

IS SUBMARINE GROUNDWATER DISCHARGE AN OVERLOOKED SOURCE OF NUTRIENTS, ACIDITY, AND ANOXIA TO NORTHERN NSW ESTUARIES?

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Abstract - Estimating how submarine groundwater discharge (SGD) contributes to estuarine acidification, deoxygenation and eutrophication can be extremely expensive and laborious if done by traditional means (i.e., modelling). We are using radon (^{222}Rn) to quantify SGD and its relative contribution to those environmental problems in the Richmond River Estuary, northern NSW. Naturally-occurring ^{222}Rn is an excellent natural tracer of groundwater because it is conservative and typically 2-3 orders of magnitude higher in groundwater than surface waters. In addition, new technology has allowed rapid and inexpensive field measurements. Our results indicate that acidic waters are entering the estuary via groundwater pathways. A radon survey along a 120-km long segment of the Richmond River demonstrates that the Wilsons River and Tuckean Swamp are areas of preferential groundwater inputs. Intensive measurements in the Tuckean Broadwater imply that groundwater inputs are highly variable over hourly and seasonal time scales and related to surface water pH. SGD rates in the Shaws Bay Lake (Ballina) were estimated to be $6.9 \text{ cm}^3/\text{cm}^2/\text{day}$. Future investigations should separate the relative contribution of surface- and groundwater-derived inputs of nutrients, trace metals and acidity. As the management approach at groundwater- and surface water-dominated sites will be different, radon data can help local Councils to manage the estuary from a proactive rather than reactive perspective.

Introduction

A number of Australian estuaries are severely and recurrently impacted by acid sulphate soil drainage, deoxygenation, and eutrophication. We suspect that submarine groundwater discharge (SGD) seeping out along channels and banks is a major but overlooked source of nutrients, anoxia and acidity to Australian estuaries. Estimating how groundwater contributes to these issues is extremely expensive and laborious if done by traditional means (i.e., modelling and hydrogeological surveys). We are using ground-breaking radon (^{222}Rn ; a powerful groundwater tracer) measurement technology to quantify SGD and its relative contribution to those environmental problems in the Richmond River Estuary, northern NSW.

The Richmond River Estuary is one of the most anthropogenically impacted estuaries on the east coast of Australia and surrounded by large areas of coastal acid sulphate soils. During summer flooding can result in fish kills, devastating fishing and tourism industries. The fish kills occur a few weeks after the flood peak, presumably when flood waters have receded and most of the surface runoff has flushed to the ocean. We suspect that SGD is highest several days after the flood peak and may be a causative agent for the fish kills (Figure 1). By performing continuous ^{222}Rn measurements, we can quantify the total and relative groundwater flux during and after floods, during seasonal de-oxygenation events, and in the

dry season. This information will help to identify the role that SGD has on the physical, chemical and biological conditions in the Richmond River Estuary.

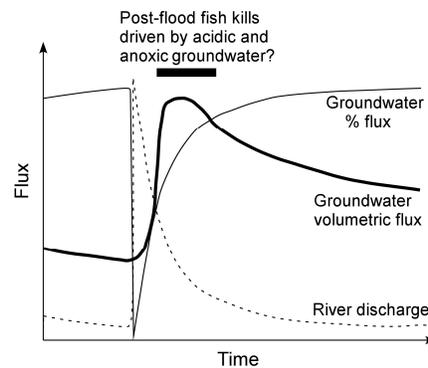


Figure 1: The theoretical temporal variability of groundwater inputs into northern NSW estuaries.

In this paper, we discuss the importance of SGD into coastal environments and how it can influence the water quality of the Richmond River Estuary. We report data obtained on two occasions: (1) an initial survey to map the distribution of radon along the river and possible groundwater hotspots; and (2) a 24-h time-series deployment at two fixed sites to quantify SGD rates.

Environmental problems in the Richmond River Estuary

Coastal acid sulphate soils (CASS) are extremely common in floodplains throughout Australia and in the Richmond River catchment. CASS often have a near-surface sulphide layer overlain by a pronounced sulphuric horizon (Sammut et al., 1996). They can be harmless if the local hydrology is not disturbed. However, thousands of km of artificial drains have been constructed on Australian's floodplains (Johnston et al., 2005), maximising the impacts of CASS by releasing large amounts of sulphuric acid to nearby waters. Acidic waters mobilize toxic metals and nutrients to concentrations that exceed by far Australian water quality guidelines (Ferguson and Eyre, 1999). As a result, commercial and ecologically-significant species are dramatically affected (Dove and Sammut, 2007).

While acidification is a chronic problem that may occur throughout the year, deoxygenation events seem to be more episodic and acute (Lin et al., 2004). In 2001, for example, a major event killed most of the life in the Richmond River estuary. This resulted in the closure of all fishing for about 6 months and a 30% downturn in the economy of several coastal towns in northern NSW, including Ballina.

It is unclear whether the transport pathways of acidic and anoxic water are associated with surface or subterranean fluxes. Nevertheless, deoxygenation events originate in the agricultural drains surrounding estuaries that are thought to be groundwater-dominated (Johnston et al., 2009). Several authors speculate that groundwater can account for a significant fraction of the acid flux even if the groundwater contribution to total drainage is

low (Cook et al., 2000; Macdonald et al., 2007). However, no investigation has yet quantified the relative contribution of groundwater and surface runoff at CASS sites.

Groundwater residence times, in contrast to surface runoff, can range from years to decades. For example, groundwater contaminated after the second world war (when fertilizer use and sewage disposal were not a concern) supplies the nitrogen that fuels widespread modern harmful algal blooms in Florida, USA (Hu et al., 2006). Similar problems may occur in northern NSW where sugar cane plantations can be a major source of nitrate to groundwaters that drain to nearby estuaries. The removal of riparian vegetation and dredging of drains may further enhance the problem.

Global significance of SGD

SGD is defined as any flow of water from the seabed to coastal areas, regardless of fluid composition or driving force. It thus includes both a terrestrial component of fresh groundwater and an oceanic component of recirculated seawater (Burnett et al., 2006; Santos et al., 2009b). Fresh groundwater discharge is thought to be <10% of the total freshwater flux to the oceans (Burnett et al., 2006). The input of nutrients and contaminants via groundwater pathways, however, may be much more important because nutrient concentrations in groundwater are often much higher than those in river and rain water.

In the last few years, the biogeochemical implications of SGD into coastal environments are becoming increasingly recognized. For example, work in the USA (Santos et al., 2008a) and Korea (Kim et al., 2008) show that groundwater-derived nutrient inputs into coastal environments are comparable or higher than regional river inputs. Global river-derived nutrient inputs into the ocean have tripled since the 1970's (Smith et al., 2003). Little is known, however, about how much of this increase is derived from groundwater inputs into rivers and estuaries.

As human activity on coastal watersheds increases, the role of groundwater-borne nutrients to the receiving waters is expected to increase (Bowen et al., 2007). SGD-derived nutrient inputs into the coastal ocean may be a key factor driving harmful algal blooms (Hu et al., 2006; Hwang et al., 2005; Lapointe et al., 2005; Lee and Kim, 2007). High N:P ratios in contaminated groundwater may even drive the global coastal ocean towards P-limitation and change the present N-limited coastal primary production (Slomp and Van Cappellen, 2004).

Measuring SGD in areas where the river flux may dominate can be extremely difficult. River discharges are usually gauged upstream of the tidal reaches. Therefore, regional and global estimations of river water and nutrient fluxes into the ocean often neglect additional inputs occurring downstream of gauging stations. Because even low groundwater volumetric inputs may be biogeochemically significant, overlooking SGD may significantly underestimate global and regional nutrient fluxes into the coastal ocean. The natural topography of estuaries results in groundwater flow lines converging towards the river mouth. We thus suspect that groundwater inputs into estuaries downstream of the gauging stations may contribute to both water and dissolved species fluxes into the ocean.

Approaches to estimate SGD

There are 3 approaches to quantify SGD: (1) seepage meters, (2) numerical modelling, and (3) geochemical tracers. Seepage meters are cut-off ends of drums that are pushed into the bottom sediment. A plastic bag is often used to collect the seeping water, allowing one quantify to volume of groundwater discharging at the deployment site. Even though seepage meters may provide useful information, some issues limit their use. First, hydrodynamic artefacts related to the deployment of a physical structure may mislead interpretations (Cable et al., 2006). In addition, as an individual seepage meter covers a very small area (usually $\sim 0.025 \text{ m}^2$), several seepage meters are needed if spatially-relevant information is to be obtained. This is usually not feasible.

Numerical models are the typical approach to study groundwater-surface water interactions (Savenije, 2009). They are fed by hydrogeological data and often assume homogeneous and steady state conditions. However, coastal aquifers are inherently heterogeneous and temporally dynamic. Tidally-driven subsurface fluxes are often ignored in model estimates. However, tidal pumping has been found to enhance the seepage of groundwater in coastal environments (Santos et al., 2009b). This process is likely to be significant in Australian (sub-) tropical tidal rivers.

The main advantage of using geochemical tracers is that the water column integrates the signal coming into the system from various pathways. Smaller scale variations are smoothed out. In contrast to models that often assume that groundwater discharge is driven only by hydraulic gradients, tracers such as ^{222}Rn integrate all the mechanisms driving seepage and thus influencing surface water quality. These include tidal pumping, density inversions, currents and waves, and bioirrigation.

The new ^{222}Rn measurement technology used in this study allows us to quantify processes ranging in time scales from hours to months. Radon is an excellent natural tracer of groundwater. It is typically orders of magnitude higher in groundwater than surface waters, providing the source strength required (Santos et al., 2008b). As a noble gas, ^{222}Rn is biogeochemically conservative, making the assessment of sources and sinks within a water body relatively easy (Burnett and Dulaiova, 2003).

Quantifying SGD by traditional means (seepage meters and numerical modeling) is a time-consuming and costly process. As a result of this situation, most coastal water quality assessments in Australia and worldwide are being performed using less than optimum data for possible groundwater inputs or even neglected groundwater inputs altogether. The new radon measurement technology we are using (Dulaiova et al., 2005) has the potential to revolutionize the way groundwater is accounted for in coastal water quality assessments, as it is an efficient, inexpensive and rapid method to assess groundwater inputs (Burnett et al., 2009).

Radon survey along the Richmond River

Our automated radon measurement technique allows one to survey a water body from a small boat and obtain a radon-in-water measurement every 5-15 minutes, depending upon the concentration of ^{222}Rn . By performing radon surveys along individual streams, one can quickly make qualitative comparisons among different segments of the streams and rank them in terms of their probable groundwater contributions. While one cannot establish a simple one-to-one relationship between radon concentration and groundwater discharge because of complicating factors that require further examination (such as different source waters, current velocities, atmospheric evasion, etc), radon is clearly a useful tool for exploratory purposes (Peterson et al., 2009b; Santos et al., 2008b). Employing such an

approach allows one to target selected individual water bodies for more extensive studies in order to quantify the groundwater input rates.

We have performed a high resolution, continuous radon survey (Figure 2) along a 120-km long river segment (from Ballina to 20-km upstream of Lismore) in June 2009. The survey took only three days to be accomplished and allowed us to identify the areas where groundwater inputs are qualitatively more important. The radon concentrations in the Richmond River immediately upstream of Coraki are much lower than in the Wilsons River. In Lismore, the radon activities in the Wilsons River are about 40% higher than in the Leycester Creek. This implies that groundwater inputs are relatively more important in the Wilsons River than in several of the other segments investigated. The Lismore City Council is currently pumping water from the Wilsons River upstream of Lismore for supplying the local population. The high radon concentrations observed at this area suggest that nutrients, pathogens, and other contaminants may enter the public supply area via groundwater pathways.

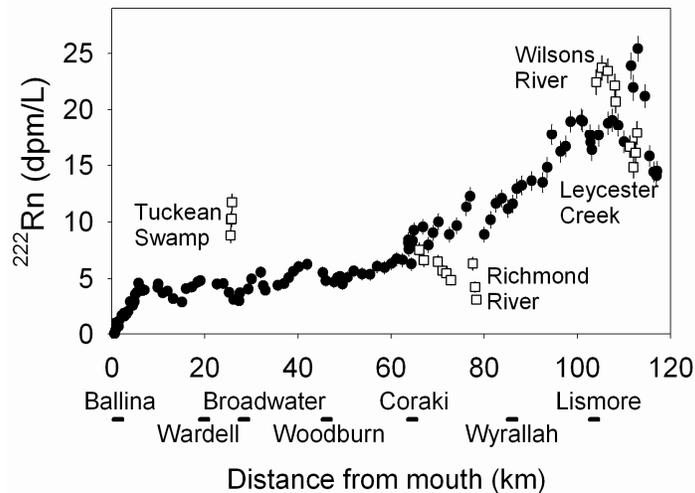


Figure 2: Radon survey along the Richmond River from Ballina to approximately 20-km upstream of Lismore. The closed circles represent observations along the main river channel, while the open squares are data from tributaries briefly “sniffed” during the survey.

In the lower Richmond River, a radon hot-spot in the Tuckean Broadwater coincided with the main source of low pH water to the Richmond River Estuary (Figure 3). This implies a link between groundwater inputs and surface water quality at this area. The Tuckean Swamp is probably the most significant source of low pH, deoxygenated water to the estuary after floods. Previous studies (Ferguson and Eyre, 1999; Sammut et al., 1996) have highlighted that surface water pH can be <4 at this area, especially a few weeks after floods when groundwater inputs are probably the highest. While our preliminary data is not enough to quantify the relative contribution of surface and subterranean acidity fluxes at this area, they highlight the need for more specific experiments.

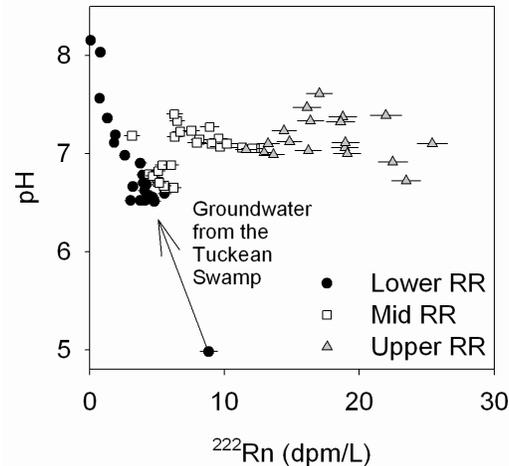


Figure 3: Relationship between radon concentration and pH during a survey of the Richmond River in June 2009. The river was separated in three sections: (1) Lower RR: from Ballina to Broadwater; (2) Mid RR: from Broadwater to Wyrallah; and (3) Upper RR: from Wyrallah to upstream of Lismore. Groundwater inputs from the Tuckean Swamp seem to control river pH in the lower Richmond River, while no relationship between radon and pH were observed in the mid and upper segments.

Time series measurements in the Tuckean Broadwater

While the radon survey provided qualitative information about groundwater inputs into the river and its estuarine area, time series observations can be extremely useful to quantify the fluxes and gain insights into its dynamics. We have performed a 24-h time series deployment in the Tuckean Broadwater about 50-m downstream of the Baggotville Barrage on 14 September 2009 (Figure 4). Our radon system was moored adjacent to a water quality monitoring station maintained by the Richmond River County Council. The area is a large estuarine habitat which is prone to severe acidification from runoff emanating from drains in the Tuckean Swamp. Monitoring performed in the 1990's indicated that large rain events flush the Broadwater with fresh acidic water (pH ~ 3.5) from the Tuckean Swamp. During the dry season, salinities rise up to 15 and pH stabilizes at about 7 (Ferguson and Eyre, 1995).

The radon concentrations were remarkably variable for a nearly-stagnant system. We were able to detect a tidal radon signal even though the tidal range was only <20 cm. Relatively high radon concentration were observed at low tide. The values at high tide were about 60% lower than at low tide. A similar tidal signal has been observed at other systems (Peterson et al., 2009a; Santos et al., 2009a) where groundwater inputs dominate radon sources in surface waters. The other possible radon sources (diffusion from the sediments and decay of its parent isotope ²²⁶Ra) generate a nearly steady-state temporal distribution which is clearly not the case at the Tuckean Broadwater.

There are two processes that are likely to act together to explain the radon temporal variability during this tidal cycle:

- (1) Hydraulic gradient-driven SGD: If the groundwater table is constant, the tidal oscillations in the Broadwater will lead to steeper hydraulic gradients at low tide which in turn would increase the amount of groundwater seepage at low tide;
- (2) Tidal pumping of surface water into the aquifer: In this case, surface water infiltrates the aquifer at high tide, changes its chemical signal, and discharges at low tide. This process was described for a swamp connected to the nearby Clarence River (Johnston et al., 2005). Even though tidal pumping does not represent a source of new groundwater into the estuary, biogeochemical transformation taking place within the aquifer would represent a net source of several chemical species, including H^+ , nutrients and trace metals.

Regardless of which process is driving higher groundwater inputs at low tide, it is clear that acidic waters are entering the estuary via groundwater pathways. The inverse relationship between radon and pH shown in Figure 4 highly supports this idea and is consistent with the data obtained during the survey (Figure 3). The Broadwater average pH during the time series deployment was about 6.4, representing much higher values than was observed in June during the radon survey (pH <5). Radon concentrations during the survey near the mouth of the Broadwater were nearly 10 dpm/L, a value 4-fold higher than during the time series deployment.

While temporal changes in pH associated with rainfall patterns are well documented for the area (Ferguson and Eyre, 1995), our recently-obtained radon data imply a previously overlooked tidal and seasonal link between groundwater inputs and estuarine acidification. Modelling the radon distributions to quantify the volumetric groundwater inputs into the Tuckean Broadwater has yet to be undertaken.

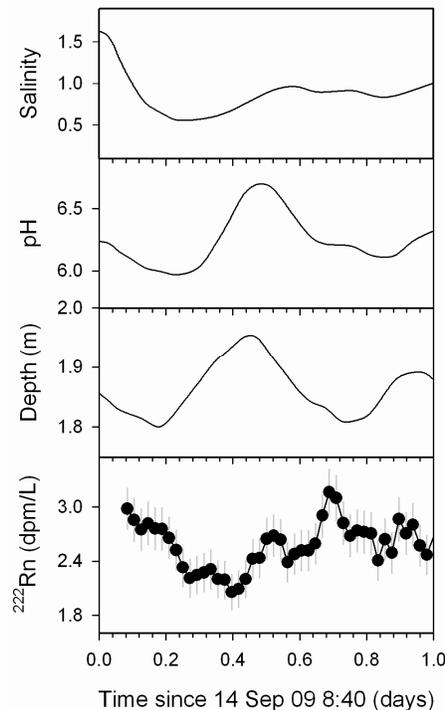


Figure 4: Results of a 24-h time series of radon, water depth, pH, and salinity in the Tuckean Broadwater about 50-m downstream of the Baggotville Barrage.

Time series measurements in the Shaws Bay Lake, Ballina

We have also performed a 24-h time series measurement study in Shaws Bay Lake in September 2009 to demonstrate how one can quantify SGD rates based on the radon data. This is a saline water body located on the north margin of the Richmond River Estuary mouth in Ballina. Tidal exchange between the Lake and the Richmond River Estuary occurs through gaps in the breakwater in the northern side of the river. The simple geometry and the availability of accessory data (i.e., weather data from the Ballina airport) allow us to apply a well-established model to estimate SGD rates at this site.

The results show a temporal variability consistent with higher groundwater inputs at low tide (Figure 5). The radon peak at low tide was associated with a slight but detectable drop in salinity, demonstrating that there is some fresh groundwater discharging into this area. Groundwater sampling was performed with a novel push point piezometer system (Charette and Allen, 2006). Radon concentrations in beach groundwaters (0.3 to 1.8 m deep) were 51 ± 22 dpm/L ($n=5$), a value about 50-fold higher than surface water concentrations.

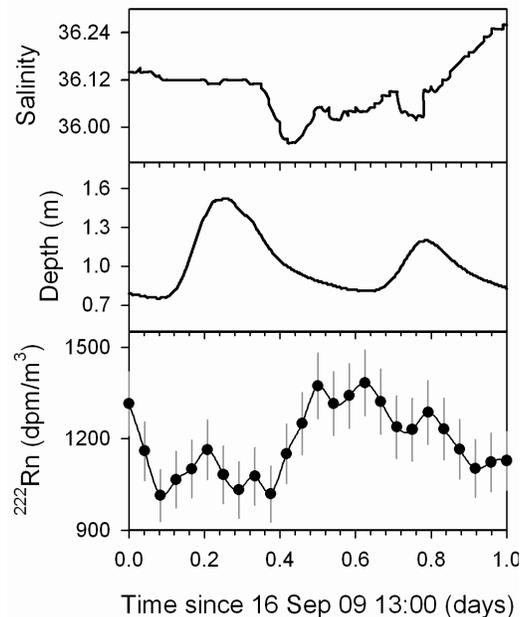


Figure 5: Results of a 24-h time series of radon, water depth, and salinity in Shaws Bay Lake, Ballina.

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 SGD rates, we applied a non-steady state mass balance described in detail elsewhere (Santos et al., 2009a). Our continuous measurements allowed estimates of groundwater discharge rates at 1-hour time steps. 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 were 6.9 ± 5.8 cm/day (or $\text{cm}^3/\text{cm}^2/\text{day}$; $n=26$) during the deployment. Because the radon model is based on nearly one day of continuous

observations (one hour for each measurement interval), the standard deviation represents natural temporal fluctuations associated with tidal pumping rather than uncertainties.

These preliminary estimations demonstrate that groundwater can be a significant source of both water and dissolved species into the lower Richmond River Estuary. Our future work will focus on the determination of seasonal changes in both SGD rates and nutrient fluxes.

Final remarks

Automated measurements of radon in water can now be made easily and quickly, allowing rapid assessment of groundwater interactions with surface water bodies in a very convenient and inexpensive manner. The radon surveying and mooring approach, therefore, should be useful in most river and estuary situations as an inexpensive and rapid method to assess groundwater inputs. For a complete understanding of contaminant loadings to surface water bodies, such evaluations are critical.

The techniques employed here allow environmental managers to quickly assess the groundwater discharge nature into rivers over large spatial ranges. As the management approach at groundwater- and surface water-dominated sites will be different, radon data can help local Councils to manage the estuary from a proactive rather than reactive perspective.

Because of technical difficulties, groundwater has been overlooked as a water quality driver in the Richmond and other Australian estuaries for decades. As result, no previous quantitative information exists on groundwater discharges along the Richmond River. Our preliminary results indicate that (1) the Tuckean Broadwater and the Wilsons River are sites of relatively high groundwater inputs; (2) groundwater inputs are likely to be linked to low-pH events in the Tuckean Broadwater; (3) groundwater inputs are highly variable over tidal and seasonal time scales.

In conclusion, groundwater seems to be a major driver of surface water quality in the Richmond River Estuary and needs to be included in future environmental monitoring and management efforts.

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