

Application of the pore water stable isotope method and hydrogeological approaches to characterise a wetland system

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Abstract

Three naturally intact wetland systems (swamps) were characterized based on sediment cores, analysis of surface water, swamp groundwater, regional groundwater and pore water stable isotopes. These swamps are classified as temperate highland peat swamps on sandstone (THPSS) and in Australia they are listed as threatened endangered ecological communities under State and Federal legislation.

This study ~~is the first application of~~ the stable isotope direct vapour equilibration method in a wetland, aiming at quantification of the contributions of evaporation, rainfall and groundwater to swamp water balance. This technique potentially enables understanding of the depth of evaporative losses and the relative importance of groundwater flow within the swamp environment without the need for intrusive piezometer installation at multiple locations and depths. Additional advantages of the stable isotope direct vapour equilibration technique include detailed spatial and vertical depth profiles of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, with good accuracy comparable to other physical and chemical extraction methods.

Depletion of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in pore water with increasing depth (to around 40-60 cm depth) was observed in two swamps but remained uniform with depth in the third swamp. Within the upper surficial zone, the measurements respond to seasonal trends and are subject to evaporation in the capillary zone. Below this depth the pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signature approaches that of regional groundwater indicating lateral groundwater contribution. Significant differences were found in stable pore water isotope samples collected after dry weather period compared to wet periods where recharge of depleted rainfall (with low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) was apparent.

The organic rich soil in the upper 40 to 60 cm retains significant saturation following precipitation events and maintains moisture necessary for ecosystem functioning. An important finding for wetland and ecosystem response to changing swamp groundwater conditions (and potential ground movement) ~~is that~~ basal sands are observed to underlay these swamps, allowing relatively rapid drainage at the base of the swamp and lateral groundwater contribution.

Based on the novel stable isotope direct vapour equilibration analysis of swamp sediment, our study identified the following important processes: rapid infiltration of rainfall to the water table with longer retention of moisture in the upper 40-60 cm

and lateral groundwater flow contribution at the base. This study also found, that evaporation estimated using stable isotope direct vapour equilibration method is more realistic compared to reference evapotranspiration (ET). Importantly, if swamp discharge data were available in combination with pore water isotope profiles, an appropriate transpiration rate could be determined for these swamps. Based on the results, the groundwater contribution to the swamp is a significant, and perhaps dominant component of the water balance. Our methods could complement other monitoring studies and numerical water balance models to improve prediction of the hydrological response of the swamp to changes in water conditions due to natural or anthropogenic influences.

1 Introduction

Stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) have been widely used to understand groundwater and surface water interaction and recharge processes in aquifer systems (Barnes and Allison, 1988; Cuthbert et al, 2014). Although less common than liquid water isotope studies, pore water (vapour) stable isotope techniques have been applied to investigate groundwater flux and interpret the paleoenvironment (Hendry et al, 2013; Harrington et al, 2013), determine slope runoff contribution to groundwater (Garvelman et al, 2012) and characterize multi-layered sedimentary sequences (David et al, 2015). Pore water stable isotope analysis was less common due to sampling difficulties (Soderberg et al, 2012) and high cost (Harrington et al, 2013), until advances in laser spectroscopy improved the speed and accuracy of the analysis (Hendry and Wassenaar, 2009; Hendry et al, 2015).

Examples of wetland research indicate that it remains challenging to quantify some components of the water balance (Bijoor et al., 2011), since only a few studies have investigated the groundwater contribution (Hunt et al., 1998). The significance of groundwater in maintaining ~~the swamp~~ the swamp ecosystem function has been discussed in the literature (Chang et al, 2009; Kaller et al, 2015). In Australia, swamp studies have evaluated geomorphology (Fryirs et al, 2016; Cowley et al, 2016), management (Kohlhagen et al, 2013), the relationship between vegetation and groundwater (Hose et al, 2014), processes that result in denudation and sedimentation in the headwaters of the swamps (Prosser et al, 1994), natural and anthropogenic vegetation change in swamps (Bickford and Gell, 2005) and the impact of mining subsidence (CoA, 2014b). However, there is limited literature on the importance of groundwater storage, flow and which water source contributes to maintain moisture in swamp systems.

The temperate highland peat swamps on sandstone (THPSS) swamps in Eastern Australia are endangered ecological communities with endemic flora and fauna that are dependent on water balance. The direct influences on the water regime of these swamps are changes in weather patterns, natural storm activity (Smith et al. 2001), fire (Middleton and Kleinebecker, 2012; CoA, 2014a) and the effects of mining subsidence (CoA, 2014b). Ecologically, the THPSS swamps are sensitive to changing swamp moisture content (CoA 2014a; Young, 2017), and the importance of groundwater in these systems has been discussed by Eamus and Froend (2006), Fryirs et al (2014) and Hose et al (2014).

There is direct and indirect evidence that the T~~H~~P~~P~~H~~S~~S swamps (Newnes Plateau shrub swamp) are mostly saturated, including vegetation patterns, specific species of plants, piezometer records (Benson and Baird, 2012) and spring discharge (Johnson, 2007). Maintaining groundwater levels is necessary for the health for such a wetland system (Clifton and Evans, 2001).

Despite the awareness of these factors, there is limited research to predict hydrogeological changes in swamps and ecological response under changing water conditions (Mitsch and Gosselink 2000; Cowley et al, 2016). Furthermore, studies describing the impact of environmental changes on swamp ecology are rare and there is insufficient understanding of natural variation in swamp ecology over time (CoA, 2014a). Although groundwater is often assumed to be important for the sustainability of wetlands and swamp ecosystems, very little is known on how these systems would respond to changing swamp groundwater and regional groundwater conditions. The existing literature recognizes that natural variation in swamp ecology is not well understood given the complexity and interaction of swamp groundwater, groundwater and surface water.

Long drought periods in Australia result in temporary drying of water bodies, pooling of water and reduction in baseflow contribution to wetlands (Lake, 2003). Following such long dry periods, the rainfall may not be sufficient for a swamp to recover its original condition (Bond et al, 2008; Middleton and Kleinebecker, 2012). For example, Smith et al. (2001) report loss of swamps in Africa and Australia as a result of climate change. Vegetation removal, drainage of swamp and undermining are known to be critical human impacts (Kohlhagen et al, 2013; Valentin et al, 2005). As such, mining and urbanisation have degraded and considerably damaged the T~~P~~H~~PSS swamps (CoA, 2014b), although the actual impact often cannot be quantified due to limited baseline and monitoring data (Paterson, 2004). However, it is generally recognized that rock fracturing, changes in elevation gradient and catchment conditions can compromise the stability and integrity of these swamps (CoA, 2014b).~~

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 is connected to the regional groundwater system.

~~Therefore, we~~Therefore, we investigate, for the first time using direct equilibration method, the vertical profiles of stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopes of pore water within the swamp. We then compare those to stable isotopes of regional groundwater, rainfall and surface water as endpoint members. Supported by sediment lithology logs, organic and carbon content of sediments these stable isotope results enabled the development of a conceptual model of the swamp water cycle.

2. Site description

The research site is located west of Sydney, NSW, Australia, in the World Heritage listed Blue Mountains on the Newnes Plateau (**Fig. 1**) between Lithgow and Blue Mountains local government areas. The elevation of the plateau ranges from 1000-1200 m Australian Height Datum (mAHD).

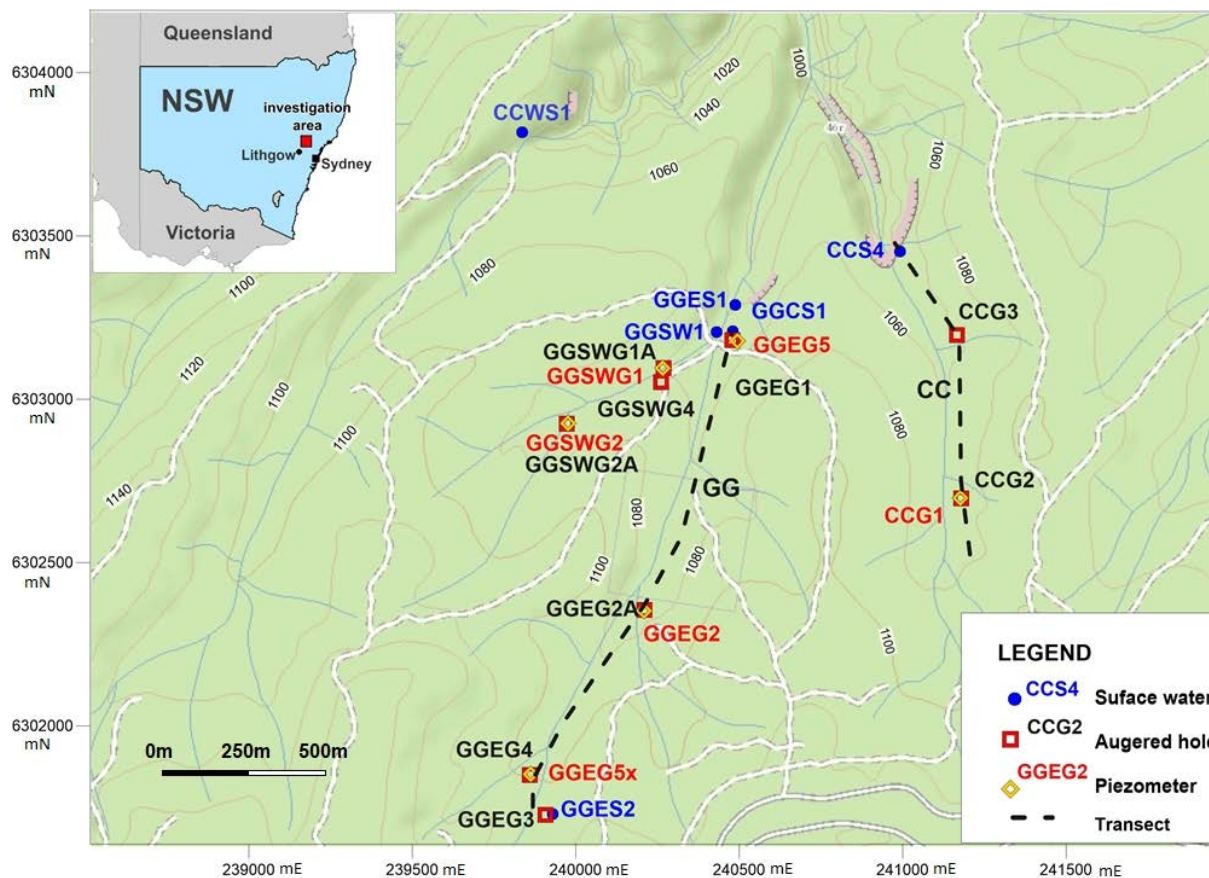


Figure 1: Map of selected Newnes Plateau swamps with location of samples and transects.

The Triassic Narrabeen Sandstone outcrops over most of the study area. It comprises mainly quartzose sandstone and minor claystone and shale (Yoo et al, 2001). The swamps on the Newnes Plateau are classified as shrub swamps (OEH, 2017) based on the dominant shrub ecological community, and they occur at the highest elevation of any sandstone-based swamp in Australia. These swamps occur in low slope headwaters of the Newnes Plateau as narrow and elongated sites with impeded drainage (OEH, 2017) and are also classified as TPPHSS belonging to both headwater and valley infill types (CoA, 2014a). Mapping by Keith and Benson (1988) and Benson and Keith (1990) indicates that the shrub swamps cover 650 ha of land on the Newnes Plateau, with the largest swamp being 40 ha and average size less than 6 ha. Keith and Myerscough (1993) relate the swamps to other upland swamps in the Sydney Basin in terms of biogeography. However, the difference from other TPPHSS is the presence of a permanent water table (Benson and Baird, 2012).

The three swamps selected: identified as CC (swamp area 7 ha, catchment area 150 ha), GG (swamp area 11 ha, catchment area 190 ha) and GGSW (swamp area 5 ha, catchment area 57 ha), are in the upper Carne Creek catchment (**Fig. 1**). Carne Creek is a tributary of the Wolgan River (catchment area 5310 ha) that ultimately flows to the Hawkesbury River and Pacific Ocean. The three swamps selected thus have a total area approximately 0.043% of the Wolgan River catchment. Except for

the headwaters including these swamps, the Wolgan River has been designated part of the Colo Wild River area recognizing substantially unmodified conditions and high conservation value (NSW Government, 2008). The swamps in this study are located to the east of current underground mining operations, with coal extraction currently occurring on the western side of the GGSW and GG swamps though not directly below these swamps. The swamps are elongated with gentle gradient and typically terminate with a sandstone rockbar. The swamp groundwater level responds rapidly to rainfall recharge (Centennial Coal, 2016) and there is indication that swamp systems are fed by lateral groundwater inflow (Benson and Baird, 2012). Further indirect evidence for regional groundwater interaction with swamp sediments and long-term saturation are the consistently stable swamp groundwater levels over time (Centennial Coal, 2016). Chalson and Martin (2009) undertook radiocarbon dating on pollen from a swamp on the Newnes plateau and found that the calibrated ages were 11,000 to 7,500 years (sampling depth 55-90 cm) and decreasing to 1,800 years at 40 cm depth. These ages support the existence of the swamps during the early wetter and warmer Holocene, through to seasonally variable climate in the period from mid to late Holocene (Allen and Lindsay, 1998). Given the seasonality of rainfall events, groundwater interaction must have existed through the mid and late Holocene to enable the swamp survival during dry periods.

Two sedimentary formations underlay the Newnes Plateau swamps: the Burrallow Formation and the Banks Wall Sandstone. The Burrallow Formation underlies the upper headwater part of the swamps and comprises of an interbedded coarse-grained sandstone sequence with frequent fine-grained, clay-rich sandstone, siltstones, claystones and shales. The thickness of Burrallow Formation ranges from around 40 m in the upgradient part of the swamps but is absent in downgradient parts of the swamps. Banks Wall Sandstone typically forms the base of lower parts of most swamps (McHugh, 2014).

Information on the natural groundwater regime in the swamps is very limited (CoA, 2014). It is generally considered that the sandstone underlying the swamps provides the barrier to water loss due to its relatively low permeability (CoA, 2014). However, in some cases, joints and bedding planes within sandstone can provide recharge to swamps (Coffey, 2008). NSW DP (2008) considers that headwater swamps, such as the ones described in this study, are likely to be perched above the regional water table. CoA (2014) indicates that regional groundwater in those swamps can interact with the swamp system, but where this occurs the connection is ephemeral as it is dependent on the perched aquifer. The groundwater residence time is short, and the water is fresh. Information available to date suggests that the dominant source of water to Sydney Basin (headwater) swamps is rainfall and run-off recharge (NSW PAC, 2009).

The climate on the Newnes Plateau is temperate with higher rainfall in November to March and lower rainfall from April to October. Average yearly rainfall at the closest long term meteorological station in Lidsdale (Bureau of Meteorology (BoM) Station SN63132, 12 km west of the study area) is 765 mm (890 mAHD) and 1270 mm at Mt Wilson (BoM Station 63246 21 km south-east (SE) of the study area) (1010 mAHD). The temperature varies from an average 19.6°C in summer to 5.8°C in winter (Lidsdale).

3. Methods

3.1 Fieldwork and sampling

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 SN63226, 900 m-AHD, 13 km SW of the study area with 139 years of data records) for February to May (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, 3 surface and 3 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.

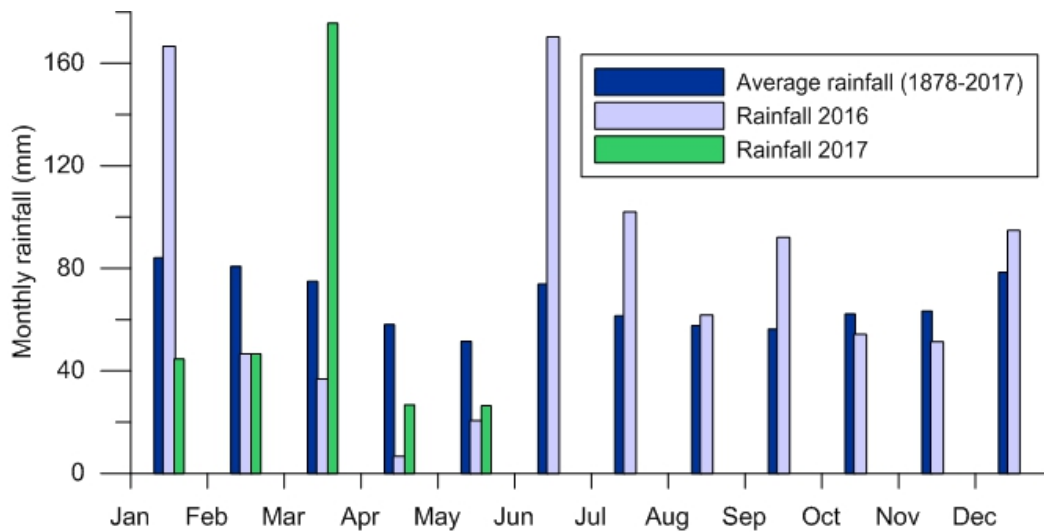


Figure 2: Long term average monthly rainfall at Lithgow station (Bureau of Meteorology Station No. 063226) compared to rainfall during 2016 and 2017.

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 (**Fig 3,4 and 5**). 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 to 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 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 from the underlying sandstone aquifer where possible.

Sediment cores were divided into subsamples of 10-20 cm length, packed into Ziploc 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 Ziploc 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 use of clear Ziplock bags for storage of samples for pore water analysis has been found (Hendry et al 2015) to result in evaporation loss and isotopic fractionation only after 10-15 days after sample collection. The same afternoon after collection, samples ~~were packed~~ 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 4°C to prevent evaporation. Vacuum packing was required to minimise atmospheric moisture contamination. 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. Storage time for samples after collection was 3 days in the cool environment (4°C) before they were analysed.

Swamp groundwater was sampled directly from the cored hole and field parameters were measured immediately (pH, electrical conductivity (EC), dissolved oxygen (DO), temperature). 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 the~~ as the cored holes. Swamp and sandstone piezometers were installed by the mining company prior to our research study. Swamp piezometers were installed to the base of the swamp, where auger refusal did not allow further progress. The typical installation depth is 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 sandstone piezometer is 10.78.5 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 the Australian Nuclear Science and Technology Organisation (ANSTO) provided event based $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 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.

3.2 Sample analysis

The swamp sediment samples were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by $\text{H}_2\text{O}_{(\text{water})}$ - $\text{H}_2\text{O}_{(\text{vapour})}$ pore water 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 [University of NSW \(UNSW\)](#), 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 during preparation and 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 samples to a tough Ziploc bag. The 1 L sample bags were inflated with dry air and left on the laboratory bench within the controlled temperature for a period of between 17 to 24 hours to allow vapour equilibration. Timing of vapour equilibration is dependent on 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 H_2O 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 a 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 during sampling 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 H_2O .

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 based on literature and air moisture (Wassenaar et al, 2008). 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 using this technique, as 1 L headspace only allows sampling once (60-90 seconds). Repeated inflating of the same sample 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. Linear regression for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was established between the liquid values for standards and raw headspace vapour (fractionation factor at 25°C) readings for the same standards. Regression was used to calibrate the vapour results for samples. Calibration was undertaken with two secondary $\delta^{18}\text{O}$ and $\delta^2\text{H}$ standards (Los Gatos 2A -16.14 ‰ $\delta^{18}\text{O}$ and -123.6 ‰ $\delta^2\text{H}$ and 5A -2.80 ‰ $\delta^{18}\text{O}$ and 9.5 ‰ $\delta^2\text{H}$) and normalised with one primary

VSMOW/VSMOW2 standard run during the analysis. LGR standards were stored in accordance with the protocol, at 4°C, and ampules were fully sealed to prevent any exchange with the atmosphere. The use of LGR standards 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 satisfactorily.

- 5 Replicate sample analyses using direct vapour equilibration method (mean difference of 6 samples) indicate reproducibility of results in our research within an uncertainty of 0.68 ‰ for $\delta^2\text{H}$ and 0.04 ‰ for $\delta^{18}\text{O}$. Reported instrument precision of 0.5 ‰ $\delta^2\text{H}$ and 0.15 ‰ $\delta^{18}\text{O}$ over 10 seconds and drift of 0.75 ‰ $\delta^2\text{H}$ and 0.3 ‰ $\delta^{18}\text{O}$ over 15 minutes was minimised by correcting the readings. The data set for each sample was corrected for drift by back correction using standards within each set and then applying the same regression analysis to the relevant samples. For each sample the standard deviation and
10 instrument drift error were calculated. Following the standard operating procedures, the precision in this research was 0.6 ‰ for $\delta^2\text{H}$ and 0.23 ‰ for $\delta^{18}\text{O}$ over 60 seconds.

- Hendry et al (2015) report the analytical precision of the vapour equilibration method (± 0.40 ‰ for $\delta^{18}\text{O}$ and ± 2.1 ‰ for $\delta^2\text{H}$) 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
15 methods as discussed in Kelln et al (2001). Based on work by Allison and Hughes (1983) and Revesz and Woods (1990), the direct vapour equilibration method precision is also better than for methods obtained by chemical water 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.

- Water samples (surface water, swamp groundwater and regional groundwater, n=21) were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by the
20 off axis- integrated cavity output spectrometry (OC-ICOS) technique using an LGR analyser located at UNSW Australia. Two secondary standards and VSMOW/VSMOW2 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 sediment samples (n=70), drying at 100°C for 24 hours and re-weighing (Reynolds, 1970). 100% gravimetric water content relates to water holding capacity and organic content of the material. The analysis was undertaken at the School of Mining
25 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.

- The vapour equilibration method is sensitive to presence of volatile organic compounds (VOC) in samples (Millar et al, 2018) and may require spectral correction post analysis, however usually the presence of these hydrocarbons is not known (Hendry et al, 2015). There are limited studies related to quantification of VOC in peat (Mezhbor and Bonn, 2014) and impact of organic matter on isotopic composition (Orlowski et al, 2016). For water samples, the LGR's post analysis software automatically applied check for spectral interference. Similar approach was reported by Millar et al (2018), Schultz et al (2011) and Orlowski et al (2018). There was no evidence of spectral contamination. However, this analysis was not possible for vapour analysis of soil samples due to the different processing method. The similarity between the isotopic
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composition of water and vapour collected from the same horizon suggests a strong interaction between groundwater and porewater; as the groundwater analyses show no evidence of VOC contamination, there is no reason to suspect that the porewater samples would contain concerning levels of VOCs despite the high peat organic content. Furthermore, in one of the rare VOC quantification studies on peat, Mezhibor and Bonn (2014) found that peat had mean concentration of isoprene and acetaldehyde (VOCs characteristic for natural plant organic emission) up to 0.26 ppb. The ecosystem in their study is similar to this one and for such low volume % concentrations the spectral corrections are not considered to be necessary.

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 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 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 (XLStat, 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 ~~Walczak~~ et al (2002). To estimate effective liquid diffusivity of isotopes, particle size and tortuosity values were obtained from the literature (Maidment, 1993; Shackelford and Daniel, 1991; Barnes and Allison, 1988).

4. Results

4.1. Stratigraphy, organic matter and moisture content

Four stratigraphic units are recognised along both Newnes Plateau swamp transects CC, GG and GGSW (**Fig. 3 to 5**), similar to a general classification derived by Fryirs et al (2014) for ~~TPH~~PSS in Blue Mountains and Southern Highlands region. The cross-sections presented in Fig. 3 to 5 were prepared on the basis of logged cores extracted as part of this research. These units are typically from the base upward medium to coarse sand, medium sand to clayey sand, silt to sandy clay and organic rich soil (sandy) at the top.

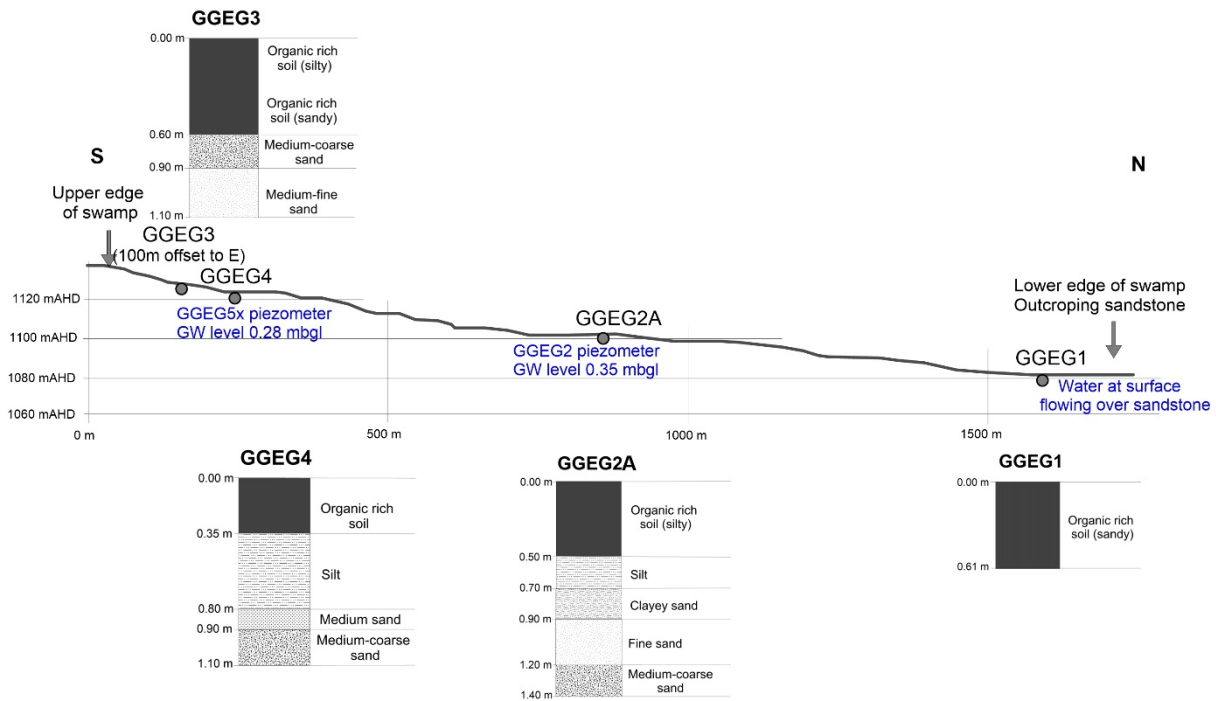


Figure 3: Interpreted long-section of swamp GG with swamp groundwater levels as measured in May 2016.

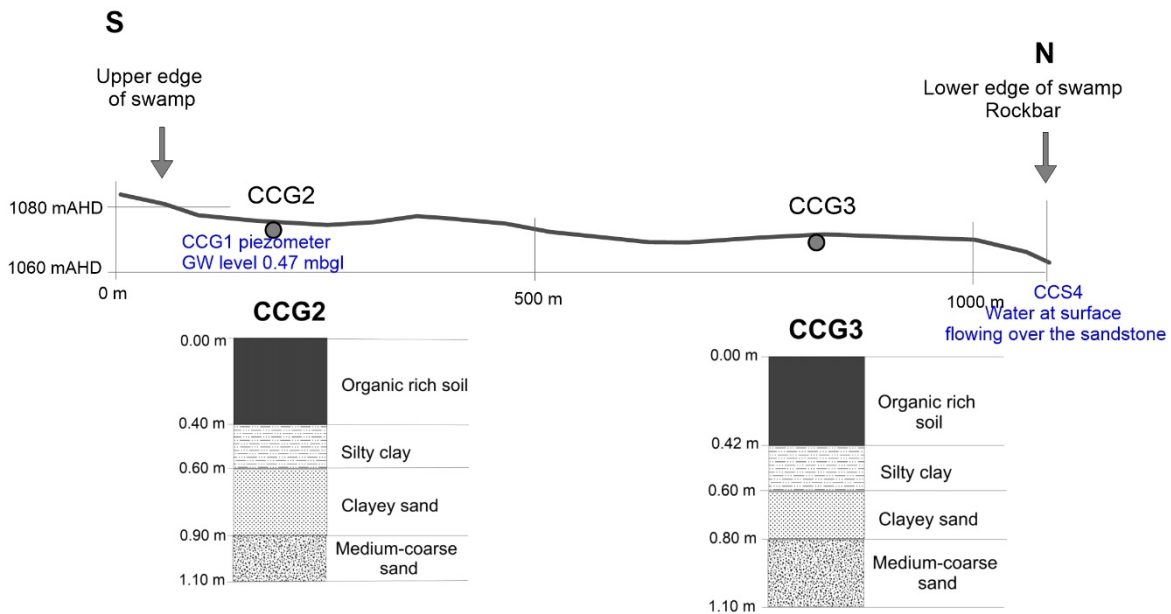


Figure 4: Interpreted long-section of swamp CC with swamp groundwater levels as measured in May 2016.

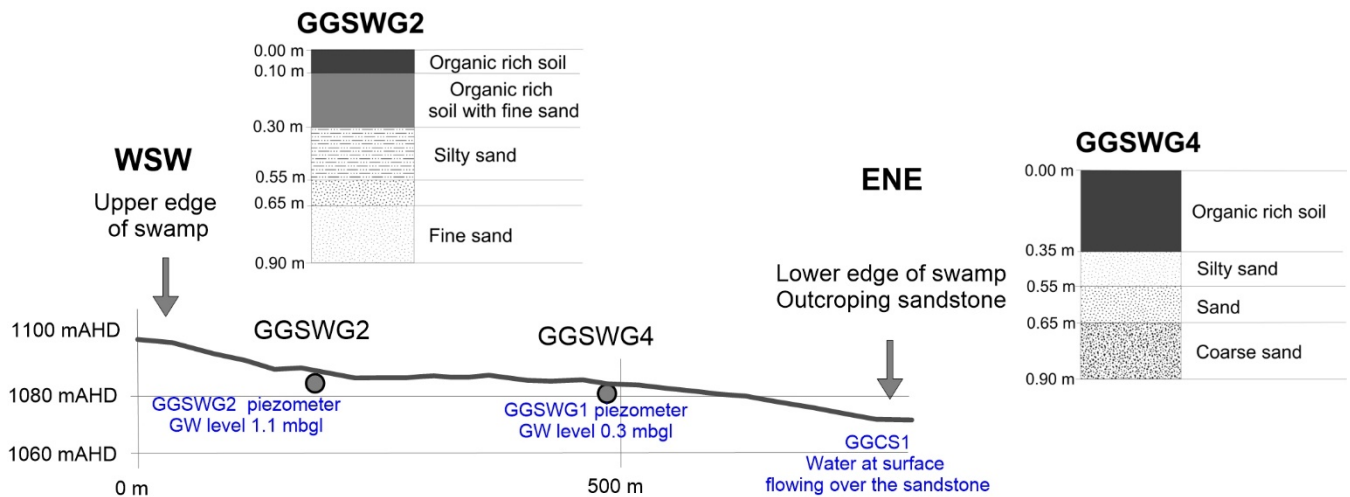


Figure 5: Interpreted long-section of swamp GGSW with swamp groundwater levels as measured in October 2016.

The base of the swamp is comprised of quartz sandstone, the Banks Wall Sandstone of the Narrabeen Group. The alluvial sands (with sub-angular quartz grains) overlying the sandstone are off-white opaque to transparent, medium to coarse grained with occasional quartz grains up to 2.5 mm in diameter. The term “sub-angular” defines the roundness of quartz or any other sediment grain. This is important as it points to material transport information, angular grains have been subject to limited transport.

These sands are overlain by medium sand grading to fine sand in the GG transect, with 15% organic matter and a minor clay component. However, in the CC transect this layer is missing and sand transitions upwards to clayey sand with iron staining. The total thickness of these two sandy units varies from 10 to 50 cm increasing in downgradient direction. At the most downgradient site on GG transect the sand layer is absent. Typically, the basal sand is overlain by a silt and silty clay that is thickest in the middle of the swamp (20–45 cm). The silt is dark grey in colour and contains approximately 40% organic matter with strong-organic smell. Organic smell relates to the likely high percentage of organic matter (peat). The uppermost unit is an organic rich soil or peat (20-60 cm thick), occasionally silty with abundant roots.

The swamp groundwater level is shallow, and it varied in piezometers (installed to 1.5 m depth) in May 2016 from 0.35 m below ground level (bgl) in GGEG2 to 0.47 m bgl in CCG1 (**Fig. 3 and 4**). The swamp groundwater level in cored holes was similar to that in shallow piezometers, however there was a significant difference represented by a rise of up to 0.4 m at all measured locations following the wetter period. The initial rise is mainly attributed to rainfall. During this wetter period, swamp groundwater levels recorded at GGSWG1 and GGEG2 were 0.05 m bgl and 0.09 m bgl, respectively. No overland flow was observed at any time, and the swamps did not have a formed channel. The only surface water observed in the swamps was at the lower edge of the swamp and flowing over the rockbar.

The swamp sediments are variably saturated, with gravimetric water content measurements exceeding 100% weight (dry mass basis) in the top 30 cm. This is typical for high organic matter proportion (GG samples) (**Fig. 6**). Within the same

vertical profile, the organic matter content varied with depth and decreased from 60 % to 10 %. At a depth from 60 to 120 cm the gravimetric water content decreased to an average of 17 % for CC and 32 % for GG swamp during both May and Oct 2016 sampling periods. The average organic matter decreased to 3.7% for all swamp locations below 80 cm depth.

During May 2016, following the dry period, upgradient and downgradient samples in CC swamp had similar gravimetric water content. A clear distinction was observed after wet weather period between the upgradient CCG2, having overall lower gravimetric water content, and downgradient CCG3, with higher gravimetric water content. A trend with an increase in moisture content downstream has been observed in all three swamps. However, at GGEG, the undulating topographic gradient means that changing moisture conditions exist along the length of the swamp. An overall increase in moisture content to around 80 cm depth in CCG3, was also recorded following the wet weather period although the increase was not statistically significant ($p>0.05$).

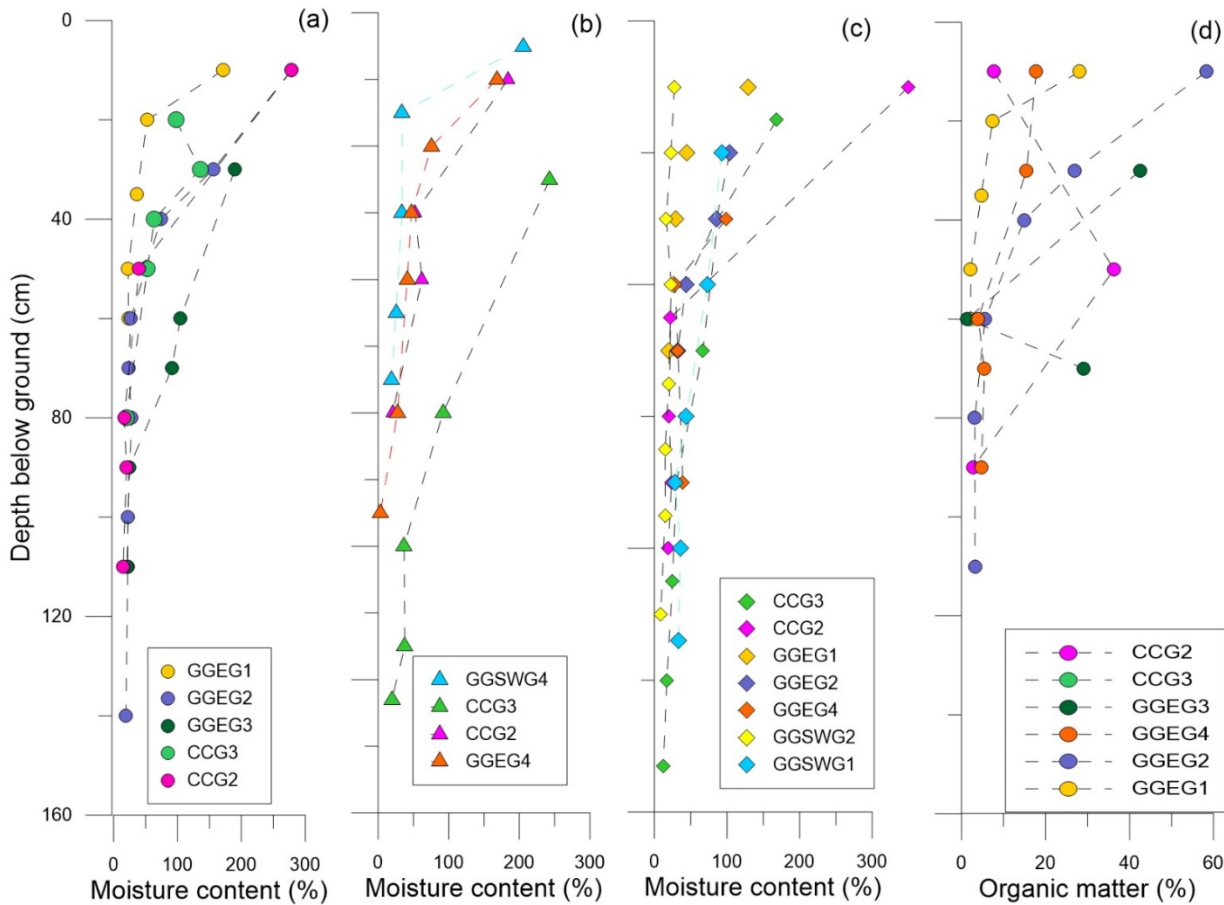


Figure 6: Gravimetric water content (% weight) for May16 (a), Oct16 (b) and May17 (c) and organic matter content in CC and GG swamps (d) shown with depth.

4.2 Stable isotopes of water and pore water

The relationship between surface water, swamp groundwater, regional groundwater and swamp pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data is presented in Fig. 7. This figure also shows the local meteoric water line (LMWL) for Lithgow ($\delta^2\text{H}=7.99\delta^{18}\text{O}+16.6$; Hughes and Crawford, 2013) and weighted rainfall average for Mt Werong which is based on the past 12 years of data ($\delta^{18}\text{O}=-6.87\text{‰}$, $\delta^2\text{H}=-37.3\text{‰}$). The $\delta^{18}\text{O}$ of rainfall varies seasonally with higher values in summer and lower in winter.

Stable isotope data from precipitation events at Mt Werong were plotted (excluding the rainfall below 5 mm) for three periods (Jan to May 2016, May to October 2016, and Jan to May 2017). The stable isotope data for these events plot on or close to previously defined LMWL for Lithgow (note that the LMWL for Mt Werong of $\delta^2\text{H}=8.08\delta^{18}\text{O}+16.6$ (Hughes and Crawford, 2013) and has a similar slope but higher intercept than that for Lithgow.

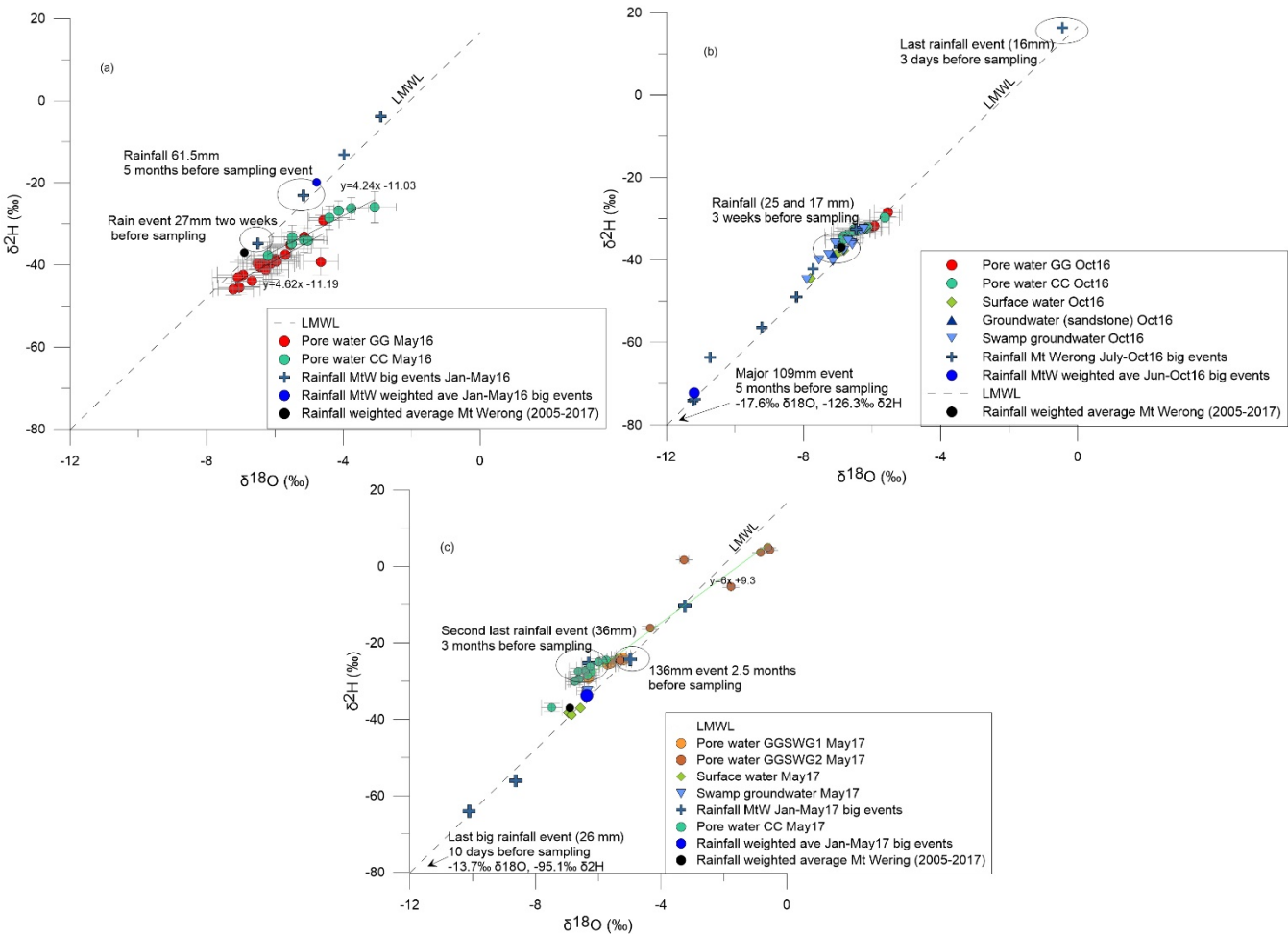


Figure 7: Stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of surface water, swamp groundwater, regional groundwater, swamp pore water, weighted rainfall average for Mt Werong (2005-2017) and LMWL for Lithgow (Hughes and Crawford, 2013) May 2016 (a), October (2016) (b) and May 2017 (c).

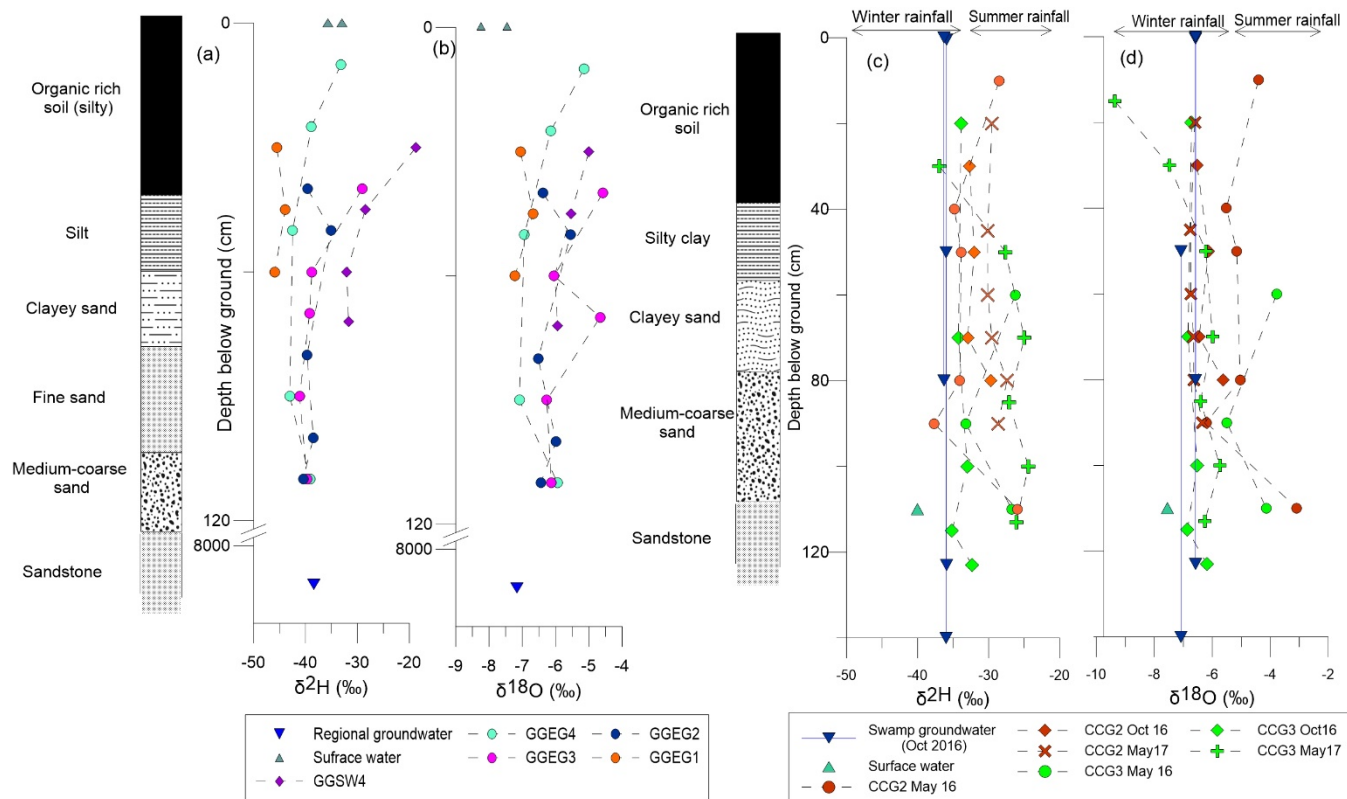
For May 2016 with dry and warm antecedent conditions, pore water stable isotope ranges ~~were~~are -7.20 to 3.10 ‰ $\delta^{18}\text{O}$ and -45.7 to -22.3 ‰ $\delta^2\text{H}$ (**Fig. 7a**). Pore water samples at CC and GG in May 2016 were clearly evaporated, lying along lines with slopes of 4.2 and 4.6 respectively, even though no single initial value for porewater evaporation was discernible. ~~Pore water samples at CC and GG in May 2016 lay along local evaporation lines with slopes of 4.2 and 4.6 respectively.~~ Two major rainfall periods (27 mm two weeks prior to May 2016 sampling and 153.5 mm in January 2016) had no noticeable influence on the swamp pore water isotope composition. The intersection points of the regressed trend lines of pore water and LMWL plot within the ~~depleted-lower~~ $\delta^{18}\text{O}$ and $\delta^2\text{H}$ rainfall range.

Stable isotopes for swamp pore water collected in October 2016 (**Fig. 7b**) ranged from -4.50 to -7.50 ‰ $\delta^{18}\text{O}$ and -25.0 to -47.0 ‰ $\delta^2\text{H}$. Pore water stable isotope values from samples collected in the wet and cool antecedent conditions, plot along the LMWL very close to the weighted rainfall average. This is consistent with a winter rainfall signature.

The pore water samples collected in May 2017 from GGSW swamp lie along a slope of 6 which aligns with a wetter period in early 2017 compared to 2016. Samples from CC swamp collected in May 2017 are more enriched in $\delta^2\text{H}$ (i.e. have a higher D-excess (d), defined as $d = \delta^2\text{H} - 8\delta^{18}\text{O}$ (Dansgaard, 1964)) than previously collected samples indicating greater evaporative influence. Rainfall samples for bigger rainfall events in the period from December 2016 to May 2017 plot along the LMWL, except events in the April prior to the 2017 sampling which have a significantly higher D-excess ($d=24.5$ ‰, rainfall of 68 mm). The pore water returned to the LMWL between May and October 2016 and shifted to the left of the LMWL for the May 2017 sampling.

Swamp groundwater samples collected in October 2016 and May 2017 are enriched in ^{18}O and ^2H relative to the rainfall weighted average for Mt Werong (2005-2017). Surface water samples collected mainly at the downstream point of the swamp plot close to the LMWL and are depleted-lower in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relative to pore water samples ~~for $\delta^{18}\text{O}$, and $\delta^2\text{H}$~~ , and relative to large rainfall events preceding the sampling event.

Surface water samples (-6.50 to -7.70 ‰ $\delta^{18}\text{O}$ and -37.0 and -44.4 ‰ $\delta^2\text{H}$) plot within the range of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for swamp groundwater samples (-6.2 to -7.9 ‰ $\delta^{18}\text{O}$ and -32.4 and -44.7 ‰ $\delta^2\text{H}$). The statistical significance of the difference between the isotopic composition of surface water and swamp groundwater on both GG and GGSW transects was analysed by comparing the means of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (October 2016 and May 2017) for these two datasets using a t -test. Based on the mean, we test the hypothesis that there is no statistical difference between the datasets (surface water and swamp water). The calculated p -value was significantly more than 0.05 (for $\delta^{18}\text{O}$ $p=0.34$ and for $\delta^2\text{H}$ $p=0.27$; $n=20$), indicating that the null hypothesis cannot be rejected and there is no significant difference between these two datasets.



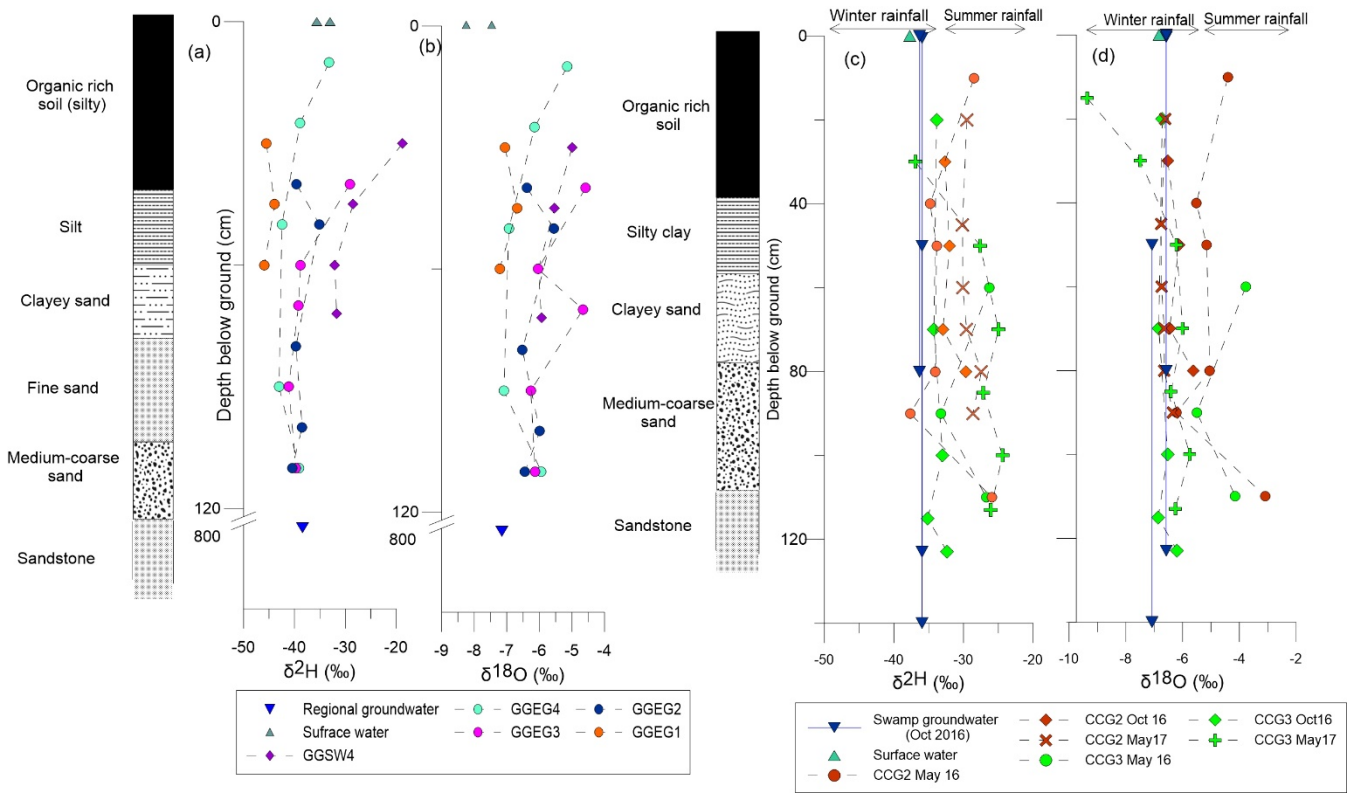


Figure 8: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ variation with depth in GG and GGSW swamps (May 2016) with typical lithology log. Regional groundwater sample was collected at the downstream point of the GG swamp (a and b). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ variation with season and depth in CC swamp (May and October 2016 and May 2017) with typical lithology log. Swamp groundwater represents cumulative water through the swamp within shallow piezometers and cored holes (c and d). Swamp groundwater samples were not collected at all locations in May 2016 due to dry conditions. Depth of augured holes was not exactly the same in all sampling events.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data for pore water is plotted with depth along with surface water and groundwater from GG and GGSW swamps (**Fig. 8a and 8b**). Seasonal pore water and swamp groundwater variations (May and October 2016 sampling) for CC swamp are compared to rainfall isotopic signature collected at Lithgow (Hughes and Crawford, 2013) (**Fig. 8c and 7d**). The $\delta^{18}\text{O}$ values of pore water (May 2016) in GG and GGSW swamps (**Fig. 8**) show a tendency of depletion with depth with greater variability at a depth of 40-65 cm. Below 100 cm depth, the $\delta^{18}\text{O}$ values of pore water approach the swamp groundwater and regional groundwater signature.

It can be observed that pore water samples from CC swamp from both upstream (location CCG2) and downstream (location CCG3) have lower $\delta^{18}\text{O}$ become depleted after longer wet and cool antecedent conditions with a $\delta^{18}\text{O}$ shift of around 1-3 ‰ (**Fig. 8c and 8d**). $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for pore water at CCG2 during May and October 2016 shows a statistically significant difference between the wet and dry period ($\delta^{18}\text{O}$ ($p=0.003$) and $\delta^2\text{H}$ ($p=0.02$)), similar to $\delta^{18}\text{O}$ of pore water at CCG3 ($p=0.01$). The CC samples collected in May 2017 have lower $\delta^{18}\text{O}$ values of pore water compared to October 2016 samples and are similar to significant rainfall in March 2017. The CC samples collected in May 2017 have similar $\delta^{18}\text{O}$ values of pore water to October 2016 samples however are slightly more depleted and similar to significant rainfall in March 2017.

Swamp groundwater samples collected from piezometers screened across both top of sandstone and the base of swamp sediments (CCG1 and GGEG2) have a similar $\delta^{18}\text{O}$ signature to pore water at a depth below 110 cm. Surface water $\delta^2\text{H}$ for October 2016 is more negative than the pore water value (-37.7‰ $\delta^2\text{H}$) in the upper 70 cm and is similar to the typical winter rainfall signature.

5 4.3 Water balance

During dry periods swamp pore water is subject to evaporation and becomes isotopically enriched in ^{18}O and ^2H . Therefore, the fractional loss of water through evaporation can be quantified if other water loss processes do not isotopically fractionate (Gonfiantini, 1986) or/and if the stable isotope composition of inflow and outflow and site weather data is known (Lawrence et al, 2007). To evaluate the evaporative losses based on isotopic composition of water, we used the Barnes and Allison (1988) analytical model to represent the change in isotopic profile in unsaturated soils due to evaporation. This model, based on deterministic approach, was selected because the stable isotopes diffusivities vary slowly with water content and a relatively good agreement is reported with experimental results (Barnes and Allison, 1988; Shanafield et al, 2015). The disadvantage of using the soil profile to estimate evaporation is that an assumption of steady state is needed and there is some uncertainty in dispersivity and tortuosity values (Shanafield et al, 2015). The support for the selection of the Barnes and Allison (1988) model for the vegetated wetland environment is shown in the recent work undertaken by Piayda et al (2017). They found that regardless of the presence of vegetation or bare soil, the total evapotranspirative water loss of soil and understorey remains unchanged. Furthermore, the modelling is considered to be applicable by focusing on vertical flow. Modelling included the samples from the base of the swamp (not sides) where vertical flow is dominant due to high permeability of the peat.

We applied the model to pore water data from all three sampling periods considering realistic input variables into the model as given in Table 1. The model ran with the evaporation factor adjusted such that it matched the observed data; all other parameters remain constant. A linear relationship was identified between particle size and tortuosity, and the final estimated tortuosity values are given in Supplement (Table 1).

The results for unsaturated soil modelling at all sampled depth points based on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ indicate an evaporative loss in the unsaturated zone of 4 mm to 9 mm/day in May 2016 (dry) period, and <1 mm/day for the wetter and cooler period between May and October 2016. Evaporation of less than 1 mm was estimated in CC swamp in both wet and dry periods, and at the upstream point on GGSW swamp.

The model was not sensitive to temperature; modelling at both 21.9°C and 10°C resulted in only minor differences in evaporation (<0.04 mm/day). Model results for drier and wetter periods are presented in Supplement (Fig. 1). The data for the May 2016 period (dry) shows a clear evaporative enrichment profile towards the surface (upper 0.4 to 0.6 m) and uniform $\delta^2\text{H}$ with depth (Supplement, Fig. 1a and 1b). No changes in isotopic composition were observed below a depth of 0.6 m.

The water balance was prepared such that it incorporates the following parameters: rainfall, runoff from each of the swamps, evaporation. The deficit in the water balance ~~was~~is attributed to groundwater contribution. Two options are considered in the water balance with respect to evaporation: evaporation based on unsaturated soil model results (E) and reference data (ET_c). The rainfall data from Lithgow BoM Station 63132 and reference evapotranspiration (ET) data from Nullo Mountain BoM Station 62100 (94 km north of the study site in the same mountain range and similar elevation and climate) indicate that in the dry period (February to May 2016) the ET significantly exceeded the rainfall (Table 1). The ET represents evapotranspiration computed from reference surface (grass) using meteorological data (Allen et al, 1998). Crop evapotranspiration (ET_c) calculation incorporates the ground cover, canopy properties and aerodynamic resistance for the specific crop into the calculation. In our case the ET_c is applied to a wetland system.

Table 1: Water/mass balance components: measured rainfall and ET data (Lithgow and Nullo Mountain), runoff, measured E and estimated regional groundwater contribution (negative values are regional groundwater contribution).

Figure 9 shows the water deficit and estimated regional groundwater contribution to each of the swamps for the ET_c and E methods. The relative regional groundwater contribution is dominant in the dry weather period when it exceeds total rainfall. This regional groundwater contribution range represents the minimum and conservative value given that discharge from the swamp is not included in the water balance and that the estimates based on the E method do not include transpiration losses.

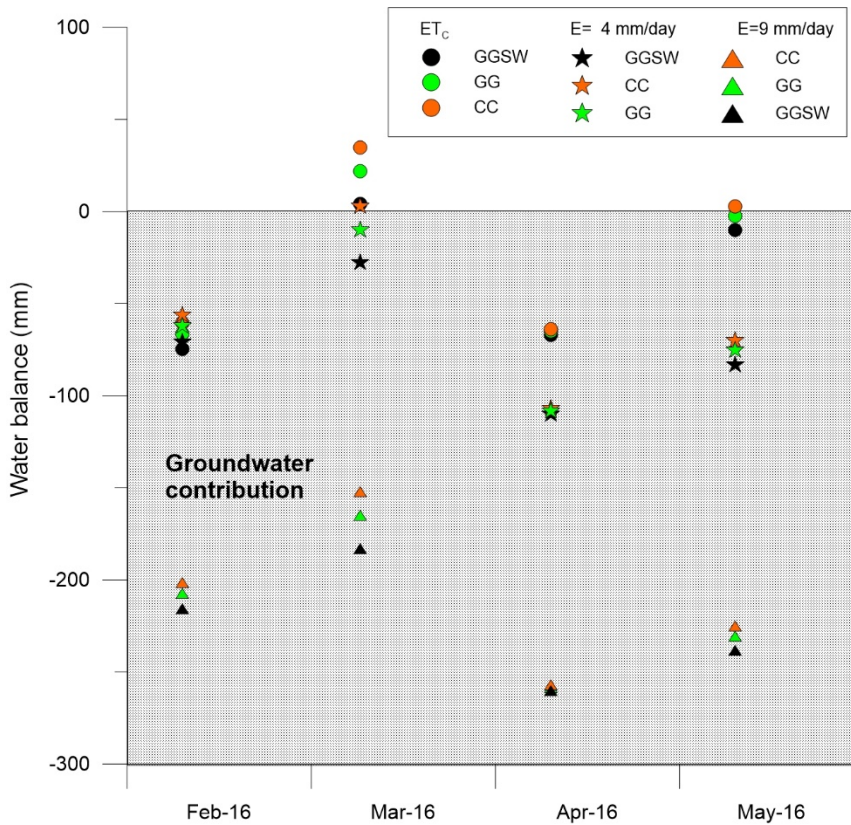


Figure 9: Water balance during dry period estimated using ET_c and E for each of the swamps.

Discussion

5.1 Swamp stratigraphy, geomorphology and groundwater condition

5 Swamp sediments are thin (less than 1.5 m) and are deposited directly on the sandstone basement. Typically, the organic soil or peat is 40-60 cm thick, underlain by unconsolidated alluvial sand and sandy silt with organic rich thin bands. The geomorphology of the Newnes swamps is consistent with the intact swamp classification as reported by Fryirs et al. (2016), and with moisture and organic matter content as reported in Blue Mountain swamps by Cowley et al. (2016). The lithology indicates that the sediment transport is alluvial, however limited and occurring over relatively short distances (length of the

10 swamp).

An important finding of this research is that no evidence was observed for a clay rich layer with sealing properties at the base of these swamps. A conceptual model of swamp sediments that are hydraulically connected with the underlying sandstone is proposed (**Fig. 10**). However, there is likely to be a decrease in permeability at this interface. A degree of hydraulic connection between the regional groundwater and these elongated gentle gradient shrub swamps (50 mm/m average (Cardno,

15 2014) is further supported by gravimetric water content results. The stable gravimetric water content below 0.4 m depth in

CC and 0.6 m depth in GG and GGSW swamps, indicates stable saturated conditions likely supported by lateral groundwater inflow.

Groundwater levels in the swamps were observed to be similar to regional groundwater level within the underlying sandstone (monitoring screen at a depth of around 10 m bgl) at the downstream end of GG swamp indicating that these two units could be hydraulically connected. Typically, the swamp groundwater levels in TPHPSS (CC swamp) rise and decline in response to rainfall recharge (Centennial Coal, 2016) with very little lag time. Rapid infiltration and discharge in the swamp groundwater system is indicated by low swamp groundwater salinity (measured in this study) (David et al, 2018). Given high moisture and organic matter content and evidence of seasonal precipitation in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ profiles ($p < 0.05$) in the upper swamp horizons, we conclude that in this zone the high water holding capacity increases residence time following the initial infiltration (vertical swamp groundwater flow). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of pore water in this variably saturated zone exhibits summer evaporation trends and a winter rainfall signature. The lateral groundwater discharge to the swamp is characterised by longer residence time compared to water exchange through the swamp based on ~~depleted-lower~~ $\delta^{18}\text{O}$ values and minor change between the sampling events. The similarity in EC and pH values between surface and swamp groundwater (David et al, 2018) further supports relatively rapid infiltration and possibility of both lateral and upward local groundwater inflow that provides baseflow to the swamp. However, local differences in swamp strata do exist: e.g. the difference in gravimetric water content in the CC swamp between the upgradient and downgradient location. This difference can be explained by higher permeability in the upgradient part of the swamp resulting in quicker drainage, increased groundwater contribution in the lower part of the swamp and/or lateral throughflow.

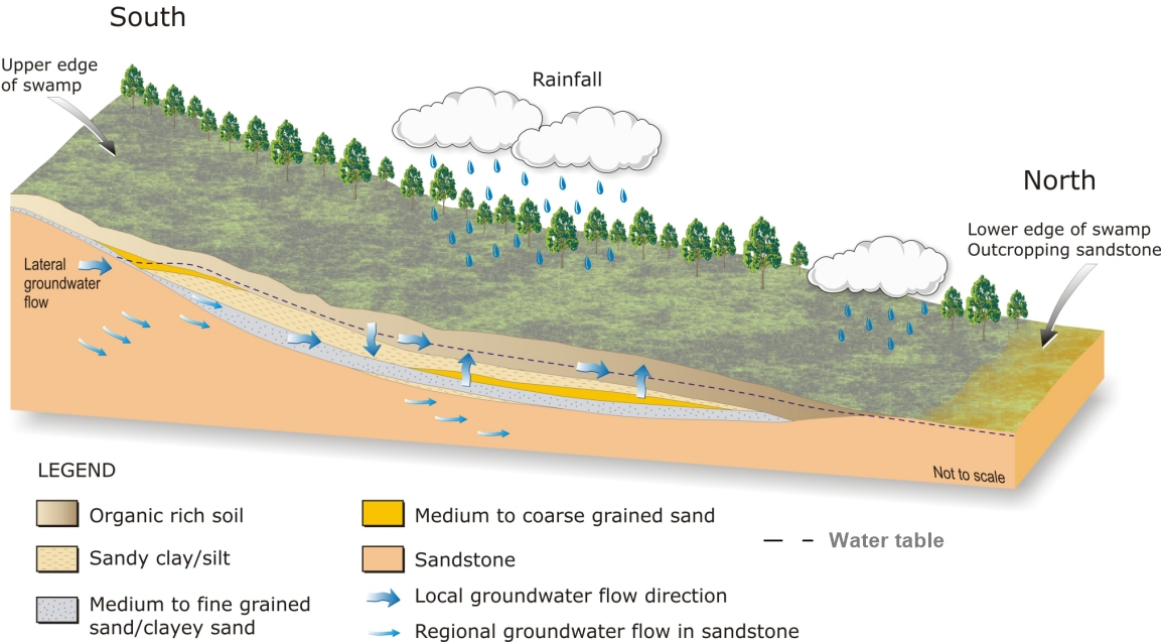


Figure 10: Conceptual representation of water dynamics in the swamp system.

To validate this conceptual model, a simple water balance was completed based on the evaporative losses estimated by analytical model (Barnes and Allison, 1988). Using the results from the dry weather period February to May 2016, we obtain evaporation estimates ranging from 1 to 9 mm/day. The evaporation occurs in the top 0.4 m of the vertical profile, with an absence of fractionation below this depth where pore water isotopes values are similar to swamp water and regional groundwater. These evaporation rates (1 to 9 mm/day) suggest high evaporation compared to rainfall in the same time period (Table 1). During the wet period (Supplement Fig. 1c and 1d) we observe the ~~lower $\delta^2\text{H}$ depletion~~ at the surface. ~~This depletion in $\delta^2\text{H}$ values~~ is related to a big rainfall event, 10 days before sampling (Fig. 7c).

With an ET_c ranging from 1.7 to 4.4 mm/day and E ranging mainly from 4 to 9 mm/d, the ET_c/E ratio for these swamps would be 0.7 to 0.3. This ratio is at the lower end of measured ET_c/E ratio for typical wetlands indicating that reference ET_c could underestimate that based on realistic evaporation rates obtained by matching the modelled to observed data. The ET_c for typical wetland vegetation (sedge) in temperate climates ranges from 0.8 to 1.2 (Allen et al, 1998; Mohamed et al, 2012) and 0.7 was reported in a swamp in the Murrumbidgee, Australia (Linacre et al, 1967). The ET_c in our case is less than the estimated E based on stable isotope data. As transpiration does not fractionate, the actual evapotranspiration in the dry and warm period would have to be greater than the estimated evaporation. This would result in higher water balance losses, requiring more water be supplied from other sources.

Runoff represents only a small component of the water budget for several reasons. Firstly, the 10% slope gradient of the ridges, 3% slope gradient along the swamp floor and densely vegetated sides and base of the swamp minimize the runoff significantly. Secondly, the upper soil layer is peat with significant water holding capacity compared to other soil types, and as indicated by the gravimetric water content measured in CC and GG swamps.

A simple mass balance comprising the rainfall (input), runoff (input) from the catchment considered two different approaches in dry period using E or ET_c . When ET_c (output), was used, March had excess water with a deficit in February, April and May of between 10 and 60 mm. However, the same mass balance calculated with E using 4 mm/day, has a water deficit of between 10 and 113 mm/month for any month. If E of 9 mm/day is used in the water balance, water deficit occurs in every month in the range from 10 to 260 mm/month (Table 1). Either way, two important output components are not considered in this mass balance: transpiration and discharge at the rockbar downgradient of the swamp. The estimation of these two components is uncertain, but inclusion in the water balance would increase the water deficit further. Importantly, if swamp discharge data were available in combination with pore water isotope profiles, an appropriate crop transpiration could be determined for these swamps, a factor that is typically a large unknown in water balance studies.

It is evident that given the water deficit, even without two output components, an additional water source must have maintained the swamp groundwater levels. We therefore conclude that groundwater is a significant contributor to swamp water balance, particularly during dry periods. For example, in GG swamp the swamp groundwater levels are in the range from 0.28 to 0.38m bgl and if groundwater inflow was not occurring under same evaporation conditions the depth to water in the swamp would be greater.

Furthermore, measured loss of moisture as shown in **Fig. 6** indicates that significant loss occurs in such a dry weather period in the top 40 cm (up to 150 % by weight), while lower parts of the swamp remain saturated. The estimate of groundwater contribution in the drier period (February to May 2016) ranges from 10 to over 113 mm/month if calculated using 4 mm/day of evaporation, and up to -260 mm/day if E of 9 mm/day is used. The water balance was undertaken for dry period only as evaporation from soil profile using stable isotopes ~~was-is~~ considered to be most accurate during that period. Thus, even in the months where water balance is positive, i. e. groundwater contribution is likely, as evident from discharge at the rockbar observed at the end of dry period. Although there is a compelling explanation for significant groundwater contribution to the swamp water balance, the actual volume of groundwater cannot be estimated without knowledge of swamp groundwater and regional groundwater recession rate and/or measurement of discharge from the swamp.

It is clear that the water balance in swamp can be obtained if all components are known (rainfall, runoff, groundwater contribution, evaporation, evapotranspiration, discharge), however due to the THPSS swamps being difficult to access and being protected under State and Federal legislation it is not possible to undertake intrusive drilling to obtain all hydrogeological information. The application of stable isotopes has enabled estimation of evapotranspiration from the swamp and assisted in development of the conceptual model.

5.2 Swamp groundwater and regional groundwater movement within the swamp system

The vertical depth profiles of pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ can provide time series information by tracing the influence of the rainfall isotopic signature in recharging water. Pore water direct vapour equilibration method is used ~~for the first time~~ in a swamp environment and results compared with end members which included surface water, rainfall and groundwater. Although stable isotope data in precipitation changes in the short term, this end member is well constrained based on the good quality dataset for precipitation. Constraining the interpretation of isotope results with these end members enabled groundwater inputs to be identified.

The evaporation response in the upper 40 cm is consistent with depth of penetration dependent on evaporation rate, soil type and time between rainfall events (Mathieu and Bariac, 1996; Melayah et al, 1996; dePaolo et al., 2004). As evaporation proceeds, capillary rise of swamp groundwater reduces the $\delta^{18}\text{O}$ enrichment closer to the surface. Moisture content data reveals variability at 30-70 cm depth, which is also observed in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ profiles and is related to interlayering of fine and coarser grained material, consistent with other studies (dePaolo et al., 2004). The ~~intercept of the~~ pore water regression line ~~intercepts with the LMWL is at a depleted lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value relative to than~~ weighted average rainfall. The isotope signature in the partially saturated zone (variable from 0.05 m bgl to 0.4 m bgl in the swamp) in the summer period (May 2016 sampling event) is a result of evaporation as observed from depth profiles and moisture content. This agrees with numerical experiments ~~conducted used~~ by Benettin et al (2018) where the soil water samples trend lines were found to be products of seasonality of evaporative fractionation. Swamp pore water in May 2016 ~~is more negative~~ has lower δ values

than rainfall and therefore likely to be from bigger, more isotopically depleted events in the autumn and winter of the prior year which are lower in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (including 230 mm in April 2015: -7.60‰ $\delta^{18}\text{O}$, -39.2‰ $\delta^2\text{H}$; 108 mm in August 2015: -9.8‰ $\delta^{18}\text{O}$, -61.6‰ $\delta^2\text{H}$; and two smaller but highly ^{18}O and ^2H depleted events in June and July). This agrees with annual weighted averages at Mt Werong of -34.9 and -46.5‰ $\delta^2\text{H}$ in 2015 and 2016, respectively. A major rainfall event in June 2016 (92.8 mm at Lithgow and 109 mm at Mt Werong, -17.70‰ $\delta^{18}\text{O}$, -126.3‰ $\delta^2\text{H}$) had not obviously affected swamp pore water.

Although the same rainfall events generally affect both Mt Werong and Newnes, and occur at the same time, the amount of rainfall at Newnes is typically smaller than at Mt Werong. Whilst we would expect that larger rainfall events would lead to the most significant infiltration and recharge of swamp groundwater and regional groundwater, and therefore influence the pore water signature more, the data seems to suggest that small recent rainfall events are very important in October 2016 and May 2017, following the wetter conditions experienced in the second half of 2016 and early 2017. The importance of smaller rainfall events on recharge is also consistent with gravimetric water content data which remained stable throughout the wetter and drier period at depth below 0.8 m in CC and 0.6 m in GG and GGSW swamps. Another contributing factor may be that groundwater provides a moderating effect particularly during wetter periods, reducing the effects that evaporation has on pore water isotope composition.

Statistically there is no difference between the mean of the surface water and swamp groundwater stable isotope samples for GG and GGSW swamp. The reason for similarity of surface and swamp groundwater samples is assumed to be short infiltration time to water table and/or mixing with lateral regional groundwater with surface water sample points being located largely in the groundwater discharge zone. There is a difference in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values ($p < 0.05$, $n = 18$) between samples collected after dry and warm versus wet and cool antecedent conditions. The October 2016 (cool weather) samples from CC swamp are typically depleted-lower in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and we conclude that these values are within the range of winter rainfall isotope values. Below 100 cm depth the pore water values of $\delta^{18}\text{O}$ remain uniform and consistent with the regional groundwater value but also with surface water. We infer this to represent swamp groundwater derived from vertical infiltration and laterally from sandstone, respectively. We therefore consider the main processes to be rapid infiltration through the swamp sediments to water table but at the same time high water retention in the upper horizons, and slow lateral exchange of pore water below the vadose zone.

The vertical topographic difference from swamp headwaters to the downstream end of the swamp (typically a sandstone rockbar) is around 40 m. This elevation difference is too small to result in any difference in isotopic signature of precipitation, therefore, given the spatial response and assuming a homogeneous environment with vertical flow, pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ should be similar (Garvelman et al, 2012). However, observed variation in profiles is not uniform, and is caused by vertical rainfall infiltration in the upper part of the profile and lateral flow at the base. The lateral flow within the swamp sediments is further enhanced by regional groundwater flow contribution from the valley sides. Such lateral flow is reported in these swamps where sandstone is underlain by a claystone layer (Corbett et al, 2014).

Factors such as fine-grained content of lithological units, reported by other studies (dePaolo et al., 2012), have been found to result in a bigger shift to ~~depleted-lower~~ $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ~~values~~ and variation in isotope signature with depth. The reason for this is related to hydraulic conductivity of the unconsolidated soil. For example, the biggest variation in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was observed in silt and clayey sand units (**Fig. 8a** and **8b**) which contain higher percentage of particles $<2\ \mu\text{m}$. Contrary to observations by Garvelman et al (2012), we did not find the variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to be a result of soil saturation and depth of vadose zone only, but also as a function of lithology and different grain size material (peat, organic soil with sand and silt). Variations in particle size, porosity and permeability would then influence groundwater flow and storage.

Conclusion

The hydrogeological and isotopic characterisation of these swamp environments provides a baseline understanding for future comparison of any hydrological changes due to natural or human activities. This study ~~is the first application of~~ the vapour equilibration method for determining stable isotopes of pore water in a wetland system. This unique pore water isotope approach combined with other data and information has significantly improved a conceptual model of wetland hydrology. As found by Wassenaar et al (2008), the pore water stable isotope method allows efficient sample collection without permanent disturbance, collection of vertically discretized data at any practicable frequency and without the need for more complex methods of water extraction.

This study found, for several upland peat swamps, that swamp groundwater is a dominant component of the water balance, its contribution being larger than rainfall during dry weather period. This finding is consistent with environmental tracer studies suggesting that 19-80 % of water in Blue Mountains swamps is from groundwater, particularly in steeper and rounder catchments (Young, 2017). Furthermore, these swamp groundwater systems appeared to be in hydraulic connection with the underlying sandstone regional groundwater, given similar groundwater levels, and the lack of a clayey layer at the base of the swamp. Although rainfall infiltration to water table occurs rapidly, the high water holding capacity of upper organic rich layers maintains the moisture for long periods. These processes are confirmed by the results of the water balance, in particular during dry periods. The majority of flow through the swamp system is via lateral groundwater flow where flow rate depends on heterogeneity within this layer and hydraulic conditions. Under natural intact conditions, upward or downward flow between the swamp system and underlying rock is controlled by groundwater heads, the slope, and the hydraulic conductivity contrast at the interface.

The conceptual model presented here provides a valuable benchmark from which to evaluate potential changes in swamps following underground mining and forestry activity. The improved understanding in the water balance in these swamps also has implications in other areas of the Blue Mountains where urbanization has a significant impact on upland swamps. The role that catchments have on the health of a swamp is important in supporting its flora and fauna, with groundwater likely to be a primary factor that contributes to the long-term survival of the ecosystem (Gorissen et al, 2017). The protection of this

ecological ~~community is~~community is therefore dependent on maintenance of catchment stability and groundwater baseflow contribution if forestry activity and ground movement or deformation due to mining occur in the swamp catchment.

Measurement of pore water stable isotopes of peat and sediment within the swamp ecosystem provides direct information on the depth at which the evaporation occurs and understanding of the water cycle. Evaporation obtained from stable isotope

- 5 direct equilibration method was found to be more realistic than reference evapotranspiration~~ET~~. In particular, based on current research of the water balance in wetland and swamp systems and ecology around the world, the application of this method could be beneficial to define water availability for flora and fauna in swamps where a thick organic soil/peat and sedimentary layer exists.

10 **Data availability**

The underlying research data can be accessed in the registry for research data repositories at <https://www.dataarchive.unsw.edu.au/>.

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Table 1: Water/mass balance components: measured rainfall and ET data (Lithgow and Nullo Mountain), runoff, measured E and estimated balance deficit (negative values are groundwater contribution).

	Feb-16	Mar-16	Apr-16	May-16
Total monthly rainfall Lithgow station (SN63132) (mm/month)	28.8	61.2	6.2	26
Reference ET Nullo Mountain (SN62100) (mm/month)	119.9	92	76.6	51
Evaporation (pore water stable isotope profiles) mm/month	117-267	123-273	120-270	123-273
Runoff estimate				
CC	31	65.6	6.6	28
GG	25	53	5.4	22.5
GGSW	16.4	35	3.5	15
Balance deficit (groundwater component) (ETc)				
CC	-60.2	34.8	-63.8	2.9
GG	-66.2	22.1	-65.0	-2.5
GGSW	-74.7	4.1	-66.9	-10.2
Balance deficit (groundwater component) (4 mm)				
CC	-56.3	2.8	-107.2	-70.1
GG	-62.3	-9.9	-108.4	-75.5
GGSW	-70.8	-27.9	-110.3	-83.2
Balance deficit (groundwater component) (9 mm)				
CC	-201.3	-152.2	-257.2	-225.1
GG	-207.3	-164.9	-258.4	-230.5
GGSW	-215.8	-182.9	-260.3	-238.2