UNRAVELLING THE SOURCES OF ACIDITY TO NSW ESTUARIES DURING FLOODS USING A NOVEL TRACER TECHNIQUE

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Abstract

The contribution of groundwater discharge to estuarine pollution has been poorly studied due to the expense involved using traditional assessment methods. Measuring groundwater inputs can be difficult as they are highly variable, both temporally and spatially, and essentially invisible. Studies over the past decade have shown that groundwater can be a significant source of nutrients and other dissolved constituents to aquatic ecosystems. This study uses 5 months of continuous ^{222}Rn (radon) and current velocity measurements to determine the relative contribution of groundwater discharge from a coastal acid sulphate catchment in the Tuckean Broadwater (northern NSW). Radon is a powerful tracer as it is greatly enriched in groundwater relative to surface water and the water column integrates the inputs of otherwise spatially-diverse groundwater pathways. The Tuckean Broadwater is a known source of acidity to the Richmond River Estuary, as a result of an extensive drainage network which lowers the water table, creating acid sulphate soils. The ^{222}Rn time series began in the dry season, when groundwater inputs were low, and captured a major rain event which raised the water table and dramatically increased groundwater discharge. Four distinct stages were identified during the time series (dry period, flood, post-flood and minor rains). The pH ranged from 7.2 to 3.6, and was significantly correlated with radon. There was an immediate drop in pH after the flood. Low pH conditions during the flood recession were sustained by increasing groundwater fluxes. This study demonstrates that using automated radon monitors combined with a hydro-phobic membrane is an effective method of assessing groundwater discharge and has shown that groundwater is a major source of acidity to this estuary. The tools described here can contribute to support management decisions in this and other acid sulphate catchments.

Introduction

In Australia a number of estuaries are affected by acidification as a result of drainage from coastal acid sulphate soil (CASS) landscapes. These discharges can trigger diseases in fish species (Johnston et al., 2003; Sammut et al., 1995), the destruction of native aquatic macrophytes (Sammut et al., 1994), mass mortalities of shellfish, crustaceans and fish (Sammut et al., 1996), and damage to infrastructure, leading to devastating financial consequences for local economies. Estimating how groundwater contributes to these issues is expensive and laborious when done by traditional means (i.e. modelling and hydrogeological surveys). Initial investigations using radon as a groundwater tracer in the Richmond River found that the Tuckean Swamp is a major source of acidity to the estuary and a regional groundwater hotspot (Santos et al., 2009b). Based on these findings, we have conducted five months of continuous observations in order to quantify groundwater discharge from the Tuckean Swamp during the transition from the winter dry season to the summer wet season, and a return to dry conditions. We report these time series data and illustrate how a new radon measurement technology can be used to link groundwater inputs to surface water quality even during extreme field conditions (i.e. a flood).

Coastal Acid Sulphate Soils

Holocene sulfidic sediments underlie large areas of coastal floodplain in eastern Australia (White et al., 1997). These sediments were formed in estuarine lowlands throughout the world following the last major sea-level rise (<10 000 years BP). Sulfidic sediments are formed in vegetated, low-energy tidal environments when sulfate from sea water is reduced to sulfides by microbes (Sammut et al., 1996). Sulfides react with iron in the sediments to form iron sulfides, the most common being iron pyrite (Macdonald et al., 2007; Sammut, 2000). The common name given to soils containing iron sulphides is coastal acid sulphate soils (CASS) (Macdonald et al., 2007). While maintained in a waterlogged and reduced condition, these sediments are stable and are termed potential acid sulfate soils (PASS) (Bierwirth and Brodie, 2005). If exposed to oxygen, which can be caused by either excavation or by the lowering of the water table via drainage or drought, oxidisation of the sulphides takes place (Indraratna et al., 1999). Once oxidised, these soils can generate large amounts of acidity, iron (Fe^{2+}) and aluminium (Johnston et al., 2003). For each mole of pyrite oxidised, four moles of acid are produced (Indraratna et al., 1999).

In the coastal zone of Australia, the impacts of disturbing CASS are a significant land and water management issue. Many of Australia's coastal floodplains have an extensive network of constructed drains, floodgates and modified water courses. These are designed to mitigate the impacts of floods and large rainfall events (Johnston et al., 2003) and have allowed agriculture and settlements to be established (White et al., 1997). Drainage of coastal floodplains has lowered the water table, allowing iron-sulphide minerals to oxidize, and creating large areas of CASS, which can result in the soil profile reaching an acidity level below a pH of 4 (Bierwirth and Brodie, 2005). The store of acid severely degrades the surrounding landscape and can mobilise trace metals and acidity, which are exported into adjacent waterways, particularly after rain events (Johnston et al., 2004). The concentration of toxic metals can exceed Australian water quality guidelines (Ferguson and Eyre, 1999). The main transport pathway of low pH water into surrounding water courses is shallow groundwater (Johnston et al., 2004). Information on groundwater's contribution to acidic conditions is therefore essential when deciding on the appropriate management actions.

Measurement of groundwater discharge

There are three basic methods used in the assessment of groundwater discharge: (1) modelling; (2) direct measurement with seepage meters; and (3) tracer techniques (Burnett et al., 2006b). Until the 1990's, the most common method for assessing groundwater seepage rates into surface water bodies has been the use of manual 'seepage meters' (Burnett and Dulaiova, 2003). Groundwater discharge studies in the past have utilised several different tracers (Peterson et al., 2010) or measurements of pore water profiles using multi-level piezometers to model advective flows (Cable and Martin, 2008). Although the use of combined methods of determining groundwater discharge offers an elegant approach, financial and logistical constraints often restrict researchers, forcing them to limit the size of the area studied (Burnett et al., 2010; Peterson et al., 2010).

In the past decade, a range of natural tracer techniques have been extensively studied in order to find an approach that enables larger scale projects to be performed without the cost constraints of traditional methods. A series of intercomparison experiments performed by Burnett et al. (2006a) demonstrated that radon (^{222}Rn) is an effective groundwater tracer, and used in isolation, produces results very close to studies using multiple methods. An important advantage of using tracers over other traditional methods of determining groundwater discharge is that the water column integrates the inputs of otherwise spatially-diverse groundwater discharge pathways (Burnett et al., 2006a).

Commonly used methods for quantifying fresh groundwater discharge such as flow equations and hydrograph separation techniques, have limitations caused by their inherent assumptions. For example, flow equations which use analytical solutions of Darcy's Law for groundwater flow in porous media often assume that the aquifer system is homogenous. However, aquifers are rarely homogenous with hydraulic conductivities varying several orders of magnitude over a very short area. Determining the varying hydraulic conductivities that occur throughout the aquifer is generally difficult (Burnett et al., 2001; Davie, 2003). This is particularly the case in areas containing CASS, where hydraulic conductivities can vary orders of magnitude (Johnston et al., 2009).

Hydrograph separation techniques estimate groundwater contribution to streamflow by separating a stream hydrograph into the different runoff components (Davie, 2003) and then assuming that baseflow represents groundwater discharge to streams. Commonly used hydrological water balances use relatively simple 'bucket' models that regard the difference between rainfall, streamflow and evapotranspiration as being groundwater. These methods can generate uncertainties larger than the estimated groundwater discharge (Burnett et al., 2006a; Cook et al., 2003). The use of radon as a natural tracer can give confidence in discharge estimates, as several of these assumptions do not need to be made. This can be particularly important at CASS sites. While not without limitations, combining the use of a natural tracer with a mass balance approach may reduce uncertainty when estimating the contribution of groundwater discharge to hydrologic budgets. This information enables groundwater resource managers to make more informed decisions regarding the protection of environmental flows and determining sustainable limits of groundwater extraction (Cook et al., 2003).

Radon as a groundwater tracer

Radon is an inert gas that is produced from the decay of uranium found in sediments and rocks. Radon is produced via the radioactive decay of Radium-226 (^{226}Ra) ($t_{1/2}$ = 1600y). Any groundwater in the aquifer which is in contact with sediments and rocks is enriched in radon (Dulaiova et al., 2008). Several researchers have demonstrated that ^{222}Rn is an effective tracer because it is enriched by approximately 2-4 orders of magnitude in groundwater relative to surface water (Santos et al., 2008), it is chemically conservative (Cable et al., 1996), and has a short half life ($t_{1/2}$ = 3.8d) (Cook et al., 2003). When groundwater containing radon discharges to surface water, radon immediately begins to exit the system due to atmospheric evasion and radioactive decay. As a result, high radon concentrations are only found in close proximity to the discharge source, and for short distances downstream of such locations (Cook et al., 2006).

The temporal change in the radon mass (inventory) in the water column can be explained by the balance between its sources and sinks. In order to quantify groundwater discharge rates, we applied a non-steady state mass balance described in detail elsewhere (Peterson et al., 2010). Daily averages of each parameter were used. The model accounts for all radon sources and sinks: atmospheric evasion, radioactive decay, mixing with low concentration waters, diffusion, and ^{226}Ra production. Any radon inputs still unaccounted for after applying the model is attributed to groundwater. By dividing the obtained radon fluxes into surface waters by the groundwater endmember concentration, we estimate that groundwater advection rates in units of m^3s^{-1} (or cm day^{-1} if the drain area is taken into account) during the deployment.

Traditionally using ^{222}Rn as a tracer has required the collection of grab samples followed by the analysis of samples in the laboratory using radon emanation or liquid scintillation techniques (Burnett and Dulaiova, 2003). Quantifying groundwater discharge using ^{222}Rn grab samples can be expensive and laborious (Burnett and Dulaiova, 2003). Burnett and Dulaiova (2003) demonstrated that a 'continuous' radon-in-air monitor, modified to detect radon-in-water, can provide accurate measurements of ^{222}Rn activities in the water column. This system allows researchers to quickly and rapidly identify areas of significant groundwater discharge without the need for samples to be analysed in the laboratory (Peterson et al., 2010). When used in conjunction with a modelling approach this has been proven to be an effective method for quantifying groundwater discharging into surface receiving bodies of water (Burnett et al., 2007). To date, there have been no studies utilising this new technology to determine the contribution of groundwater discharge to acidification in coastal waters.

The continuous radon monitor has been successfully used to quantify radon fluxes at fixed moorings and when used with current meter measurements, to quantify groundwater fluxes in tidal rivers (Peterson et al., 2010). The system can also be used to perform radon surveys by mounting it on a boat travelling at low speeds (Burnett et al., 2010). This allows researchers to quickly make quantitative comparisons over large areas and detect areas of high groundwater inputs (Burnett et al., 2010).

Previous studies (Burnett and Dulaiova, 2003; Burnett et al., 2010; Peterson et al., 2010; Santos et al., 2009a) utilising automated radon measurements have used an air-water exchanger (Figure 1a) connected to a RAD7 radon-in-air monitor (Durridge, USA). Utilising the air-water exchanger connected to a RAD7 has recently been used by several researches conducting short term (~24 hour to a few days) time series measurements. Radon is measured from a continuous stream of water passing through the air-water exchanger that distributes radon from the running water to a closed air loop (Dulaiova et al., 2010). The RAD7 has been shown to detect radon level changes in the loop every 10-30 mins, depending on the radon concentration (Burnett and Dulaiova, 2003; Burnett et al., 2010; Peterson et al., 2010). The disadvantage of this configuration is the requirement of a power source (i.e. 12 V batteries) to pump water to the exchanger.

To overcome the limitations of using the air-water exchanger for extended periods when in a remote location, the newly developed Radon-in-Water Probe (Durridge, USA) (Figure 1b) could be useful as an alternative. This system does not require water to be pumped into the system, therefore eliminating the risk of flooding and the need for a separate water pump. The membrane is a semi-permeable tube mounted on an open wire frame. It is placed in a closed loop with the RAD7, which is equipped with its own air pump. When the probe is lowered into water, radon diffuses through the membrane until the radon concentration in the loop is in equilibrium with the water. The air stream passes through a cylinder of desiccant, prior to entering the RAD7, to ensure no moisture enters the detector.

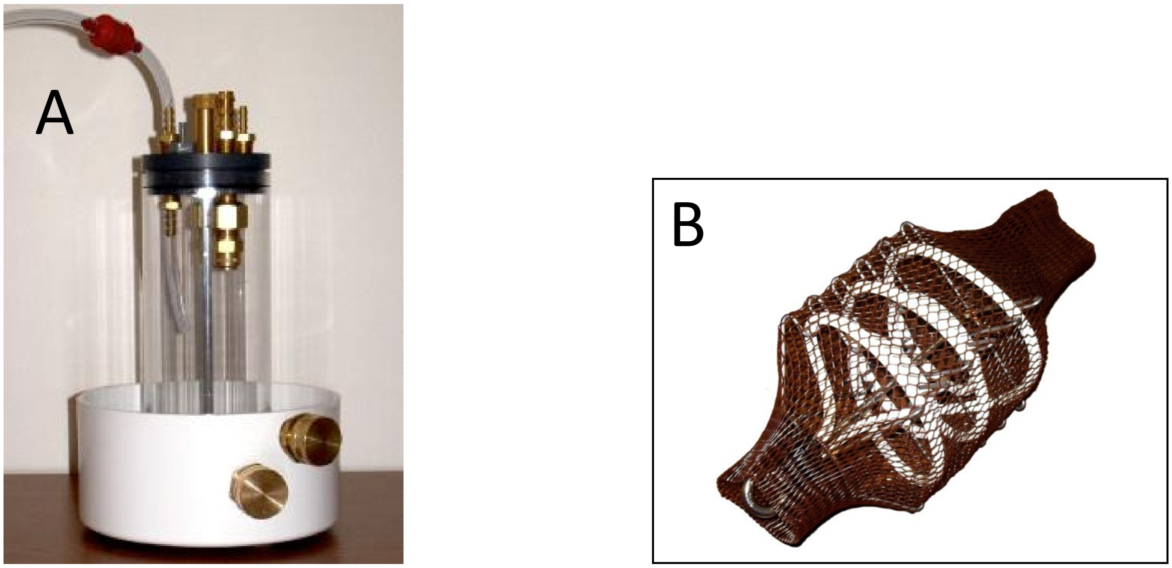

Figure 1: Different radon extraction systems for measuring ^{222}Rn in the water column when connected to a RAD7 radon monitor. (A) The air-water exchanger responds to ^{222}Rn concentration changes between 5 and 30 mins but consumes a car battery every ~12 hours and requires daily attention to avoid flooding and damaging the RAD7. (B) The Radon-in-Water Probe (membrane) consists of a hydrophobic tubing that diffuses ^{222}Rn from the water column. The membrane has a response time of 3-4 hours but does not require power and constant attention. The membrane approach is thus ideal for long-term deployments in remote river systems.

The Tuckean Swamp

Prior to European settlement, Tuckean Swamp formed a large wetland that was tidally linked to the Richmond River by the Tuckean Broadwater (Figure 2). The first drain was dug in the Tuckean Swamp in 1888 (Wolf, 2002). Since then, the swamp has been progressively cleared and drained, with the majority of drains constructed between 1912 and 1915. This resulted in a change in the environment from a boggy swamp to relatively dry land suitable for agriculture. Pressure from landholders after several large floods in the 1970's resulted in the construction of a tidal barrage (Baggotville Barrage) approximately 4 km upstream of where the Tuckean Broadwater meets the Richmond River. The Barrage allowed floodwaters downstream and prevented tidal flow upstream (Taffs et al., 2008).

In order to quantify the volumetric groundwater inputs into the Tuckean Broadwater, the radon system was deployed about 50 metres downstream of the Bagotville Barrage (Figure 2). A submersible multi-parameter water quality data logger installed at the site by Richmond River County Council recorded hourly measurements of dissolved oxygen, pH and salinity, and was calibrated fortnightly. Water level, current velocity, salinity and temperature were continuously recorded with appropriate loggers.

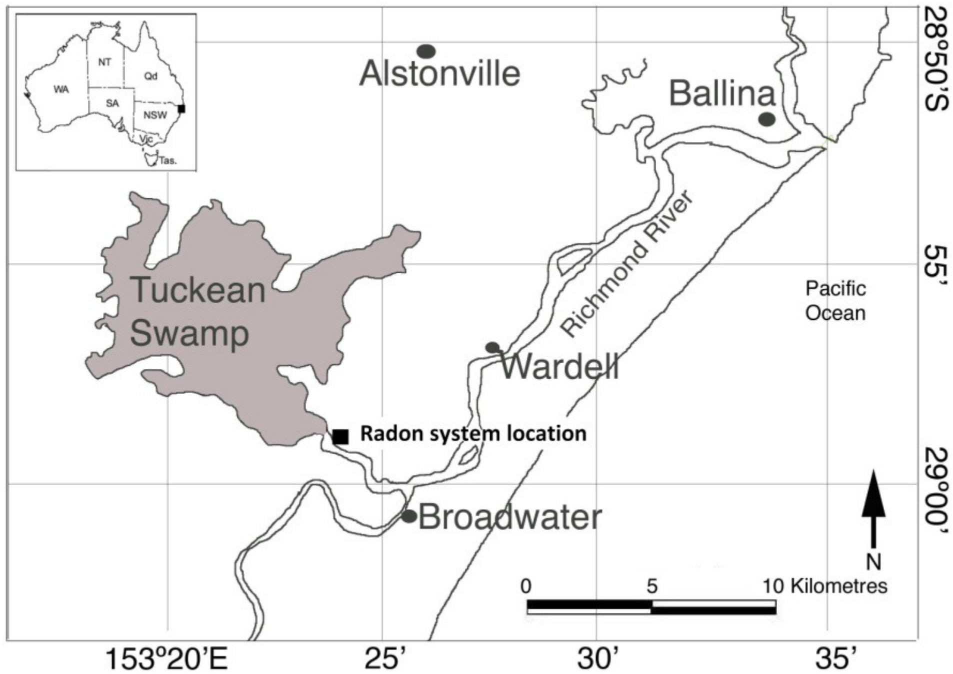

Figure 2: Location of Tuckean Swamp and the radon system series location.

Long term groundwater monitoring using radon as a tracer

The long term time series covered nearly 5 months, with a total of 133 days of radon and water quality data and 117 days of current data. A large rainfall event occurred during the time series (214 mm in 24 hours), which created an immediate decrease in pH, followed by a peak in groundwater discharge. Figure 3 shows the information obtained, with four distinct stages identified by the vertical lines (dry conditions, flood, post flood and minor rains), and Table 1 provides descriptive statistics of the data.

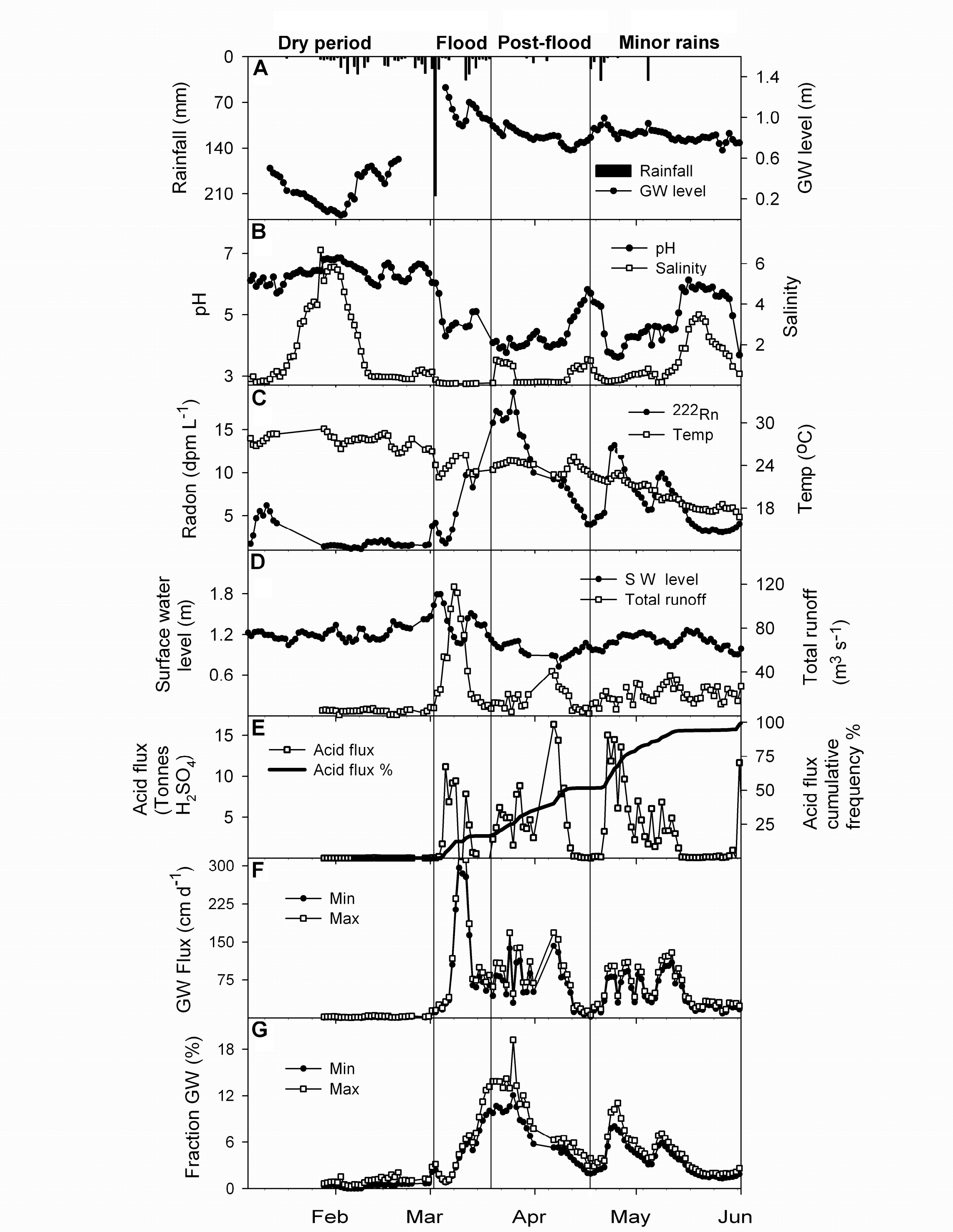

Figure 3: Daily averages of selected variables between 6 January and 1 June 2010. (A) Rainfall and shallow groundwater level; (B) pH and salinity; (C) radon and surface water temperature; (D) surface water level and total runoff; (E) acid flux and the acid flux cumulative frequency; (F) groundwater flux; and (G) groundwater flux as a percentage of total runoff. The vertical lines represent the four stages observed during the time series.

Table 1: Descriptive data of information collected during the time series deployment.

	1. Dry	2. Flood	3. Post-flood	4. Minor rains
Dates	6/1 to 1/3	2/3 to 17/3	18/3 to 17/4	18/4 to 1/6
Total rainfall (mm)	259	337	24	117
Av. Salinity	1.84	0.10	0.53	1.15
Av. GW level (m)	0.33	1.06	0.81	0.83
Av. radon (dpm L^{-1})	2.3	7.3	11.5	6.4
Max radon (dpm L^{-1})	6.2	15.3	19.3	13.2
Av daily runoff (m3)	375458	4104160	1218609	1687408
Av daily GW flux (m3)	1727	145079	81554	60191
Daily GW flux (%)	0.46	3.53	6.69	3.57
Daily acid flux (T H_2SO_4 day^{-1})	0.01	3.2	4.4	3.4

Over 330 mm of rain fell in the Tuckean catchment over 13 days from 2 March to 17 March, including 213 mm in one day on 2 March. This rain was sufficient to inundate the swamp for approximately one week. The surface water height and the groundwater table height peaked two days after the large rain event. There was an immediate drop in pH from 6.05 to 4.31 in the first four days of the flood stage. Radon concentrations steadily increased from 2 to 15 dpm L^{-1} seven days after the rain event. The fraction of groundwater steadily increased during this period, while total discharge steadily decreased and pH remained low.

Rainfall only occurred on three days during the post flood period with a total of only 24 mm recorded. During the post flood period, the highest fraction of groundwater (as a percentage of surface flow) peaked at 12% or 19% using the minimum and maximum approach respectively. This period coincides with the highest radon concentration (19 dpm L^{-1}) and a fall in pH of 0.54 from 4.63 to 4.09 when radon activity peaks. A further 72 mm of rainfall in 5 days defined the start of the minor rains stage. A spike in the groundwater fraction and radon concentration during the minor rains period resulted in the lowest pH value (3.62).

The groundwater flux peaked seven days after the significant rain event (296 cm day^{-1}), and was heavily influenced by the increased current recorded. In the absence of surface runoff during the post flood period, the average daily pH fell to 3.77 as the groundwater fraction reached its peak. Towards the end of this stage, radon activities and the groundwater fraction decreased, with a corresponding increase in pH to 5.82. This implies that during this time, groundwater was the source of acidity rather than surface water. This trend is repeated during the minor rains, with a sudden marked increase in the groundwater fraction coinciding with pH falling to its lowest level, adding further support to groundwater being the source of acidity to the Tuckean Broadwater.

The significant correlation (r^2=0.65; n=119; p>0.01) between radon and pH during the time series (Figure 4) implies that groundwater is a major driver of surface water pH in the Tuckean Broadwater. The removal of eleven dates which correspond with heavy rains in the Swamp increases the correlation coefficient from r^2=0.65 to r^2=0.77. A decrease in pH was observed immediately following the rain, before the increase in the groundwater flux.

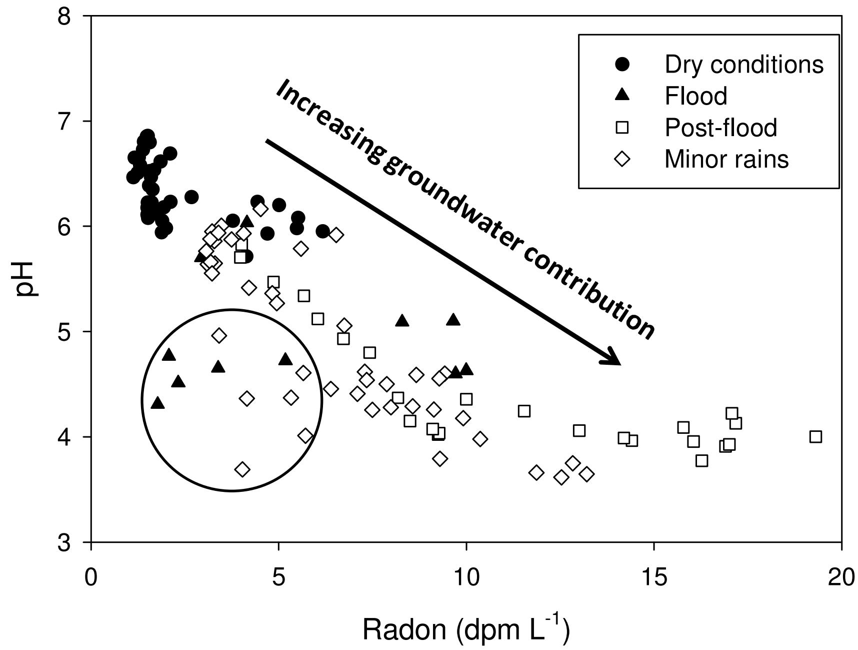

Figure 4: Scatter plot showing the relationship between radon and pH. Each point represents an integration of 24 hour periods. The circled outliers represent days immediately after the large rainfall causing the flood and the minor rains stage defined in Figure 3. Resuspension of bottom sediments and surface runoff are the likely source of acidity during those days.

Sources of low pH waters other than groundwater

There are three possible sources of low radon and low pH associated with the eleven outliers shown in Figure 3:
1) The 'first flush phenomenon' observed by Macdonald et al. (2007) which resulted in the mobilization of salts present in the upper soil profile. Due to the short residence time of the flood waters in the upper soil profile in contrast to the ingrowth time of radon, there may be insufficient time for radon ingrowth, resulting in low pH and low radon values.

2) The remobilization of monosulfidic black ooze (MBO). MBO deposits are found in areas containing CASS, and can be scoured by the strong currents created by floodwaters. This release of acid products has been reported by Macdonald et al. (2007) in a subcatchment of the Tweed River to lower pH levels to 3.5. It has been conservatively estimated that Tuckean Swamp drains contain 200 000m^3 of MBO (Sullivan and Bush, 2000 in Bush et al., 2004).

3) Overland sheet flow, which is the exporting of acidity from already inundated areas of very low relief. It was observed during this study that large sections of the swamp remained inundated for long periods even after only moderate rainfall. The pH of this overlaying water was observed to be as low as 3.7 in some areas. Sammut et al. (1996), in

a study of the Tuckean Swamp, observed that surface water with a mean pH of 3 inundated 40% of the swamp after a flood event. After periods of heavy rain, when overland sheet flow is occurring, low pH water from already inundated areas is exported into drains.

Acid exports

The estimated acid flux ranged from 0.1 and 16.3 tonnes of H_2SO_4 a day, assuming that all H^+ is present as dissociated H_2SO_4 (Sammut et al., 1996). During the time series deployment when current data is available, it is estimated that 320 tonnes of acid was exported from the swamp, with the highest average discharge occurring during the post flood period when groundwater discharge controls surface water pH (Table 1). The estimated annual export of acid from the Tuckean Swamp is estimated to be 332 kg H_2SO_4 ha^{-1} $year^{-1}$, assuming that the CASS area is 3000 ha.

The export of acid to the Tuckean Broadwater is primarily driven by the H^+ concentration. This can be seen in Figure 3, with acid exports being highest when pH was low. The highest daily average acid flux occurred during the post-flood stage, which was also the stage that had the highest daily average groundwater flux and radon activity. During the later stage of the post-flood period, the acid flux approaches zero, coinciding with a drop in radon activity and the groundwater flux. Approximately seven days into the minor rains stage, radon activity and the groundwater flux experienced a spike, with an immediate corresponding increase in the acid flux, providing further evidence of groundwater being the main source of acidity.

Our estimated production of acid exports (~332 kg ha^{-1} $year^{-1}$) is comparable to the estimates of Sammut et al. (1996) of ~300 kg ha^{-1} $year^{-1}$ for the Tuckean Swamp. Estimates of acid production from other CASS sites in Australia have shown similar rates of production. A study by Wilson et al. (1999) in the another artificially drained floodplain, located approximately 75 km north of the Tuckean Swamp, estimated acid production to be 276 kg ha^{-1} $year^{-1}$. It has been estimated by Sammut et al. (1996) that the Tuckean Swamp contains 1.3 x 10^6 tonnes of sulphuric acid. Using this estimate, and assuming no further oxidisation of pyrite is occurring, the Tuckean Swamp will continue exporting acid products to waterways for the next 1000 years.

Conclusion

Many authors (e.g. Sammut et al. 1996; Wong et al. 2010) have suggested that groundwater discharge is the source of acidity to the Richmond River Estuary. This study is the first to quantify the groundwater flux from the Tuckean Swamp and the first to use radon to quantify groundwater inputs from a CASS catchment over monthly time scales. This study successfully captured the transition from the dry season to the wet season and back to dry conditions, including a flood event that caused significant inundation of the Swamp. There was an immediate drop in pH after the flood, which may be attributed to surface water interactions with acid products. The radon concentration started to increase 7 days after the flood, with a further decrease in pH coinciding with the highest groundwater flux. This trend was repeated during the minor rains, with a spike in groundwater discharge coinciding with the lowest pH recorded during the study.

Continuous radon time series measurements have provided useful insights into the drivers of low pH conditions in the Tuckean Broadwater. The significant correlation between high radon and low pH, combined with the sustained low pH conditions experienced for several weeks in the absence of surface runoff, indicate that groundwater is the main source of acidity in the Tuckean Broadwater. This information is essential for land and water managers when making decisions regarding management of CASS priority areas.

As groundwater can be a major driver of surface water quality, management decisions in other CASS sites would benefit from similar studies to enable decisions to be made in a proactive, rather than reactive way. The advent of portable radon-in-air monitors is now allowing rapid, inexpensive assessment of groundwater discharge, and decreasing uncertainty in hydrologic budgets.

Acknowledgements

This project is supported by the Hermon Slade Foundation. Bruce Heynatz kindly allowed us to deploy our radon monitor, and Maria Matthes allowed us to install a monitoring well on their respective properties in the Tuckean Broadwater. Michael Wood and the Richmond River County Council supplied the water quality data used in Figure 3. We thank Ben Shepherd and Douglas Tait for assistance during field work and the NSW Office of Water for allowing the use of monitoring bores. The author would like to thank George Lewin for his continued support of the George Lewin Honours Scholarship.

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