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Interactive comment on "Application of pore water stable isotope method to characterise a wetland system" *by* Katarina David et al.

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Dear Reviewer, Thanks for the review and comments that have improved our manuscript. We have included a detailed response to the questions below in responses.

General Reviewer's Comment This review follows the assessment of Anonymous Reviewers 1 and 2 – this reviewer concurs with their suggestions and adds only the following comments. I must reject this paper due to serious concerns about the accuracy of porewater isotope analytical methods. If there is no clear confidence in the analytical isotopic results the subsequent modeling does not matter.

Response Thanks, it is acknowledged that the description of porewater isotope analytical methods was relatively brief. This section has now been improved and expanded to include additional details on the analytical method sampling technique. Section 3 provides more information on accuracy and confidence. This section has also has been updated based on comments from Reviewer 1 and 2.

General Reviewer's Comment This paper, if revised and resubmitted, further requires hard editing and a lot of trimming. Please conduct a thorough review for basic grammar and sentence structure. Check for imprecise or vague terminology usage. Please consider reducing the length – in many places there is unnecessary "filler text" (i.e. "International publications/ example : : : why not just say "research has shown: : : (refs). Remove a lot of the ancillary information (detailed lithology) that is not explicitly needed for your objectives of using pore water isotopes.

Response Thanks for the comments, further editing has been undertaken on this paper, and grammar and sentence structure checked. However, we respectfully disagree with the suggestion to trim the text. Our response is justified by Reviewer 1 who requested more ancillary information (detailed lithology), who for example requested that an additional cross-section be prepared to help with understanding the lithology. We have therefore added more information and additional cross-section in response to Reviewer 1 comments. We have reduced the length and removed the text which does not related to wetlands in the Introduction section. Please note some of the text is necessary to understand the background, and follows the response to Reviewer2. For example, the "international publications" is not a "filler text", the difference between the international and local literature is important as the swamp systems in Australia have formed under very different climate conditions compared to other swamps in the Northern hemisphere as discussed in Fryirs et al. (2014). This has resulted in different formation and evolution model for the upland swamps on sandstone in Eastern Australia. For all other items of discussion in the paper, the reviewer 3 comments were used to correct the text. The text in the manuscript has been reduced and edited as recommended by Reviewer.

General Reviewer's Comment - Method's section The entire Methods section, upon which this work hinges entirely, is insufficiently described or referenced. For example, page 7 lines 13-17 – no citations are give for this sampling methodology.

Response Thanks, this is acknowledged, and the entire Methods section and Section 3.1 has been considerably expanded and rewritten based on Reviewer's suggestion and suggestions from Reviewers 1 and 2 (please see below). For example, the citation is now provided for the sampling methodology (Wassenaar et al (2008) and Hendry et al (2015)).

"3.1 Fieldwork and sampling The fieldwork was undertaken during 2016 and 2017 with the swamps in a natural state and recovered from earlier wildfire in 2013. The first sampling event 24th to 25th May 2016 occurred following an extremely dry weather period of four months below the long-term average rainfall (BoM Lithgow Station 0630132, 900 m AHD, 13 km SW of the study area with 139 years of data records) for February to April (46.6 mm, 36.8 mm, 6.6 mm and 20.8 mm for each of the months). A total of 34 pore water samples and 5 surface and groundwater samples were collected. A repeat sampling on 25th to 26th October 2016 occurred after four months of above average rainfall from June to September (170.2 mm, 102 mm, 61.8 mm and 92 mm for each of the months). During October 2016 sampling event 14 pore water samples and 13 surface and groundwater samples were collected. Sampling on 30th May 2017 occurred under different climate conditions with both above and below average rainfall trend in the months preceding the sampling event. A total of 27 pore water samples and 6 surface and groundwater samples were collected in May 2017. The spatial depth resolution varied from 10 to 20 cm depending on the penetration of the corer. Figure 2 shows the variation in monthly long-term rainfall (139 years) and comparison with rainfall in 2016 and 2017. In total seven sediment cores were obtained by coring using a Russian D hand corer (40 mm diameter) to rock refusal (between 0.45 to 1.4 m), and three transects (CC, GG and GGSW) were prepared along the length of the swamps (Figures 3,4 and 5). The samples were geologically logged after extraction, by noting the lithology, grain size and roundness, matrix and colour. The hand cored holes were restored by returning soil material to the hole immediately after sampling. This was undertaken to ensure no change occurred in this endangered and protected ecological system as a result of sampling. The coring on CC transect was repeated in October 2016 at a distance of less than 0.5 m from the original hole. The coring locations were selected to represent the swamp stratigraphy from upstream to downstream and to provide a spatial coverage across the three swamps. In addition, three cored locations were selected such that they were adjacent to an existing piezometer (CCG1 on transect CC and GGEG2A and GGEG4 on GG transect). The purpose of this, in addition to determining the stable isotope profiles, was to enable comparison with the swamp groundwater measurements and to collect regional groundwater sample from the underlying sandstone aquifer where possible. Sediment cores were divided into subsamples of 10-20 cm length, were packed into Ziplock bags and kept in cool storage for later analysis of moisture content and organic matter content. The samples for pore water analysis were temporarily double packed in ziplock bags by minimising the airspace in the bag, stored in the cooled ice box in accordance with the sampling protocol developed by Wassenaar et al (2008) and further improved by Hendry et al (2015). The same afternoon after collection, samples were packed in tough high-grade food storage plastic bags with air extracted, double sealed, separately stored in an additional plastic bag and were kept at a temperature of 4°C to prevent evaporation. Vacuum packing was required to minimise atmospheric moisture contamination. Storage time for samples after collection was 3 days in the cool environment (4°C) before they were analysed. All isotopic field controls during sampling and analysis were implemented; this included: quick storage in tough plastic bags, immediate double bagging during collection and vacuum packing the same afternoon with storage at 4°C. Swamp groundwater was sampled directly from the cored hole, field parameters were measured immediately (pH, EC, DO, temperature) and samples field filtered (0.45 micron). This was repeated for all three sampling events; however, some bores were dry and some not accessible. Swamp groundwater and regional groundwater from existing piezometers (CCG1, GGEG2, GGEG5x, GGEG5 and GGSWG1) was gauged and sampled by bailing three volumes and then the same procedure was followed as for the cored holes. Swamp and sandstone piezometers were installed by the mining company prior to our research study. The swamp piezometers were installed to the base of the swamp, where auger refusal did not allow further progress. The typical installation depth was around 1 m to 1.3 m. To minimise disturbance of the swamp, all swamp piezometers were installed by manual coring an 80 mm diameter hole to refusal and pushing the slotted 50 mm diameter PVC tube into the hole. A full PVC casing was attached to the top of the pipe. The piezometer installed in the sandstone is 10.7 m depth with 50 mm diameter PVC casing that includes a 3-meter length of screen at the bottom of the hole. The piezometer installation was extended with casing to the top. The top was sealed by grout, and a steel monument constructed for protection. Surface water samples were collected at the downgradient end of the swamp but also at one upgradient location (GGES2) where this was possible. For this study ANSTO provided event based δ18O and δ2H data for precipitation from Mt Werong for the period covered in this research. Mt Werong (Hughes and Crawford, 2013) is located around 70 km south of this research site, however, within the same climatic environment and at similar elevation to the investigated swamps."

Reviewer's Comment -Section 3.2 needs to be entirely re-written – the analytical descriptions are incoherent. You need to give the delta values of all calibration standards. There is insufficient detail given to give confidence in the results.

Response Thanks, Section 3.2 was considerably expanded and fully re-written with additional detailed information on the sample analysis, secondary standards used along with their delta values and primary standard and reproducibility of the results. Please see below for fully revised Section 3.2.

"3.2 Sample analysis The swamp sediment samples were analysed for δ18O and δ2H by H2O(water)-H2O(vapour) porewater equilibration (Wassenaar et al, 2008; Wassenaar and Hendry, 2008) and off-axis ICOS. The Los Gatos (LGR) water vapour analyser (WVIA RMT-EP model 911-0004) located at UNSW, Australia was used for sample analysis. All samples and standards have been stored at 4°C prior to the analysis, and all have been allowed the same time on the laboratory bench in the temperature controlled laboratory. All samples have followed the same treatment. Samples (n=34, 14 and 27 for each of the sampling events) were prepared in the lab by transferring the sample to a tough clean zip lock bag. The 1 L sample bags were inflated with dry air and left on the laboratory bench at the controlled temperature for a period of between 17 to 24 hours to allow vapour equilibration. The timing of vapour equilibration is dependent on the compactness of the core sample, whether it is broken in pieces and if it is unconsolidated (Wassenaar et al, 2008). The timing varies for different geologic materials and must be determined experimentally (Hendry et al, 2015) for each material. Work by Wassenaar et al (2008) and David et al (2015) indicates that for compact, low permeability, consolidated materials around 3 days is required for core samples equilibration. The samples in this research are broken down, unconsolidated, saturated and high permeability therefore shorter equilibration time is considered justified. In addition, the optimal equilibration time in this research is considered to be achieved when headspace water content of 23,000 to 28,000 ppm H2O was measured in the bag. This headspace water content is important for accurate sampling (Hendry et al, 2015). Once the sample has reached complete isotopic equilibrium, the vapour was collected by perforating the bag containing sample with a sharp needle and transferring it directly from the bag to the LGR vapour analyser. The connection between the needle and the LGR inlet fitting was via the flexible, thick wall, soft plastic tube, fitted tightly with fittings on both sides. The tight fitting was required to limit the atmospheric air ingress into the LGR. The contamination by atmospheric air is considered negligible. This is based on the measurement of ambient air moisture of around 14,000 to 15,000 ppm, while the headspace for samples had a range of 23,000 to 28,000 ppm H2O. The analysis of the vapour sample was undertaken along with the standards (1 ml) prepared in the similar manner to the core samples. The equilibration time for standards was around 20 minutes. A new set of three standards (one primary and two secondary) were run after every third sample. It is not possible to sample the headspace repeatedly, as 1 L headspace only allows sampling once. Repeated inflating with dry air results in incorrect readings. Following each set of samples and standards, the analysis was suspended for a period of around 10-15 minutes, to allow the LGR to reach the stable atmospheric air readings and reduce any memory effect. The linear regression was used between δ18O and δ2H vapour values for standards (expressed as water using the fractionation factor) and liquid standards. The regression was used to calibrate the vapour results for samples. Calibration was undertaken with two secondary δ18O and δ2H standards (Los Gatos 2A -16.14‰ δ18O and -123.6‰ δ2H and 5A -2.80‰ δ18O and 9.5‰ δ2H) and normalised with one primary V-SMOW2 standard run during the analysis. LGR standards were stored in accordance with the protocol, at 4°C, and after usage the top was fully sealed to prevent any exchange with the atmosphere. The use of LRG as secondary standards has been used in other studies such as Penna et al (2010) on reproducibility and repeatability of the laser absorption spectroscopy measurements and was found that LGR standards performed satisfactory. Replicate sample analyses using direct vapour equilibration method (mean difference of 6 samples) indicate reproducibility of results in our research within 0.68‰ δ2H and 0.04‰ δ18O uncertainty. Reported instrument precision of 0.5‰ δ2H and 0.15‰ δ18O over 10 seconds and drift of 0.75‰\$$\delta$2H and 0.3‰ δ18O over 15 minutes was minimised by correcting the readings. The data set for each sample was corrected for drift by back correction of standards within each set and then applying the same regression analysis to the relevant samples. For each sample the standard deviation and instrument drift error were calculated. Following the standard operating procedures, the precision in this research was 0.6‰ δ2H and 0.23‰ δ18O over 70 seconds. Hendry et al (2015) report the analytical precision of the vapour equilibration method (±0.40‰ for δ18O and ±2.1‰ for δ2H) to be comparable or better than physical extraction from cores using high-speed centrifugation, cryogenic micro-distillation, azeotropic and microwave distillation or isotope ratio mass spectrometry (IRMS) based direct equilibration methods as discussed in Kelln et al (2001). Based on work by Allison and Hughes (1983) and

Raves and Woods (1990), the direct vapour equilibration method is better than results obtained by physical and chemical extractions (Hendry et al, 2015). This is achieved through limiting fractionation losses by short storage time, single procedure once the samples are in the laboratory and use of standards and water isotopic data as a cross check. The advantage of the method is that it is particularly suitable for samples with high moisture content which shortens the equilibration time. Water samples (surface water, swamp water and groundwater, n=21) were analysed for δ18O and δ2H by the off axis- integrated cavity output spectrometry (OC-ICOS) technique using an LGR analyser located at UNSW Australia. Two secondary standards and V-SMOW2 standard were used to calibrate and normalise the samples. Gravimetric water content (ASTM D2974-14, 2014 and ASTM D2216-10, 2010 was measured by weighing the sample (n=70), drying at 100°C for 24 hours and re-weighing (Reynolds, 1970). The 100% gravimetric water content relates to water holding capacity and organic content of the material. The analysis was undertaken at the School of Mining Engineering, UNSW Australia. Organic matter content was measured by loss on ignition method (LOI), by weighing (following initial drying at 100°C) and drying in furnace oven at 550°C (Heiri et al, 2001). The analysis was conducted at the Water Research Laboratory, UNSW Australia. Precipitation samples were analysed at the ANSTO Environmental Isotope Laboratory using a cavity ring-down spectroscopy method on a Picarro L2120-I Water Analyser (reported accuracy of ±1.0, ±0.2‰ for δ2H and δ18O respectively). The lab runs a minimum of two in-house standards calibrated against VSMOW/VSMOW2 and SLAP/SLAP2 with samples in each batch. For simple statistical analysis of moisture content, precipitation and organic matter content, an XLStat software package (XL-Stat, 2017) was used. The Barnes and Allison (1988) model was implemented for this project using R (R core team, 2013), to investigate the evaporative losses based on isotopic composition of water. For the Barnes and Allison (1988) model volumetric water content was calculated from the measured gravimetric water content and bulk density. Bulk density was obtained from known lithology and measured data (Cowley et al, 2016) and porosity data from a swamp study by Walzsak et al (2002). To estimate effective liquid diffusivity of isotopes, tortuosity values were obtained from the literature (Maidment, 1993; Shackelford and Daniel, 1991; Barnes and Allison, 1988)."

General Reviewer's Comment I have grave doubts about the results for porewater stable isotopes and suspect the trends (or differences) between samplings may be due to evaporation artifacts. What was neglected to mention is the time lapsed between core sample collection (coring, stored in Ziplok) and the sample preparation (ie inflation) for isotope analysis. Was this storage hours, weeks, days? Ziplok bags are only good for a couple of days before evaporative loss occurs.

Response Thanks, the updated Section 3.1 and 3.2 explains how samples were collected and prepared and how any potential evaporation was avoided during sampling, storage and preparation for and during the analysis. Samples were collected in accordance with the methods reported in Wassenaar et al (2008), they were stored at 4°C for three days after collection (coring) and were then prepared following methods of Hendry et al (2015), which improved on methods developed by Wassenaar et al (2008). The use of clear Ziplock bags, Isopack and clear bags for storage of samples for pore water analysis has been found (Hendry et al 2015) to result in evaporation loss and isotopic fractionation after 10-15 days after sample collection. In our research, we stored samples for only 3 days before analysis, in tough plastic bags (rather than Ziplock bags) sealed twice on each side after extracting air. Additionally, each vacuum packed (packed in the tough high-grade food plastic bag with air extracted) and double sealed sample was placed in an additional tough plastic bag with air space removed. Therefore, it is improbable that the results were artefacts of the storage process.

General Reviewer's Comment If variable periods of times elapsed for the samplings, the samples could have been subjected to differential evaporative loss (ie why is the groundwater isotopic composition constant). There were no gravimetrics controls used, nor isotopic field controls to give confidence in this method (at least as it is described).

Response We agree with the reviewer that different time periods were subject to different evaporation losses. This is observed in difference between the samples collected in May 2016 after dry and warm period compared to October 2016 after wet and cool period. All isotopic field controls during sampling and analysis were implemented; this included: quick storage in tough plastic bags, immediate double bagging during collection, vacuum packing with double seals in tough plastic food grade bags and double sealing. It is assumed that Reviewer relates gravimetric control to the weight of sample taken in the field. In the field the sample size was not weighted, as this was not considered important. What was considered important was that there was enough sample which will have a minimum of 5% moisture content to allow vapour equilibration method to be used. Water samples were also collected and analysed for cross refence with pore water. The isotopic field controls were added to Section 3.1 of the manuscript.

General Reviewer's Comment The Los Gatos "standards" used are not certified RMs, and should never be used for calibration. They have been revised at least 5 times due to improper storage (at LGR) in the past years.

Response: We used V-SMOW2 as primary reference standard, and Los Gatos standards as secondary. We are aware that there is SLAP which is the secondary standard distributed by IAEA, but have not used it. LGR standards in our lab were stored properly, at 4°C, and after usage the top was fully sealed to prevent any exchange with the atmosphere (opened once prior to this analysis). The use of LRG as secondary standards has been used in other studies such as Penna et al (2010) which undertook a study on reproducibility and repeatability of the laser absorption spectroscopy measurements and found LGR standards to work satisfactorily. In addition, the water samples analysed separately in a different LGR apparatus with in house standards and V-SMOW2 as the primary standard, returned the δ2H and δ18O similar to the pore water results, confirming the accuracy and calibration. Text has been added to manuscript in Section 3.1 to explain the LGR storage protocol was followed in the lab.

Reviewer's Comment SMOW / VSMOW do not exist – VSMOW2 does. Which was it?

Response It was V-SMOW2, this is now corrected in the manuscript.

Reviewer's Comment The introduction is too long – suggest deleting lines Page 1, lines 12-18 (unrelated to wetlands)

Response The text has been removed from Page 3, lines 12-18 as suggested.

Reviewer's Comment Continuous line numbering would have been useful for reviewers.

Response: This manuscript was prepared on the template suggested by HESS, and conversion to pdf is outside of the control of Authors of this paper.

Reviewer's Comment Many places have a "the" or "a" added or missing. (i.e. title, Page 3 line 1, etc.).

Response Thanks, "a" and "the" were added or removed, as suggested in the title and Page3 line 1, and at other places in the manuscript.

Reviewer's Comment Page 1 line 4, not climate change (aka CO2)-> rather, paleoclimate.

Response Thanks, this was reworded to paleoclimate in manuscript.

Reviewer's Comment Page 4, line 8 "Following such extreme setttings: : : (what does that mean?)

Response: Thanks, this has been clarified as "long dry periods"

Reviewer's Comment Page 4, line 16-20 – please rewrite the objectives in a clearer manner. A hypothesis would be a good place to start.

Response: Line 16-20 related to objectives has been rewritten and hypothesis added. The paragraph now reads: "The objective of this research was to improve understanding of intact swamps under natural conditions by characterizing the sediments, waters and organic materials and developing the conceptual model for the swamp system. We hypothesise that groundwater is an important contributor to the swamp water balance and for this we investigate for the first time using direct equilibration method the vertical profiles of stable δ18O and δ2H isotopes of pore water within the swamp. Groundwater contributions to pore water could be determined by comparison of end members stable isotope values. A conceptual model of the swamp water cycle was developed by combining stable isotope results with information from sediment lithology logs, organic and carbon content of sediments. "

Reviewer's Comment Page 8 line 25-26 - IRMS cannot be an LGR analyser!

Response: Thanks, this typing error is now corrected in manuscript to Off axis- integrated cavity output spectrometry (OA-ICOS).

Reviewer's Comment Figure 6 caption error and use of d18O/d2H – the slash suggests 'or' when you mean'and'. Superscripts missing. Suggest using the same Y-axis scaling on all figures. Why are the symbols for the same thing different in each panel? Very confusing to look at and compare!

Response Thanks, the caption has been changed to say δ18O and δ2H and superscripts added to Figure 6. Same y- scaling has been used on all figures as suggested, and all symbols for the same sample types are the same in each panel as recommended by the Reviewer3. Please see attached Figure 6 (now Figure 7).

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-237, 2018.

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Discussion paper

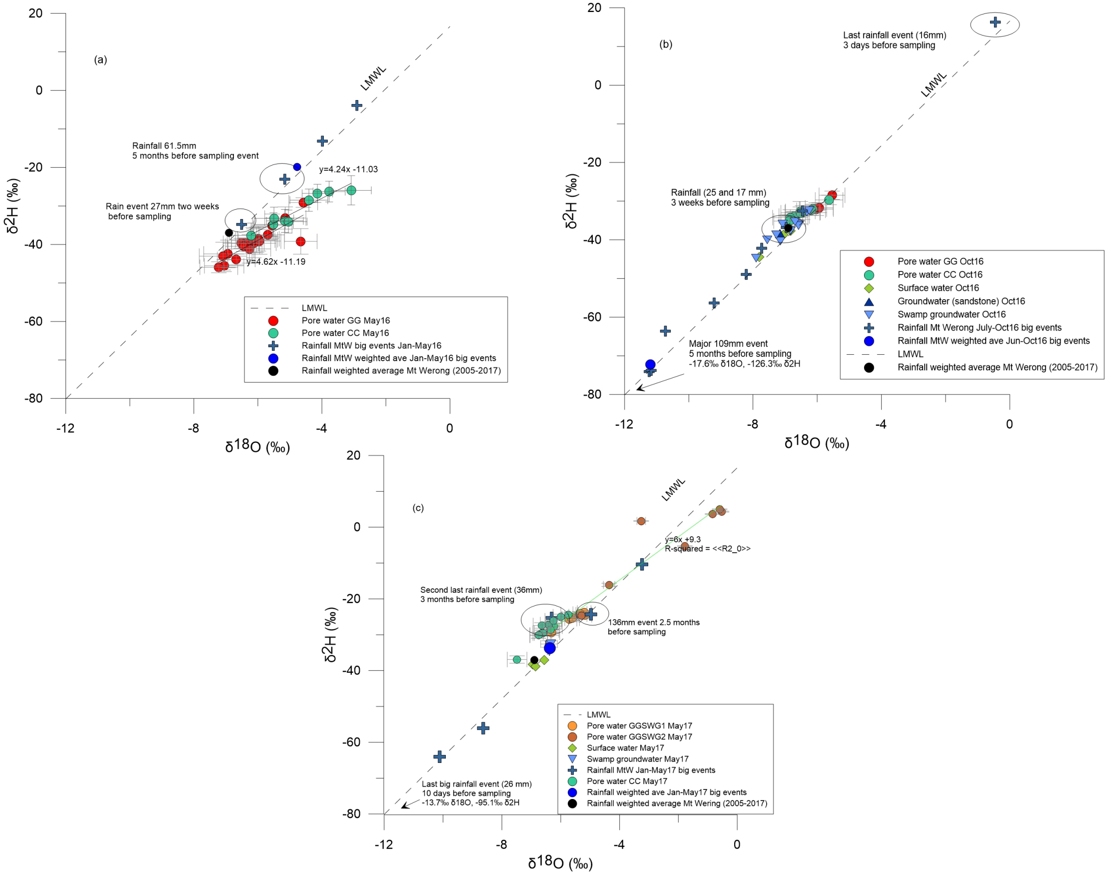

Fig. 1.

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