Hydrogeochemical characterisation of swamps near underground mining development ◎

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Abstract

Underground mining developments in many areas have little influence on surface waters and ecosystems, however, there are considerable risks in some locations due to ground movement and subsidence. Many swamps are mapped in the proximity of underground coal mines on the Newnes Plateau, Eastern Australia. These swamp ecosystems depend on wet and moist conditions, however there is concern that effects of mining may reduce groundwater flow and contribute to drying of swamps.

We collected water and organic matter samples from three swamps near longwall panels prior to their extraction to complement baseline studies of the swamps. We use the geochemistry of water samples along with carbon and nitrogen stable isotopes (δ^{13}C and δ^{15}N) of organic matter to provide information on the functioning of this ecosystem.

Results of δ^{13}C and δ^{15}N indicated that microbial activity is highest from surface to 60 cm depth, decreasing with depth and confirms organic matter sources. Hydrogeochemistry indicates that rainfall quickly reaches groundwater and that its residence time is relatively short. Natural seasonal trends in geochemistry indicate dissolution of plagioclase and mobilisation of Mg and no change in naturally occurring trace metal concentrations.

Keywords: stable isotopes, hydrogeochemistry, swamps, longwall mining

Introduction

Underground mining developments in many areas have little influence on surface waters and ecosystems, however, there are considerable risks for these natural assets in some locations due to ground movement and subsidence. Upland swamps in the Sydney region are elongated narrow features which occur high in the landscape at the headwaters of the creeks (above 600 mAHD) (Fig. 1). The swamps provide a moist environment for a number of protected and endangered flora and fauna species, and also contribute to stream flow and water quality (Fryirs et al 2014, Cowley et al 2016, Hose et al 2014). However, several swamps have been degraded due to urban development, forest plantations, recreational activity and longwall mining (Young, 2017). Variable climate and wildfire are also threats to these swamp ecosystems that are protected by government regulation.

Information on the influence of subsidence on ecology and its response to changes in the shallow groundwater and surface water balance are currently limited (CoA, 2014), so additional studies and monitoring of the swamps are in progress.

Before potential changes related to mining can be considered, it is important to understand the behaviour of swamps in the natural conditions along with their temporal variations. These include changes in the water regime, water quality, and groundwater. Both lithology and topography play an important role in the control of the swamp morphology and its spatial extent (McHugh, 2012). Recently published literature has considerably improved the understanding of the swamps by investigating their morphology and ecosystems. For example, Fryirs et al (2014) propose the swamp model where the swamps comprise the mineral rich sand and loam deposits,

which reflect the mineral–sand trapping and accumulation on the floor of the valley. Cowley et al (2016) identifies contemporary sands unit, which underlay the peat, with low water holding capacity and low organic content such that it impedes the water flow. Hose et al (2014) discussed drainage from the swamp indicating that the hillslopes and marginal zones drain more quickly than the main swamp axis. They conclude that the changes in vegetation types spatially and over time are directly related to groundwater levels which influence moisture in the overlying peat.

This paper aims to characterise the hydrogeochemistry of several swamps, to complement other baseline studies and monitoring prior to potential effects of subsidence by longwall mining. The paper focuses on hydrogeochemical data and stable isotopes of carbon, nitrogen, oxygen and hydrogen to provide information on organic matter and water within the swamps.

Methods

Fieldwork to collect water, sediment and organic matter samples occurred during relatively dry (May 2016) and wet (October 2016) period, and also during May 2017. The water and groundwater samples for major ion analysis and stable isotopes were collected from temporary hand augered holes located in three swamps: GG, CC and GGSW. Each narrow auger hole was refilled with the materials sourced from each hole immediately following sampling. Sediment samples for pore water analysis were collected from augered holes. Organic matter was collected from both the augered holes and from the swamp surface and side of the swamp. The location of the samples is shown on Fig. 1, along with
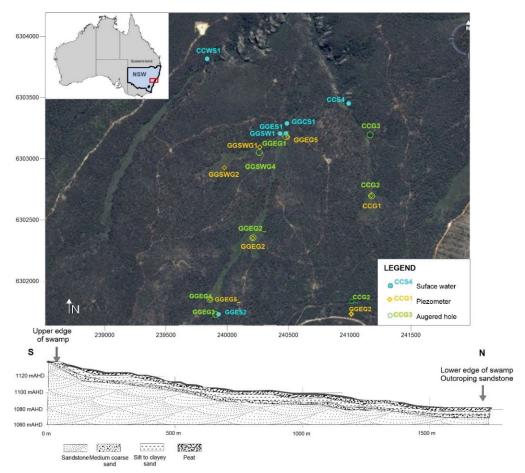

Figure 1 Map with sample locations and typical stratigraphic cross section

the typical cross section based on the augered holes along three transects.

Groundwater was sampled directly from augered holes, field parameters were measured immediately (pH, EC, DO, temperature) and samples field filtered (0.45 micron) for major ions aanalysis. Groundwater from existing piezometers (CCG1, GGEG2, GGEG5x, GGEG5 and GGSWG1) was sampled by bailing three volumes and then the same procedure was followed as for the augered holes. Surface water samples were collected at the downgradient end of the swamp and at one upgradient location (GGES2) where this was possible. Major ion water samples (n=18) were analysed for chloride and sulphate by ISPMS and calcium, potassium, magnesium, sodium, silica and sulphur by inductively coupled plasma–optical emission spectroscopy (ICP-OES) at the UNSW Mark Wainwright Analytical Centre. Selected elements and trace metals were analysed by ISPMS.

Carbon and nitrogen stable isotope ratios on organic matter was analysed by Flash 2000 elemental analyser coupled to Delta V Advantage IRMS (mass spectrometer) at the UNSW Mark Wainwright Analytical Centre. Samples (n=37) were prepared by drying, grinding by mortar and pestle, weighing the samples and preparing in tin capsules, typically 0.5 mg in weight. Given that the signal for carbon was too high and for nitrogen too low, the samples size was adjusted to around 0.2 mg for carbon and over 1 mg for nitrogen. Two standards (USGS40 and USGS41) were included in the analysis after every tenth sample. The isotope ratios were reported as the relative ‰ difference between sample and conventional standards (Vienna Peedee Belemnite (VPDB) for carbon and atmospheric nitrogen (Air-N_2) for nitrogen isotopes). Measurements were to an instrument precision of approximately 0.2% for $\delta^{15}N$ and $\delta^{13}C$. The sampling error was assessed as a difference between the duplicate samples of the same organic matter sampled at the same depth. These differences were larger than the instrument precision, with the median difference 0.13 ‰ for $\delta^{15}N$ (n=14) and 0.68 for $\delta^{13}C$ (n=34).

Pore water samples for stable isotopes were collected, preserved and prepared based on Wassenaar and Hendry (2008) method.

Sediment samples were collected every 10-20 cm with depth. The pore water samples were analysed for δ^2H and $\delta^{18}O$ in the UNSW laboratory using a LGR water vapour analyser (WVIA RMT-EP). Three LGR standards and SMOW were used for calibration.

Results and discussion

Water chemistry

The chemistry for groundwater samples (n=12) was typical of a natural uncontaminated environment, with low salinity (23.7-190.4 µS/cm) and relatively low concentrations of dissolved oxygen (DO) (0.8 to 7.2 mg/L, and the mean of 3.5 mg/L). The highest DO value was possibly affected by pumping and purging of a 10-m deep piezometer GGEG5, installed in the Hawkesbury Sandstone (HBSS) on the side of the swamp. Surface water samples (n=6) were more oxidised as expected from 8.6 to 9.1 mg/L, and had low electric conductivity (EC) of 4.5 to 21.8 µS/cm. pH was acidic ranging from 3.9 to 6.0 for groundwater samples and pH 3.7 to 4.8 for surface waters. These results reflect the organic content of swamp sediments and decomposition.

Although, the groundwater was fresh, the major ion composition for GG, GGSW and CC swamps indicates domination by sodium-chloride (Na-Cl), followed by lesser contribution from calcium (Ca)and sulphate (SO_4) (Fig. 2) during May and October 2016. These periods include both dry and wet weather conditions, respectively. Bicarbonate (HCO_3) was calculated assuming cation balance equilibrium, with overall HCO_3 concentration low except for several groundwater samples. Groundwater samples have increased Ca concentration compared to surface water samples resulting from plagioclase dissolution. Plagioclase along with quartz is the main constituent of sandstone. Samples collected in May 2017 (average rainfall conditions) have same anion but different cation composition, with abundance of magnesium (Mg) in both surface and groundwater, and reduction in Na. Mg is highly mobile element, and can occur in sandstone due to weathering of aluminosilicates containing Mg. It needs to be noted that sampling in May 2017 occurred after substantial rainfall event (20 mm) which

resulted in mobilisation of Mg. However, there were no changes in naturally occurring element concentrations (Al, As, Mn, Zn, Sr, Ba) with p>0.05 (T-test for means) therefore no mobilisation in groundwater occurred as a result of rainfall event (with all concentrations above the level of reporting).

Stable carbon and nitrogen isotopes in organic matter

The results showed large variability in the isotopic composition: $\delta^{15}N$ ranged from -0.1 to 11.85 ‰ (average 4.7‰, standard deviation 3.1‰, n=35) (Fig 3a) while $\delta^{13}C$ ranged from -25.3 to 33‰ (n=31) where highest value

sample is the outlier possibly an error in measurement. The range of $\delta^{15}N$ is consistent with values from literature for pristine groundwaters (Heaton, 1986). $\delta^{13}C$ occurs in a much narrower range with an average of -27.8‰ and standard deviation 1.64‰. It is observed that the samples follow an enrichment trend in $\delta^{15}N$ with depth (from 0 to 12‰), which is followed by uniform trend towards the base of the swamp sediments at 120 cm depth. The reason for depleted values in the upper horizons can be explained by higher microbial activity compared to deeper horizons but also by presence of past fire events (Schmidt and Stewart, 2003).
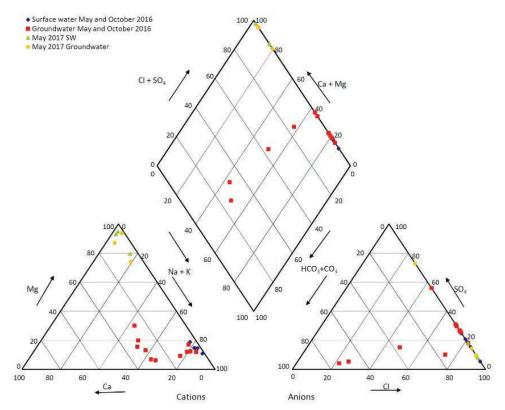

Figure 2 Percent cation (a) and anion (b) in groundwater samples from CC, GGSW and GG and surface water draining those swamps, samples include all sampling periods.

Table 1. Difference between swamps based on $\delta^{13}C$ and $\delta^{15}N$ (P-value is significance level derived from one-way ANOVA test).

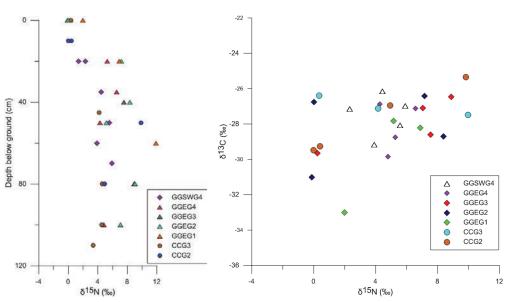| Swamp	CCG	GGEG	GGSW	p-value
$\delta^{15}N$ mean (SD)	4.26 (3.07)	5.61(3.54)	4.43(1.42)	0.49
$\delta^{13}C$ mean (SD)	-27.568(1.66)	-28.119(1.75)	-27.522(1.15)	0.58

Figure 3 *Plot of $\delta^{15}N$ with depth for GG, GGSW and CC swamps and nitrate values in surface and groundwater during dry (May 2016) and wet weather (October 2016) (a) and $\delta^{13}C$ and $\delta^{15}N$ of organic matter samples in swamp sediments from CC, GG and GGSW swamps, separated based on individual swamps (b)*

To investigate further this change in $\delta^{15}N$ with depth, a dual isotope plot of carbon versus nitrogen isotope is presented to determine if a discrete domain exists and define the source of material for the swamp (Fig. 3b). The results are compared to typical isotopic values from literature (Deegan and Garritt, 1997) which confirms that the swamps are typical of terrestrial environments. Depleted $\delta^{13}C$ values (around -29‰) occur in a narrow range and indicate landscape dominated by woody vegetation (Fry, 2006). The $\delta^{13}C$ values of organic samples from these swamps thus suggests sources influenced by woody vegetation, such as Boronia shrubs within the swamp. Although these isotopes show variability within each of the swamps. neither $\delta^{13}C$ or $\delta^{15}N$ were found to be considerably different between three swamps (p>0.05) (Table 1).

Stable oxygen and deuterium isotopes in waters

Preliminary results of stable oxygen and deuterium isotopes indicate that all surface, pore water and groundwaters were similar to rainfall, with some samples enriched due to evaporation. The local meteoric water line (LMWL) and weighted rainfall average shown in Fig. 4 is from Lithgow rainfall data ($\delta^2H=7.99\delta^{18}O+16.6$; Hughes and Crawford, 2013).

Pore water samples from GG and CC swamps collected in May 2016 after long dry period, plot below the LMWL indicating an evaporation trend (slope of 4.2 for CC and 4.6 for GG swamp). If the regression lines are extended for both swamps to LMWL, they fall within the rainfall range for Lithgow. Pore water samples collected in October 2016 after a relatively cool and wet period plot mainly along the LMWL, with samples from May 2017 (average rainfall conditions) plotting along and above the LMWL. These results from the wetter period reflect the rainfall signature as observed from mean weighted rainfall average. Additional more detailed work will quantify the relative importance of rainfall and shallow groundwater flow to the swamp water balance (David et al, 2018 in review).
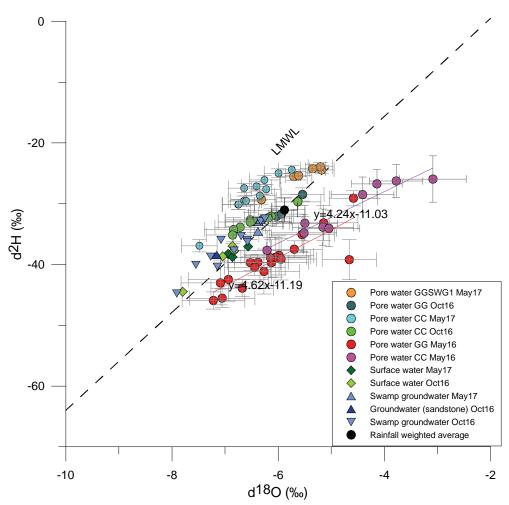
Figure 4 Isotopic composition of pore water, groundwater and surface water samples in three swamps

Conclusion

Multiple investigation techniques have provided some important insights into the sources of organic material and water to the swamp, and hydrogeoochemistry of the swamp in the natural condition. Depleted $\delta^{15}N$ indicates microbial activity in the upper peat and soil horizons, while $\delta^{13}C$ results point to terrestrial swamp environments with woody vegetation. Slightly higher groundwater EC compared to surface water, and slightly elevated calcium compared to surface water is indicative of short residence time within the swamp. Rainfall recharge changes the cation composition of natural groundwaters, however mobilisation of naturally occurring trace metals was not observed. Recharge to the swamp sediments is sourced from rainfall during wet periods, with evaporative losses during dry periods. Further detailed studies will quantify the relative importance of rainwater and groundwater in relation to peat and sediment within the swamp, and to the overall water balance during varying hydrological conditions.

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