014) and reducing the total SO_4^{2-} pool of CASS landscapes. While the AVS concentrations found within the permanent wetland (up to 18.5 µmol g^{-1}) were a result of sulphate reduction induced by CASS wetland restoration, they nonetheless represent a relatively volatile form of sulphur, which is at risk of rapid oxidation during drought periods (Johnston et al., 2014;Karimian et al., 2017). The AVS concentrations of the permanent wetland sites were more than 20-fold higher than the three adjacent seasonal wetland sites, and represent a potentially volatile by-product and consequence of re-flooding CASS soil landscapes, in addition to leading to increases of CH_4 emissions (Table 1).

The soil profile from the seasonal wetland Juncus/ Forest~~Veg C~~ habitat featured abundant $Fe(III)_{HCl}$ ($Fe(III)_{HCl}$ to $Fe(II)_{HCl}$ ratio of 136) and also SO_4^{2-}. This was associated with the lowest fluxes of CH_4 for both ~~seasonal~~ sampling periods (~~Fig. 5~~Fig. 3, Table 1). Relatively low CH_4 fluxes from Juncus/ Forest~~Veg C~~ are likely due to the more oxidising conditions present at this site and the surfeit of thermodynamically favourable terminal electron acceptors (i.e. Fe(III) and SO_4^{2-}), which would competitively exclude organic matter degradation by methanogenic archaea (Postma and Jakobsen, 1996).

At the other seasonal wetland sites ~~(Veg A and B)~~, the average Fe(III) and SO_4^{2-} concentrations were intermediate, (i.e. lower than ~~Veg C~~Juncus/ Forest, but higher than the permanent wetland), although in the upper profile ~~Veg B~~the Phragmites had more SO_4^{2-} while ~~Veg A~~Juncus had more Fe(III) (~~Fig. 5~~Fig. 3, Table 1). CH_4 flux values from these sites were also intermediate (Table 1). Sediment profiles from both ~~Veg A~~Juncus and ~~Veg B~~Phragmites indicated a degree of Fe reduction based on the ratio of Fe(III):Fe(II) which were 7.2 and 3.6 respectively. The redox potentials from Phragmites~~Veg B~~ during both C1 and C2 ~~seasons~~ campaigns (9.6 mV and -89.0 mV respectively) were consistently lower than Juncus~~Veg A~~ during C1 and C2 ~~seasons~~ campaigns (46.5 mV and 12.0 mV respectively), which is consistent with the more reducing conditions encouraging CH_4 production in Phragmites~~Veg B~~ habitat. Further, as iron reduction yields more free energy than SO_4^{2-} reduction ~~(which yields more free energy than methanogenesis)~~ (Burdige, 2012), then Fe reduction ~~at~~ at the Juncus site ~~Veg A~~ may outcompete CH_4 production ahead of SO_4^{2-} reduction ~~at~~in Phragmites~~Veg B~~, which may help explain some of the differences in CH_4 production between the two sites. The

~~Regression analysis and Spearman rho coefficients summarise the spatial trends occurring between the average sediment parameters versus seasonal CH_4 fluxes from the different sites (Fig. 7). p~~Positive significant trends ~~occurred for~~between Fe(II), AVS and the $Cl:SO_4^{2-}$ ratios with CH_4 flux rates (r_s=0.88, p<0.01) further support~~ing~~ our hypothesis that reducing conditions and a smaller pool of sediment Fe(III) and SO_4^{2-} facilitate higher CH_4 production rates (Fig. 7). Alternatively, the negative trends observed between soil redox potentials, SO_4^{2-}, Fe(III) and CH_4 fluxes affirm that the abundance of thermodynamically favourable terminal electron acceptors play~~s~~ a role in attenuating CH_4 production at each site.



476

477 **Figure 7.** Regression analysis of average daily CH_4 fluxes (mmol m^{-2} d^{-1}) vs subsoil parameters
478 of 0-20 cm core depth (i.e. CH_4 'active' zone). Note: Log scale y-axis of CH_4 fluxes from the
479 four wetland ecotypes over two ~~seasons~~campaigns. Note: The r_s values were calculated using
480 Spearman rho are for C1 (black shapes) and C2 (white shapes).

481

482 **4.2 Plant-mediated CH_4 fluxes from the seasonal wetland**

483 Plant-mediated CH_4 fluxes were highest during C1 under post-dry/flooded conditions
484 with 20-30 cm of standing waters in the seasonal wetland (Table 1). While waterlogged
485 conditions are an obvious driver of higher CH_4 production rates from saturated sediments in
486 addition to the geochemical differences (previously discussed), other drivers which may
487 explain these trends include differences in ~~diurnal~~diel variability in temperature, PAR and plant
488 physiology, which may influence CH_4 gas transport pathways.

489 In vegetated seasonal wetlands, plant-mediated gas transport is recognised as a
490 dominant pathway for CH_4 emission to the atmosphere and accounts for up to 90% of total
491 wetland fluxes (Sorrell and Boon, 1994;Whiting and Chanton, 1992). For plant survival in

near-permanent inundation environments, oxygen transport occurs via the araenchyma downwards to the rhizome. This increases the plant performance by mitigating (i.e. oxidising) the accumulation of phytotoxins such as sulphides and reducing metal ions around the roots (Armstrong and Armstrong, 1990;Armstrong et al., 2006;Penhale and Wetzel, 1983). As oxygen transfer to the rhizosphere occurs, an exchange of sedimentary CH_4 can be efficiently transported from the rhizosphere to atmosphere, bypassing sedimentary oxidative processes along the way (Fig. 8). This process in plants can be either convective (i.e. pressurised) or via passive diffusive gas flow, both of which are adaptive traits of many wetland species (Konnerup et al., 2011;Armstrong and Armstrong, 1991).

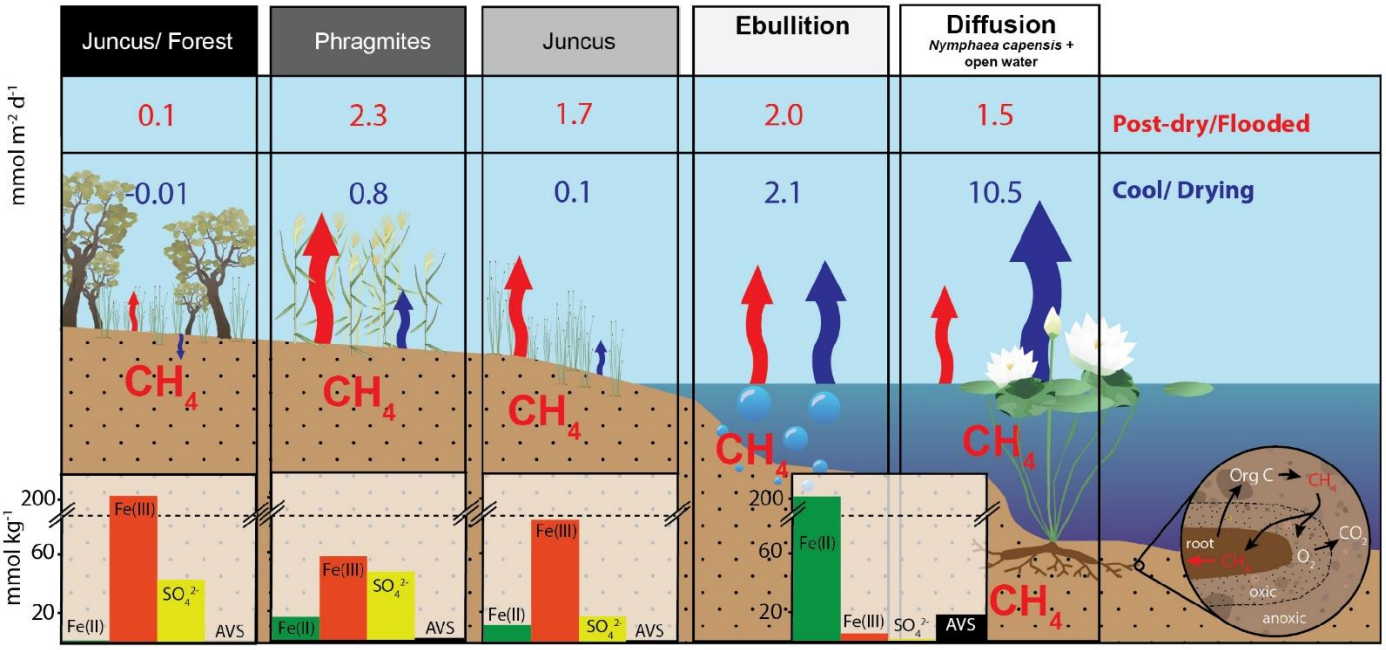


Figure 8. Conceptual model summarising the terrestrial and aquatic CH_4 fluxes (mmol m^{-2} d^{-1}) and sediment core profile parameters (mmol kg^{-1}) of the permanent and seasonal wetlands during C1 (post-dry/flooded conditions) and C2 (cool/drying conditions) of Cattai Wetland. Conceptual diagram rhizome process insert adapted from (Conrad, 1993). Note: Dashed line highlights y-axis break.

During both ~~seasons~~ campaigns the highest CH_4 fluxes from seasonal wetland vegetation were emitted from Phragmites ~~*Phragmites australis* (Veg B)~~ and always occurred during daylight (Table 1, Fig. 8). In *Phragmites australis* ~~(Veg B)~~, the presence of pressurised

lacunar leaf culms drive a mass flow of oxygen to the rhizome and back to the atmosphere via older (non-pressurised) efflux culms (Sorrell and Boon, 1994;Henneberg et al., 2012). This process has been widely studied in wetlands featuring *Phragmites australis*~~this species~~, as it is one of the most productive and wide spread flowering wetland species (Clevering and Lissner, 1999;Brix et al., 2001;Chanton et al., 2002;Tucker, 1990). Milberg et al. (2017) found no apparent diel patterns of CH_4 fluxes from *Phragmites australis* during seven campaigns within the Swedish growing season. In a midlatitude prairie wetland, Kim et al. (1998) showed that CH_4 emissions ~~from *Phragmites australis*~~ peaked around midday and that daytime emissions were about 3-fold higher than night time emissions, positively correlating with temperature and PAR. These were similar to our findings with highest CH_4 fluxes of each ~~seasonal~~ time series occurring near midday (4.88 mmol m^{-2} d^{-1} at 10:50 am during C1~~; 4.88 mmol m^{-2} d^{-2}~~ and 2.06 mmol m^{-2} d^{-1} at 12:15 pm during C2~~; 2.06 mmol m^{-2} d^{-2}~~) (~~Fig. 3~~Fig. 4). We also found a positive significant relationship between CH_4 flux and both temperature and PAR during C2 (r^2=0.35, p<0.001 and r^2=0.18, p<0.01 respectively) (Fig. 6). The often high ~~diurnal~~diel variability in CH_4 fluxes from *Phragmites australis* occurs as convective gas transport increases rhizospheric oxygen and CH_4 exchange via living culms during the daytime, whereas molecular diffusion during the night time facilitates a more passive and lower CH_4 flux pathway through dead culms (Chanton et al., 2002;Armstrong and Armstrong, 1991).

One possible reason CH_4 fluxes were lower from Juncus~~Veg A~~ than Phragmites~~Veg B~~ despite their close geographical location, may be due to the passive gas diffusion mechanism utilised by *Juncus sp*. (Henneberg et al., 2012). Unlike the pressurised conductive gas flow mechanisms of Phragmites~~Veg B~~, many wetland rush species (such as *Juncus sp.*~~Veg A~~) employ passive diffusive gas flow to survive within water logging environments (Konnerup et al., 2011;Brix et al., 1992). Despite diffusion being a less efficient gas transport mechanism (Konnerup et al., 2011), plant-mediated CH_4 diffusion is recognised as the dominant pathway for CH_4 emissions from many seasonal wetland species. During C1 and C2, day time fluxes (diffusive) from Juncus~~Veg A~~ were only 19% and 33% higher than night time fluxes (diffusive). In comparison, ~~a~~in~~t~~ Phragmites~~Veg B~~ these day:night ratios were almost triple this (67% and 94% higher) during the same periods. This may potentially be due to the more efficient daytime conductive gas transfer pathway of CH_4 through ~~Veg B (~~*Phragmites australis*~~)~~ compared to the more passive diffusive CH_4 gas transfer pathway of ~~Veg A (~~*Juncus kraussii*~~)~~ and/or the effectiveness of these different species to alter sedimentary redox conditions. This suggests that non-pressurized pathways may result in lower net rhizosphere-

atmosphere gas exchange of CH_4 from seasonal wetland vegetation. Alternatively, root depth and root density differ between these two species (Moore et al., 2012;De La Cruz and Hackney, 1977), which may further influence redox dynamics in the rhizosphere, and the potential extent of net gas exchange.

The Juncus/ Forest ~~*Juncus kraussii* below *Casuarina sp.* trees (Veg C)~~ habitat emitted ~~nominal~~ significantly lower fluxes of CH_4 during both time series campaigns and was a net sink for CH_4 during C2 (Table 1, Fig. 8). Although wetland trees have recently been shown to contribute significantly to CH_4 fluxes from flooded environments (Pangala et al., 2017), we could not quantify or constrain the role of trees as a conduit of methane to the atmosphere at this site. Regardless, there were clearly lower CH_4 fluxes through the *Juncus kraussii* at the Juncus/ Forest habitat ~~Veg C (*Juncus kraussii*)~~ compared to the Juncus only habitat ~~Veg A (*Juncus kraussii*)~~. As the species at ground level were identical, these differences are not related to vegetative gas transport mechanisms, nor organic carbon content (Table 1). Shading by the overhanging trees may inhibit the daytime diffusive CH_4 gas transport through Juncus/ Forest habitat ~~Veg C~~ assumable to lower rates of photosynthesis, however PAR was only lower during C2 (Fig. 7) and so does not appear to explain the CH_4 flux differences observed during C1. The differences are therefore likely explained by the higher positive redox potentials (Table 1) that may be partially attributable to rhizome aeration by the nearby trees, and more abundant thermodynamically favourable terminal electron acceptors (i.e. Fe(III) and SO_4^{2-}) (~~Fig. 5~~Fig. 3) all of which can inhibit methane production within the sediments (Burdige, 2012).

4.3 Permanent Wetland CH_4 fluxes

Diffusive CH_4 fluxes from the permanent wetland varied considerably between ~~seasons~~campaigns; however, ebullition fluxes were similar (Table 1, Fig. 8). The highest ~~seasonal~~ CH_4 fluxes for both ebullition and diffusion (2.1 mmol m^{-2} d^{-1} and 10.5 mmol m^{-2} d^{-1} respectively) occurred during C2 despite cooler conditions (Fig. 2. Fig. 8). This however was the opposite trend to the seasonal wetland CH_4 fluxes (Table 1, Fig. 8). One reason may be due to the antecedent hydrological conditions before C1 (Fig. 2). Jeffrey et al. (2019) reported that a water level drawdown of the permanent wetland after a hot and drying summer period exposed some of the permanent wetland sediments to oxidative conditions. This may have oxidised a portion of the labile sedimentary carbon pool prior to C1 sampling of the permanent wetland, therefore reducing the total CH_4 pool observed during C1 sampling. A lag time

(ranging from weeks to months) for recovery of the CH_4 pool post-drought has been observed in other systems (Boon et al., 1997) and also during lab-based experiments (Knorr et al., 2008; Freeman et al., 1992). Further, during C2 the return of macrophyte species *Nymphaea caspensis* most likely enhanced CH_4 gas transport from the rhizosphere to the floating chambers, as discussed in detail in Jeffrey et al. (2019). Therefore this combination of ~~This~~ drivers most likely ~~may~~ explain the higher CH_4 fluxes during C2 when the system and lilies had had sufficient time to recover, despite lower water column temperatures that would normally reduce microbial metabolism rates. This hypothesis is also supported by the shift of net positive redox potential of the permanent wetland during C1 (71.7 ± 65 mV), to a strong negative redox potential during C2 (-216 ± 42 mV) indicating that there was a time lag for reducing conditions to recover within the permanent wetland for C2. Further, although aquatic vegetation can facilitate root zone aeration therefore increasing sedimentary redox potentials, as no aquatic vegetation was present in the permanent wetland during C1, this suggests that water level drawdown was the main driver of redox conditions. This highlights the critical role of antecedent hydrological conditions and how dynamic weather oscillations of drought and floods (a common occurrence of many Australian wetland systems), strongly influence the redox potentials, soil geochemistry and ultimately CH_4 fluxes.

4.4 Implications and conclusions

~~Permanent wetland emissions account for the majority of~~Within the global wetland CH_4 budget, ~~however~~ both subtropical systems and southern hemisphere systems are poorly represented (Bartlett and Harriss, 1993;Bastviken et al., 2011) (Fig. 9). Further, the fluxes from seasonal wetlands are poorly constrained (Pfeifer-Meister et al., 2018) due to their intermittent nature and variability of intra-seasonal areal extent, which may compound why natural wetlands have the largest uncertainty of the global methane budget (Saunois et al., 2016;Kirschke et al., 2013). Although the temporal resolution of our study cannot be up scaled to realistic annual estimates, our high resolution sampling strategy provided insights to daily CH_4 flux rates revealing distinct differences between different vegetation types across the terrestrial aquatic wetland boundary. Our ~~seasonal~~ CH_4 emissions rates were at the low end of the scale of measurements made in southern hemisphere subtropical systems but within range of northern hemisphere subtropical systems of similar latitudes (Fig. 9).

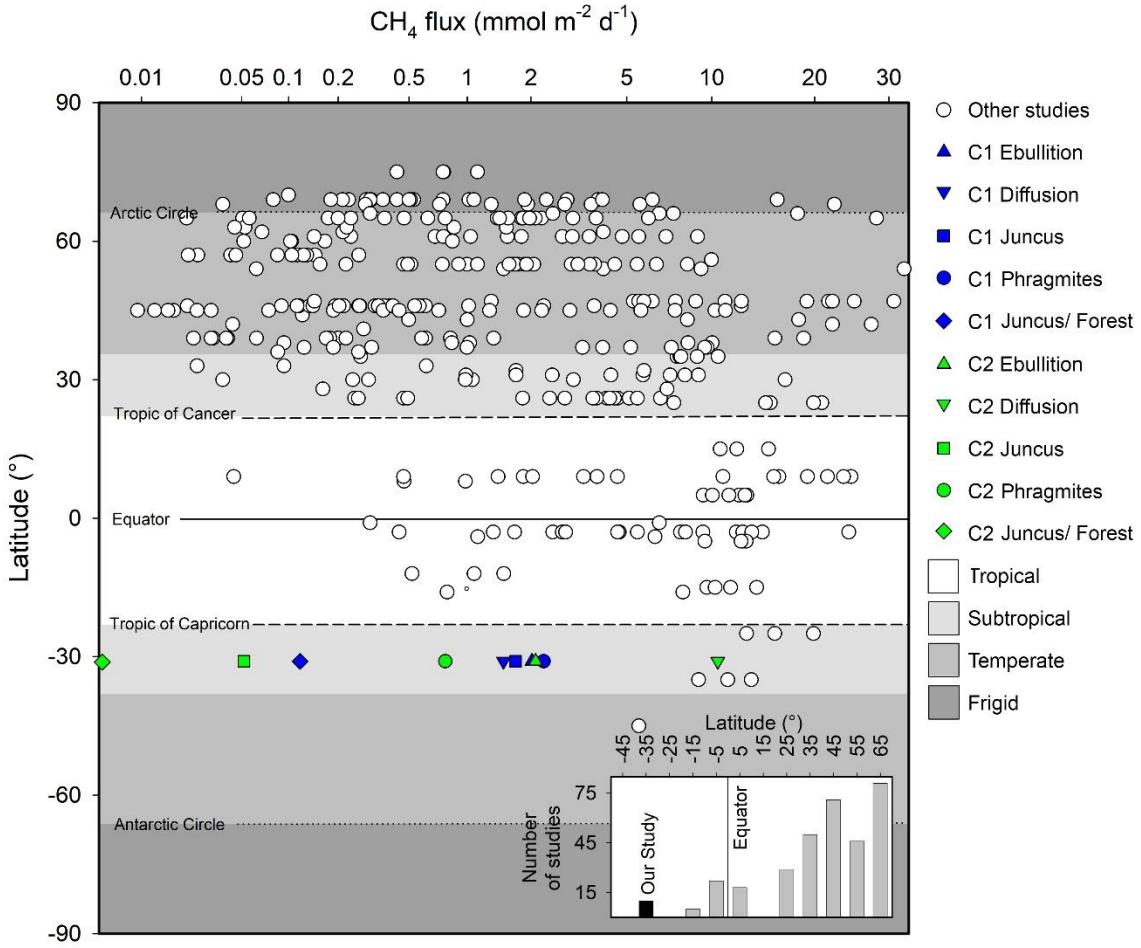


Figure 9. Summary of major CH_4 wetland reviews by Bartlett and Harriss (1993), Bastviken et al. (2011) and modelled fluxes by Cao et al. (1998) adapted from Jeffrey et al. (2019) highlighting latitudinal trends and bias from a variety of wetland systems. Inset figure highlights number of studies in these reviews by latitudinal increments of 10° poleward of the equator. Note: x axis scaled to highlight subtle differences between studies.

Although remediating degraded wetlands through re-flooding is a common technique to improve biodiversity, increase C sequestration and improve downstream water quality issues (Johnston et al., 2014;Johnston et al., 2004), our results propose a nuanced dilemma for land use managers, as wetland remediation~~storation~~ can potentially have net positive radiative forcing effects on the Earth's climate due to high rates of CH_4 production (Petrescu et al., 2015). This has also been shown to be particularly high during early remediation periods (Hemes et al., 2018). Our results suggest that seasonal wetlands emit less CH_4 on an areal basis

than permanent wetlands, yet carbon accumulation in these soils may be lower (Brown et al., 2019) ~~(Brown et al. (in publication))~~. Longer-term studies over annual cycles encompassing seasonal drivers and CH_4 fluxes would further test this hypothesis of the different drivers between seasonal and permanent wetland systems.

Our results also suggest that selective hydrological restoration of wetlands featuring sediments with abundant thermodynamically favourable terminal electron acceptors (i.e. Fe(III) or SO_4^{2-}) may be a (partial) biogeochemical solution (also suggested by Hemes et al. (2018)) to both remediate degraded sites whilst simultaneously mitigating some CH_4 emissions. When Fe(III) and SO_4^{2-} are abundant in anaerobic environments they provide preferential terminal electron acceptors for microbial metabolism and thus limit methanogenesis via competitive exclusion (Achtnich et al., 1995). However, high rates of sulphate reduction coupled with Fe reduction can also lead to the accumulation of metal sulphide minerals e.g. pyrite and AVS (Johnston et al., 2014). Under permanently saturated and low oxygen conditions, metal sulphides will steadily accumulate and remain relatively benign. However, if the saturated state of remediated sites cannot be maintained, AVS may react with oxygen resulting in undesirable production of acidity and low pH conditions. Therefore the remediation of wetlands for carbon storage should involve careful site selection to both limit CH_4 production and to avoid redox related geochemical by-products with detrimental environmental effects.

This study has highlighted how sediment geochemistry is intimately related to CH_4 production and consumption. While high sulphate and Fe(III) favour lower CH_4 production, sites featuring more reducing conditions and depleted sulphate and Fe(III) favour the highest CH_4 fluxes. Results reveal distinct differences between the areal CH_4 fluxes of four different eco-types located within a remediated subtropical Australian wetland and indicate high ~~seasonal~~ variability between campaigns. By combining novel and well established techniques we delineated several CH_4 pathways of both seasonal and permanent wetland sources (ebullition, diffusion and plant-mediated pathways) and linked these to hydrological~~seasonal~~ drivers. This provided evidence that soil geochemistry is an important factor to consider for wetland remediation in the context of CH_4 production and mitigation strategies. The CH_4 emissions results were comparable to other wetlands of similar latitudes and contribute important data for both the understudied southern hemisphere wetlands and seasonal subtropical wetland ecotypes.

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~~**References to add manually**~~

~~(Association et al., 1915)~~

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