Submarine Groundwater Discharge and Associated Nutrient Fluxes to the Corpus Christi Bay System

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1 Abstract

The naturally occurring radium isotopes ^{228}Ra and ^{226}Ra were used to quantify SGWD to Nueces Bay, and to investigate the process of SGWD to the upper Laguna Madre and to the Corpus Christi Bay system as a whole. Samples for dissolved radium were collected from Nueces Bay and the Upper Laguna Madre as well as the Gulf of Mexico, the Nueces River, and area water wells. A mathematical mixing model was used to determine the necessary SGWD to support the observed radium concentrations. The model results indicate a range for SGWD of from 6 to 16 x 10^6 m^3/month. The average dissolved nitrate concentration of the regional groundwater is 2.56 mg/L N as NO_3^- (182 μM) based on 274 samples collected from 176 wells in Nueces and San Patricio counties during the period of 1950 to 2001 (*TWDB*, 2003). Assuming this is representative of SGWD and using the range of 6 to 16 x 10^6 m^3/month the NO_3^- supply would be between 15,000 and 40,000 kg as NO_3^- per month or 180 to 480 x 10^6 g/year. This estimate is exceeded as a source of nitrogen to the entire Nueces Estuary (including Corpus Christi Bay) only by wastewater and by the Nueces River only during high inflow years (*Brock*, 2001). We conclude that SGWD is an important source of water and particularly of nutrients to regional bays. Large uncertainties in current model estimates of SGWD can be resolved with additional measurements focussed on poorly constrained elements of the hydrological balance and of radium cycling.

2 Introduction

The direct discharge of groundwater to the coastal ocean (Figure 1) was once considered a negligible component of the hydrologic cycle. This process, termed submarine groundwater discharge (SGWD), will occur to some extent whereever the hydraulic gradient favors coastal flow and the land and sea are hydraulically connected (*Moore*, 1999). This discharge may be ecologically important even if the rate is small compared to surface inputs because groundwater is often enriched in natural and anthropogenic nutrients (*Burnett et al.*, 2002; *Drever*, 1997; *Kehew*, 2000; *Kreitler and Jones*, 1975). In recent decades, there has been increased interest in characterizing and quantifying SGWD (*Burnett et al.*, 2002) largely in response to concerns about coastal water quality. Two widely expressed concerns are that 1) anthropogenic increases in groundwater NO_3^- concentrations are partially responsible for the increasing eutrophication of coastal waters (e.g. *Johannes*, 1980; *Laroche et al.*, 1997; *Valiela et al.*, 1992); 2) fluctuations in SGWD rates or water quality are related to the initiation of nuisance algal blooms (*Laroche et al.*, 1997; *Sewell*, 1982). Results from a growing body of work support the hypothesis that groundwater discharge is a significant component of the water and nutrient budgets in many coastal areas (e.g., *Basu et al.*, 2001; *Charette et al.*, 2001; *Johannes*, 1980; *Kooi and Groen*, 2001; *Laroche et al.*, 1997; *Moore*, 1997, 1999; *Mortimer et al.*, 1999; *Nowicki et al.*, 1999; *Scott and Moran*, 2001; *Sewell*, 1982; *Swarzenski et al.*, 2001; *Valiela et al.*, 1992; *Yang et al.*, 2002).

SGWD is by nature challenging to measure. Techniques based on naturally occurring chemical tracers have proven especially useful in quantifying of SGWD because they represent an integrated spatial and temporal signal across entire bay systems (e.g., *Cable et al.*, 1996; *Charette et al.*, 2001; *Corbett et al.*, 2000; *Hussain et al.*, 1999; *Kelly and Moran*, 2002; *Krest and Harvey*, 2003; *Krest et al.*, 1999; *Rama and Moore*, 1996; *Schwartz*, 2003; *Scott and Moran*, 2001). The ideal chemical tracer of SGWD is a dissolved constituent which 1) exhibits a substantial enrichment in groundwater relative to other potential endmember waters (e.g. seawater, river water, rain, and runoff) and 2) behaves conservatively within the coastal zone (*Charette et al.*, 2001).

Radium isotopes come close to this ideal because they behave conservatively in brackish and marine waters and are enriched in groundwater (*Krest et al.*, 1999). The four naturally occuring Ra isotopes are members of the three long lived uranium-series radioactive decay chains and are each the daughter nuclides of thorium isotopes (Figure 2). While thorium readily adsorbs to particles Ra is much more soluble and will partition into the liquid phase. The activity of ^{228}Ra in groundwater is generally higher than that of ^{226}Ra due to the greater natural abundance of thorium over uranium (*Michel*, 1990). In southern and central Texas, major deposits of uranium are present in Eocene and younger formations which outcrop well inland of the coastal bay system (*Cech et al.*, 1988). These deposits are associated with the Burkeville confining unit in the deepest portion of the Evangeline aquifer. Since ^{238}U is the progenitor of ^{226}Ra the location of these U deposits could influence the activity of ^{226}Ra in regional groundwaters and surface waters.

We have undertaken a study to estimate SGWD to the greater Corpus Christi Bay, motivated by several factors. Previously published nitrogen budgets of Nueces and Corpus Christi Bays have not been able to reconcile nitrogen supply and nitrogen export (*Brock*, 2001). This region has also experienced problems associated with eutrophication, specifically loss of seagrass and blooms of harmful algae such as the Texas brown tide *Aureoumbra lagunensis* (*Buskey et al.*, 1998). In this study we use ^{226}Ra and ^{228}Ra to quantify the SGWD and nitrogen supply to Nueces Bay and the upper Laguna Madre and by extension to the Corpus Christi Bay system during four different sampling periods over the course of a year. Samples for dissolved radium were collected from Nueces Bay and the Upper Laguna Madre as well as the Gulf of Mexico, the Nueces River, and area water wells. Samples for dissolved nutrients and salinity measurements were taken coincident with bay water radium samples. A mathematical mixing model was used to determine the necessary SGWD to support the observed radium concentrations. The associated nutrient supplies were estimated by applying average regional groundwater nitrogen concentrations to the values of SGWD.

3 Sampling and Methods

3.1 Study Area

The objective of this study was to quantify SGWD to the Corpus Christi Bay system. Prior to this effort, there was no information concerning the spatial extent of SGWD in the study area except that which could be deduced from regional hydrogeology. An equipotential surface (Figure 3) developed during study planning suggested that SGWD would be focused by the regional gradient into Nueces Bay. There was also no information prior to this survey concerning the magnitude of SGWD in the study area; however, the flat topography and semi-arid climate suggested magnitudes at the lower end of measurement capability. We thus chose to focus our study on Nueces Bay, where SGWD was expected to be highest, and a location within Bird Island Basin in the Upper Laguna Madre which would be taken as representative of SGWD at the lower end of what would be expected in the Corpus Christi Bay system. In addition, a detailed study of the nitrogen budget of Nueces Bay had previously been published (*Brock*, 2001) which provided a context in which to interpret our SGWD nutrient fluxes. This survey plan provided a means to focus survey resources where they would be most beneficial while still being able to draw conclusions about SGWD to the larger Corpus Christi Bay system.

3.2 Study Periods

The initial study plan called for quarterly sampling periods. The first of these surveys was conducted in Nueces Bay in late April of 2002. In early July, just prior to the second quarterly survey, an unusually large storm system caused massive flooding in the Nueces, San Antonio, Guadalupe, and Lavaca watersheds. This was an exceptional event which dramatically increased inflow to Nueces Bay over the next half year as shown in Figure 4.

The second quarterly survey was postponed several weeks due to the initial flooding. Consideration was also given to postponing the survey further until a time when bay hydrology approached steady state with respect to inflow, since this is an important assumption in the mixing model used to calculate SGWD. However we concluded that collecting data during such exceptional watershed conditions was more important. The second survey was conducted approximately two weeks after the initial storm and local flooding. Inflow to Nueces Bay peaked several weeks after the survey due to drainage of the upper watershed.

The timing of the subsequent surveys was reassessed after the July survey. At that point the two completed surveys had resulted in the collection of data from the driest and wettest conditions the watershed was likely to experience over a span of years. The storm and subsequent flooding had emphasized the wet/dry seasonality of the regional climate and quarterly surveys no longer appeared appropriate for the goals of the study. It was decided that the study would be better served by using the third and fourth surveys to examine SGWD variations that occurred within a monthly tidal cycle. It was also decided that the third and fourth surveys should be postponed until Nueces Bay returned to a state more representative of average conditions. The third and fourth surveys were performed on 19 and 27 May 2003.

The timing of data collection in the Upper Laguna Madre was notably different than the Nueces Bay surveys. Data was collected roughly once a week at the same nearshore location for the entire study period.

3.3 Sampling

Surface water samples from Nueces Bay were collected for Ra (75 L) and nutrient (50 mL) analysis during April and July 2002 and on 19 and 27 May 2003. Roughly weekly surface water samples were collected from the Upper Laguna Madre near the Bird Island boat basin at the Padre Island National Seashore from June 2002 to May 2003. Samples were also collected from a variety of potential source waters in the region to assess the radium and nutrient concentrations of the endmember fluids which contribute to the bay water samples. Sample locations are shown in Figures 5 and 6.

Nueces Bay was sampled at 19 locations in April 2002 and 20 locations in July 2002 (Figure 6 and Tables 1 and 2). Heavy flooding just prior to the July sample collection was evident in a lowering of the average salinity of the bay water from 33 ppt in April to <1 ppt. A subset of ten of the 2002 sample stations were resampled in May 2003 (Tables 3 & 4) on two separate days chosen to be near the predicted spring and neap tides. One station outside Nueces Bay in Corpus Christi Bay was sampled on 27 May 2003 (Table 4). Water samples from Nueces Bay were collected by submersible pump from approximately 30 cm below the water surface, filtered to 1 μm in the field, and stored in 25 L polyethylene bottles. Nutrient samples were stored in 25 mL polyethylene bottles, filtered to 0.45 μm using silica-free filters, and frozen (-10°C) until analysis.

At the Bird Island site, a total of 36 samples were collected from the same location on a roughly weekly basis from June, 2002 to May, 2003 (Tables 5 and 6). Surface water samples were collected approximately 15 m from the shoreline at a point where the depth abruptly drops from 0.5 m to 1 m. Water samples were collected by hand, stored in 25 L polyethylene bottles, and filtered to 1 μm in the laboratory.

During December 2002 radium and nutrient samples were collected from Lake Corpus Christi reservoir at the shoreline within the state park, from the Nueces River less than a kilometer downstream of Lake Corpus Christi dam, and just below the saltwater barrier on the Nueces River in Calallen, Texas (Table 7). Water samples were collected by hand, stored in 25 L polyethylene bottles, and filtered to 1 μm in the laboratory.

Water was collected from nine wells in the region (Figure 5 and Table 8). The wells sampled had either pumps or windmills (Table 9) and water samples were collected by hand from the outlets, stored in 25 L polyethylene bottles, and filtered to 1 μm in the laboratory.

Radium samples (100 L) were also collected from the Gulf of Mexico in September 2002 along a transect starting from just offshore of Aransas Pass to a point approximately 70 km from shore (Table 10). At this farthest point two samples were also collected from depths of 500 and 1130 m using Niskin bottles. The surface water samples along this transect were collected by the ship seawater collection system.

3.4 Measurement of Dissolved Radium Activities

Radium was quantitatively extracted from water samples and precipitated as $Ba(Ra)SO_4$ following the procedure outlined by *Rutgers van der Loeff and Moore* (1999). Radium was extracted onto MnO_2 impregnated acrylic fiber at a flow rate of less than 1 L/min. The fiber was then rinsed in deionized water and placed in a Soxhlet extraction apparatus where the Ra was leached from the fiber using 500 mL of 6 N HCl. Radium was precipitated with $BaSO_4$ by adding 10 mL of saturated $BaNO_3$ and 25 mL of H_2SO_4 to the heated extraction solution. The white precipitate was then allowed to settle overnight after which the fluid was decanted and the precipitate was rinsed with 6N HCl and transferred to polystyrene counting vials.

The precipitates were aged at least 15 days prior to gamma counting for ^{228}Ra and ^{226}Ra on a high purity germanium well detector (*Moore*, 1984). This holding period allows the ingrowth of the daughter nuclides ^{228}Ac and ^{214}Pb. The 911 kev gamma ray of ^{228}Ac and the 351 kev peak of ^{214}Pb were used to determine the activities of ^{228}Ra and ^{226}Ra, respectively:

$$\frac{dpm}{L} = \frac{Counts}{br \cdot de \cdot t \cdot v \cdot fe \cdot e^{-86400\,k\,t_{spl}}} \tag{1}$$

where br is the branching ratio of the gamma decay, de is the detector efficiency at that gamma energy, t is the duration of the count (in minutes), v is the sample volume, k is the radioactive decay constant (in days), t_{spl} is the time elapsed from sample collection, and fe is the filter extraction efficiency of the Mn fibers.

In most studies, Mn fibers prepared in this way are assumed to quantitatively extract Ra from water samples at flow rates of <1-2 L/min. Extraction effieciency in this study was verified to be >95% by using two MnO_2 columns in series for several samples and determining the relative amounts adsorbed to the primary and secondary columns. A combined collection and counting efficiency for the gamma dectector was determined by preparing two solutions of known ^{228}Ra and ^{226}Ra activity from standards and precipitating, collecting, and counting the samples in the same way as the samples. The uncertainty in the reported activities was determined by propagating the errors associated with the eight variables in Equation 1.

3.5 Mixing Model

To determine SGWD into a body of water by conservation of tracer mass, all other sources and sinks of the tracer must be quantified:

$$\frac{dV_{bay}}{dt}[T_{bay}] = Q_{S.IN}[T_{S.IN}] - Q_{S.OUT}[T_{S.OUT}] + SGWD[T_{GW}] \tag{2}$$

where V_{bay} is the volume of the embayment, [T] is the tracer concentration, Q is the volumetric flow rate, and the subscripts S.IN, S.OUT, and GW refer to the total surface inputs, total surface outputs, and groundwater. If steady state is assumed then SGWD is the flow rate of groundwater necessary to balance the other tracer contributions:

$$SGWD = \frac{-Q_{S.IN}[T_{S.IN}] + Q_{S.OUT}[T_{S.OUT}]}{[T_{GW}]} \tag{3}$$

Accounting for radioactive decay of tracers such as ^{228}Ra or ^{226}Ra is only necessary when the residence time of water in the bay is more than a significant fraction of the isotope half life (*Cable et al.*, 1996) which in this case are 5.7 and 1620 years respectively. In May, 2003, samples were processed quickly enough to determine ^{224}Ra (half-life of 3.6 days) in addition to ^{226}Ra and ^{228}Ra.

The important sources and sinks of Ra to a bay are generally river inputs, tidal exchange with the coastal ocean, diffusion from sediment porewaters, and groundwater. In the literature, steady state conditions are assumed and the generalized conservation of mass Equations 2 and 3 are rewritten in the form of Equations 4 and 5 (e.g *Charette et al.*, 2001):

$$Ra_x = \left[(Ra_B - Ra_{GM}) \cdot \frac{V_B}{\tau}\right] - [Ra_R \cdot Q_R] - [Ra_{sed} \cdot A_B] \tag{4}$$

$$SGWD = \frac{Ra_x}{Ra_{GW}} \tag{5}$$

where Ra_x is the excess Ra activity supplied to the bay, Ra_B is the average Ra activity of the bay water, Ra_{GM} is Ra activity of the coastal ocean, V_B is the bay volume, τ is the bay water residence time with respect to outflow, Ra_R is the Ra activity of Nueces

River water, Q_R is the river discharge rate, Ra_{sed} is the Ra flux from sediments, A_B is the bay area, and Ra_{GW} is the Ra activity of the groundwater. For the Texas coastal bend, an additional term must be added to Equation 4 to account for the concentrating effect on bay radium activities from excess evaporation (E) over precipitation (P):

$$Ra_x = \left[(Ra_B - Ra_{GM}) \cdot \frac{V_B}{\tau}\right] - Ra_R \cdot Q_R - Ra_{sed} \cdot A_B - Ra_B \cdot (E - P) \quad (6)$$

Ra activity in excess of that accounted for by export to the coastal ocean, supplied by river input, emanating from sediments, or due to an imbalance in evaporation and precipitation is attibuted to groundwater discharge. SGWD is then the flux of excess Ra divided by the average concentration of Ra in the local groundwater (Equation 5).

The July sampling period called for a different approach. During July 2002 the bay was rapidly flushed by river water and rain giving a water residence time of 14 days. In this case the influence of tidal flux appeared negligible and was removed from the model. Excess radium was taken to be that activity above Nueces River water activity, and the diffusive flux of radium from the sediments is reduced by the weaker ionic strength of the fresh water:

$$Ra_x = \left[(Ra_B - Ra_{NR}) \cdot \frac{V_B}{\tau}\right] - Ra^*_{sed} \cdot A_B \quad (7)$$

3.6 Nutrient Concentrations

Dissolved nutrient concentrations (nitrate+nitrite ($NO_3^- + NO_2^-$), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), and amorphous silica (SiO_2)) were measured following traditional methods (*Grasshoff*, 1976) using a Lachat Quikchem 8000 autoanalyzer.

Samples were run in duplicate against standards prepared in low-nutrient Gulf of Mexico seawater (*Yamane and Asito*, 1992). Problems were encountered in some sample runs with consistency between sample duplicates that could not unequivocally be attributed to sample collection procedures or contamination. We have reported in Tables 1-10 the nutrient data (average of replicate analyses) in which we have confidence. For calculations of groundwater-borne nutrient fluxes we have used dissolved nitrate values averaged from the TWDB database(*TWDB*, 2003). Regional well water nitrate levels range between a maximum of 25.21 mg/L N as NO_3^- (1800 μM) to below detection. The average nitrate concentration is 2.56 mg/L N as NO_3^- (182 μM) (Figure 13).

3.7 Environmental Data Collection

During each sampling period pan evaporation, precipitation, and water surface elevation data were obtained from area weather and tidal stations (e.g., Lake Corpus Christi Reservoir (*Nueces River Authority*, 2003) and Texas Coastal Oceanographic Observation Network (TCOON) (*TCOON*, 2003)). Temperature and salinity in Nueces Bay were determined using a YSI Model 6000 Sonde (April & July, 2002), a SeaBird Electronics SeaCat CTD profiler (May 19, 2003), and bottle samples run on a Guildline Autosal salinometer (May 27, 2003; no temperature data). For Bird Island samples, temperature, pH, dissolved oxygen, specific conductivity, and salinity were determined using a YSI Model 6000 Sonde (not available for all samples) (Table 6).

4 Results and Discussion

4.1 Results of Radium Activity Measurements

The activities of ^{228}Ra and ^{226}Ra, their isotopic ratio, and salinity are the variables most relevant to characterizing SGWD. The activities of ^{228}Ra to ^{226}Ra in the end-member waters are used to model mixing of radium within the bay (Equations 6 and 7). The ratio of ^{228}Ra to ^{226}Ra is indicative of the source of radium. Salinity is an indication of the relative amounts of fresh and saline waters and provides an additional constraint on the associated water fluxes. The distribution of these values are summarized as box plots for the four Nueces Bay sampling periods, the Bird Island sampling, and all other water types collected in the region (Figures 7-10). Box width is proportional to the square root of the number of samples, the height of the box encompasses the 25th and 75th quantiles, the median is represented by the horizontal line which divides the box, the mean is shown by a triangle, and the whiskers extend to the extreme values of the sample set. These plots are drawn assuming an underlying normal distribution; however, the distribution is skewed if the median and mean values are offset which is the case for the majority of these sets. If significant unsupported radioactive decay of radium was occuring within these systems the activity distribution would be geometric. This is likely the case for the activity values obtained from the Gulf of Mexico transect which includes waters more than 80 kilometers apart and of different ages relative to cycling through coastal waters. Significant radioactive decay of ^{228}Ra relative to ^{226}Ra will not occur within coastal waters with residence times substantially less than 5.7 years. The more likely explanation for the skewness of the distributions is that the sampled waters are not homogenous with respect to mixing and therefore represent a combination of more than one distribution.

The activities of ^{228}Ra fall between 0.01 and 2.6 dpm/L (Figure 8). The highest values occurred within Nueces Bay; the April 2002 and 19 and 27 May 2003 values were significantly greater than the next highest mean from Bird Island (p-value<0.027, $\alpha=0.05$). The activities of ^{228}Ra at Bird Island were significantly greater than in the groundwater samples, the Nueces River, and the Gulf of Mexico (p-value$<10^{-4}$, $\alpha=0.05$). The July 2002 Nueces Bay samples have activities comparable to river water.

The activities of ^{226}Ra are between 0.05 and 1.0 dpm/L (Figure 9). Again, the highest values occurred within Nueces Bay; the April 2002 and 19 and 27 May 2003 values were significantly greater than the next highest mean from Bird Island (p-value<0.003, $\alpha=0.05$). The activities of ^{226}Ra for Bird Island, the groundwater samples, the Nueces River, and the Gulf of Mexico were progressively lower (p-value<0.047, $\alpha=0.05$). The results suggest that there is more regional variability in ^{226}Ra activity than for ^{228}Ra activity. This may partially be due to the presence of significant uranium deposits inland of the bay system. The July 2002 Nueces Bay samples have activities comparable to river water.

The activity ratio of ^{228}Ra to ^{226}Ra (Figure 10) is particularly useful in distinguishing sources and understanding the evolution of bay water activities because the activity ratio is unaffected by evaporation and direct precipitation. The average activity ratios for the April 2002 Nueces Bay samples and the Bird Island samples are similar at 3.8. The July 2002 Nueces Bay samples and the river and groundwater samples all average 1.2 in ^{228}Ra/^{226}Ra activity ratio. The average activity ratios of the 19 and 27 May 2003

Nueces Bay samples are intermediate between these two values which suggests that the bay during this period was in transition from essentially river water to an evaporation dominated hydrology represented by the April 2002 Nueces Bay and Bird Island activity ratios. This activity ratio of roughly 3.8 is close to that of well sample 4 (the closest groundwater sample to the bay, within half a kilometer of the north shore) which had an activity ratio of 4.03 (Table 8).

4.2 Comparisons between Radium Activity, Water Level and Water Fluxes

The daily tidal range within the Nueces Bay system is typically less than 0.3 m but the spring/neap tidal range can be greater than 0.5 m (Figure 11). The 19 and 27 May 2003 sampling periods were designed to sample the bay at different portions of the spring/neap tidal cycle for that period in May. The May 19 samples were collected at the end of a spring tidal period while the May 27 sample followed a brief neap phase (Figure 11). In the May 19 sample set, there is a gradient of Ra activities that trends from a high for ^{228}Ra and ^{226}Ra of 2.23 and 1.00 dpm/L at Station 16 near the head of the bay to a low of 1.03 and 0.37 dpm/L at Station 1 near the mouth (Figure 6 and Table 3). A similar gradient exists in the May 27 sample set with highs for ^{228}Ra and ^{226}Ra of 2.18 and 0.96 dpm/L at Station 18 near the head of the bay to a low of 0.96 and 0.31 dpm/L at Station 1 near the mouth (Figure 6 and Table 4). There was no significant difference in average radium activities or ratios between these two periods.

The data from Bird Island in the upper Laguna Madre suggest that there is at least an indirect relationship between radium activities and seasonal water level (Figure 12).

During the intial half of this period radium activities and water level exhibit an inverse relationship after which radium activities increase despite smaller fluctuations in water level. This initial inverse relationship is likely the result of increased runoff from regional flooding which dilutes the bay water. After this initial dilution, the radium activities appear to increase independently of water level fluctuations. It appears; therefore, that there is small but persistent flux of radium to these waters on which daily water level fluctuations due to wind or tide have a negligible impact.

4.3 Estimates of SGWD to Nueces Bay

SGWD to Nueces Bay was estimated for the April 2002 and May 2003 sampling periods using the data provided in Tables 1 - 8 and Equations 5 and 6. The calculations are summarized in Table 11. The first step is to estimate the excess radium (^{226}Ra or ^{228}Ra) in the bay. For the April 2002 and May 2003 samplings, this is done using Equation 6 as written. The near shore sample Station 1 from the Gulf of Mexico transect was used as the ocean endmember (Table 10). The mean of the Nueces River radium samples collected in December 2002 were used to represent the river endmember. The magnitudes of the diffusive fluxes of radium from bay sediment porewaters were approximated using the maximum values reported from the literature, 0.048 and 0.192 dpm/m^2/day for ^{226}Ra and ^{228}Ra respectively, multiplied by the area of the bay (*Charette et al.*, 2001; *Rama and Moore*, 1996). Mean radium activities were used to represent Nueces Bay during the different sampling periods. Excess evaporation is a dominant term in the hydrologic balance of Nueces Bay and acts to increase radium activities relative to those in the source waters. Variation in bay area was assumed to be negligible but the volume of the bay was varied with the water level reading from the Texas State Aquarium TCOON Station (*TCOON*, 2003).

Monthly averages of precipitation, evaporation, and river discharge from Lake Corpus Christi (*Nueces River Authority*, 2003) were used to determine the values for Nueces Bay. It would be more relevant to use evaporation, precipitation, and river inflows averaged over the mean bay water age (instantaneous residence time) rather than monthly averages, however our current understanding of Nueces Bay residence time is insufficient for this purpose. The rainfall recorded at Lake Corpus Christi was applied to the area of Nueces Bay and the watershed below the dam. Evaporation recorded at Lake Corpus Christi was applied to the Nueces Bay area.

Bay residence time (τ) is the most uncertain term in the calculations, largely due to the real variability of this quantity. Assuming tidal flux, river inflow, evaporation, and precipitation are controlling and tidal flux approximately balances the other terms, then these terms and the bay volume can be used to estimate the residence time. If monthly averages of evaporation, precipitation, and river inflow are used, bay residence time varies from 14 to >800 days during this study period; further, estimating residence time from values averaged over different time scales (from three to six months) also produces variable results. For consistency between sampling periods a value of 250 days was used for the April 2002 and May 2003 Nueces Bay residence times, which is in keeping with published estimates (*Schroeder and Wiseman Jr.*, 1999).

For July 2002, the flushing of the bay by rain and flood waters renders a calculation of excess radium with respect to the Gulf of Mexico meaningless in that the flow is more nearly unidirectional. Therefore, the excess activity has been calculated relative to (December 2002) river water (Equation 7). In addition, the diffusive fluxes from the sediments are reduced in the July 2002 model because the lower ionic strength of the bay water will lead to less desorption of radium produced in sediments during this time period.

In all cases, the excess radium inventory in the bay is divided by the activity in groundwater to estimate SGWD (Equation 5). Well sample 4 (Table 8) was used to represent the groundwater endmember because it was closest to the bay and the only groundwater sample to exhibit an activity ratio similar to the bay water. For the July 2002 flood period, there is little or no discernible excess Ra in the bay, and so no calculation of SGWD is possible.

There are large uncertainites in several of the terms used to estimate SGWD, most notably residence time (estimate: ±50%) which determines the radium exported to the ocean as well as the relevant time scale for averaging evaporation, precipitation, and river inflow. Uncertainty is also introduced when deciding on the most appropriate value to use for the radium activities of the endmember fluids (estimate: ±30%). Other terms such as the water fluxes and the diffusive flux of radium from sediment porewaters have uncertainties but the results are less sensitive to changes in these values. Specifically, setting the diffusive flux of radium from sediments to zero causes only a 10% increase in the SGWD estimate (Table 11). In addition to uncertainties in the inputs, our measurements indicate that the bay system is not at steady state over this time period; therefore, some additional error must be introduced into the results by this assumption. Overall, ±100% is a reasonable estimate of the total uncertainty in the final results. Despite these uncertainties there are at times measurable significant excesses of ^{228}Ra and ^{226}Ra over Nueces River, Gulf of Mexico, and in fact all measured groundwaters. This model attributes those excesses to SGWD.

For each period, both ^{228}Ra and ^{226}Ra were used to make independent estimates of SGWD. There is a systematic difference in the ^{228}Ra and ^{226}Ra based calculations that is partially an artifact of the particular values used to represent the endmember activities. A portion of this difference may also be real as ^{226}Ra is considered to be a more sensitive indicator of SGWD because the longer half life allows greater proportional enrichments (*Rama and Moore*, 1996). For 19 and 27 May 2003, there was no excess of ^{228}Ra that could not be accounted for by other sources. The results from the remaining periods indicate values for SGWD between 6 and 16 x10^6m^3/month, which are comparable to the other water fluxes for non-flood periods given in Table 11.

4.4 Nutrient Fluxes to Nueces Bay from Groundwater

The average dissolved nitrate concentration of the regional groundwater is 2.56 mg/m^3 N as NO_3^- (182 μM) based on 274 samples collected from 176 wells in Nueces and San Patricio counties during the period of 1950 to 2001 (*TWDB*, 2003). Assuming this is representative of SGWD and using the range of 6 to 16 x 10^6 m^3/month the NO_3^- supply would be between 15,000 and 40,000 kg N as NO_3^- per month or 180 to 480 x 10^6 g/year. This estimate is exceeded as a source of nitrogen to the entire Nueces Estuary (including Corpus Christi Bay) only by wasterwater and by the Nueces River only during high inflow years (*Brock*, 2001).

4.5 Recommendations for Future Work

These results can be tested and verified by further sampling in Nueces Bay and in neighboring bays. A multi-bay study will also allow comparisons to be made of bays across the regional precipitation gradient and with different patterns of land and water usage.

Specific needs to be addressed in future studies that have been identified in this pilot project include:

1. Better constraints on the bay water residence times relevant to the mixing model. One means by which this will be addressed in the future is through the use of short-lived radium isotope measurements (Moore, 2000; Charette et al., 2001). This provides a way of determining the most relevant values of evaporation, precipitation, and river fluxes (average over the actual average bay water age) for the model calculations.

2. Much greater sampling of near-surface groundwater most likely to be in contact with bay waters, in order to characterize the radium activities and isotopic ratio of SGWD. This can be accomplished by driving piezometers near the shore of the bay.

3. Direct measurement of the diffusive flux of radium from bottom sediments, through measurement of thorium isotope inventories in surficial sediments.

4. Incorporation of additional tracers (e.g. short-lived Ra, radon-222, and/or methane) as well as direct (e.g., seepage meter) measurements of SGWD. The

use of multiple, complementary approaches will enable a more robust estimate of SGWD to be obtained.

5 Summary

Based on this study, we conclude that SGWD is an important source of water and particularly nutrients to regional bays. Large uncertainties in current model estimates of SGWD can be resolved with additional measurements focussed on poorly constrained elements of the hydrological balance and of radium cycling. Excess radium inventories, and thus calculated SGWD fluxes, are particularly sensitive to the bay water residence time.

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A Figures and Tables

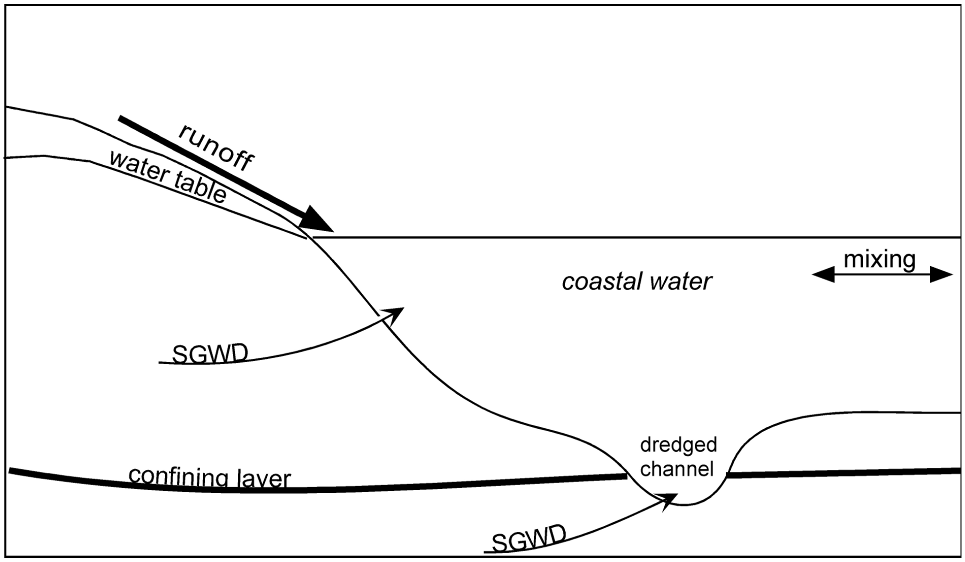

Figure 1: A schematic representation of SGWD to coastal waters from confined and unconfined aquifers. Discharge from unconfined aquifers occurs at the sediment water interface and may be focused if the hydraulic conductivity of the sediments varies. Discharge from confined aquifers may occur at locations where the confining layer is absent or fractured. This can occur naturally along fault lines and it can also occur where human activities such as channel dredging have breached the confining layer.

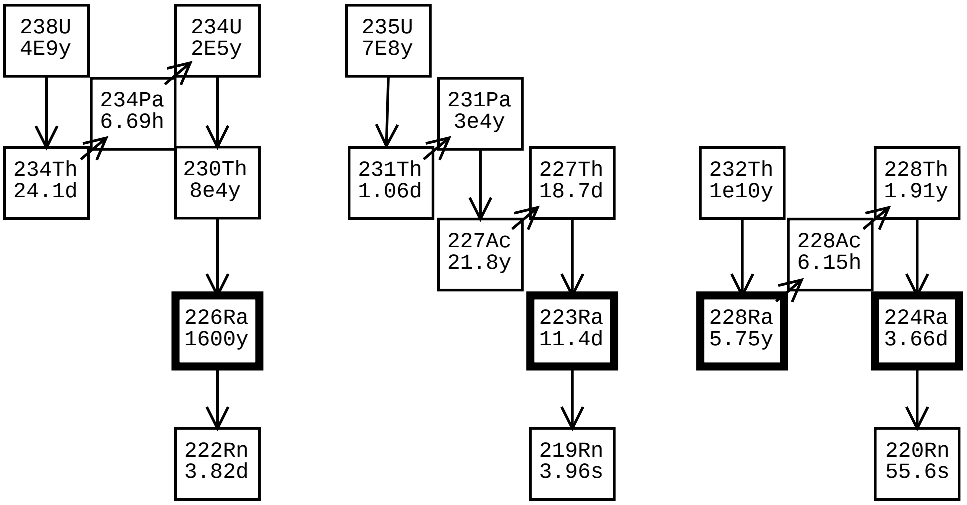

Figure 2: The portions of the three naturally occurring radioactive decay chains in which Ra isotopes are present. The half-life of each isotope is reported directly below its identity.

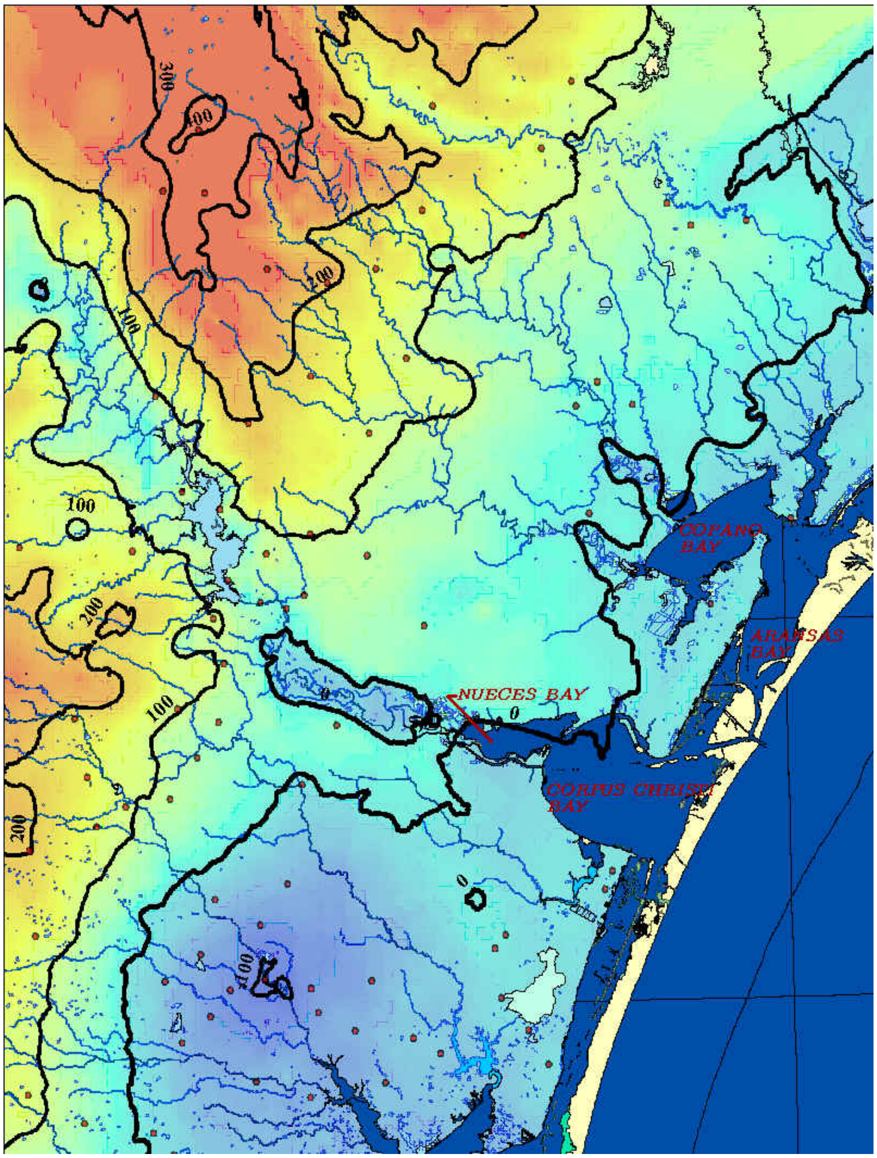

Figure 3: A groundwater equipotential map created as a preliminary aid in selecting study areas for this project. The map is based on well data from the TWDB groundwater database for the year 2000. The contours are based on a spherical krige interpolation of water levels in feet above mean sea level taken from the wells shown on the map. The contour interval is 100 ft (30.5 m). The ground coloration also reflects water levels, starting with red at 400 ft (122 m) and ranging to blue at -100 ft (-30.5 m).

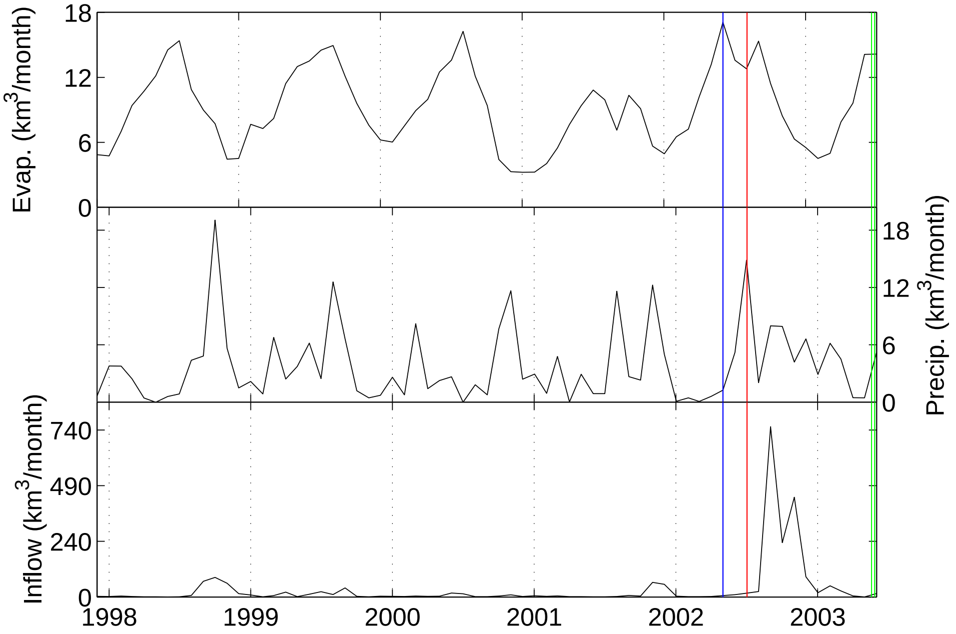

Figure 4: Time series of Nueces Bay evaporation, precipitation, and river inflow from 1998 to 2003 (*Nueces River Authority*, 2003) show 1) this study's sampling periods, 2) the general dominance of evaporation over local precipitation, and 3) the episodic nature of precipitation and river input. The April and July 2002 Nueces Bay sampling periods are shown as blue and red solid vertical lines and the 19 and 27 May 2003 sampling periods are shown as solid green vertical lines. Note the high rate of evaporation relative to precipitation during the April sampling period, the large amount of rainfall prior to the July sampling period, and the large amount of river inflow after July to the end of 2002.

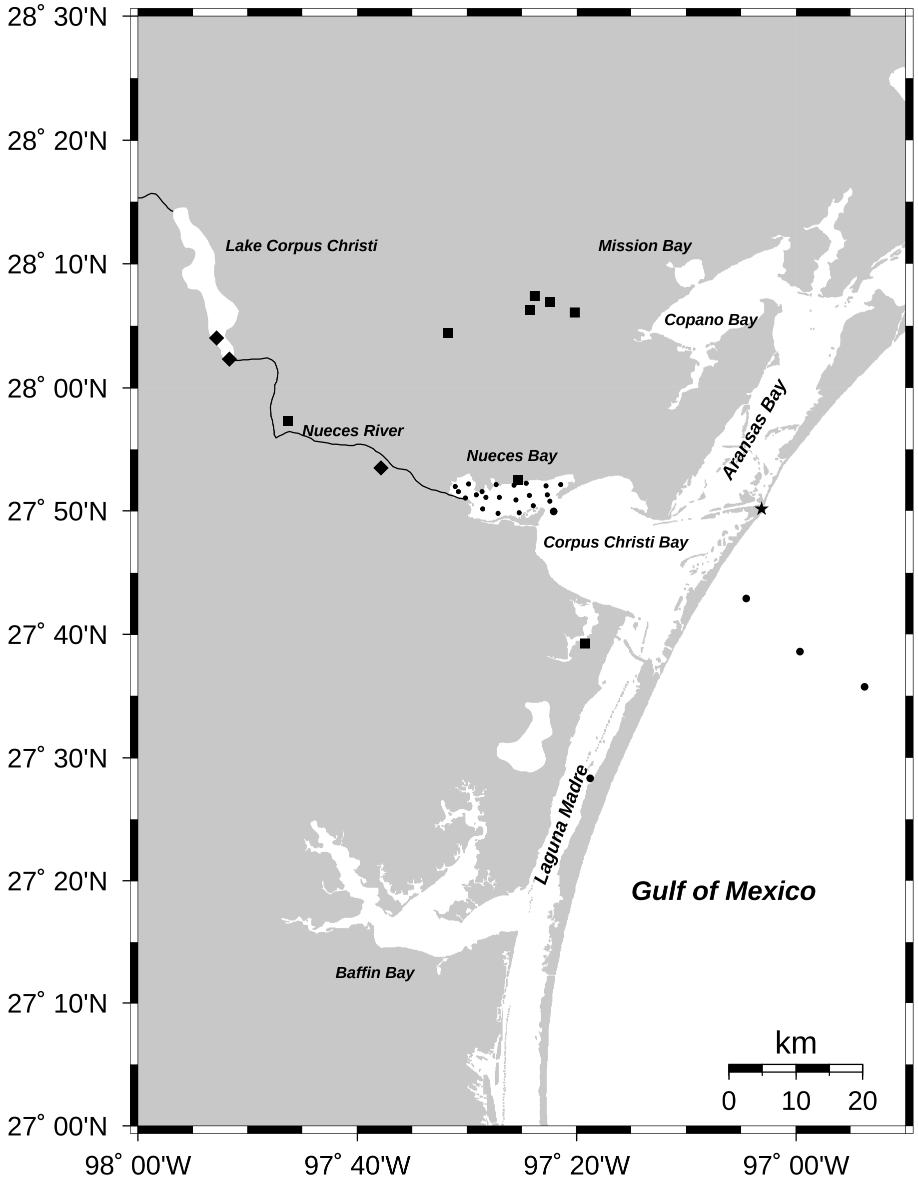

Figure 5: Locations of the samples collected for this study. The inland squares represent well samples and the inland diamonds are surface water samples. The farthest offshore samples are not shown on the map.

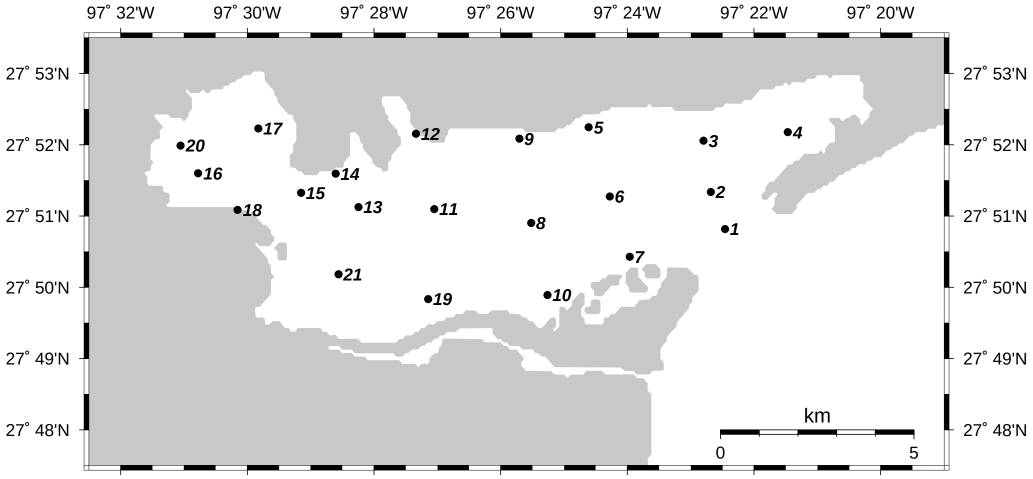

Figure 6: Station locations within Nueces Bay.

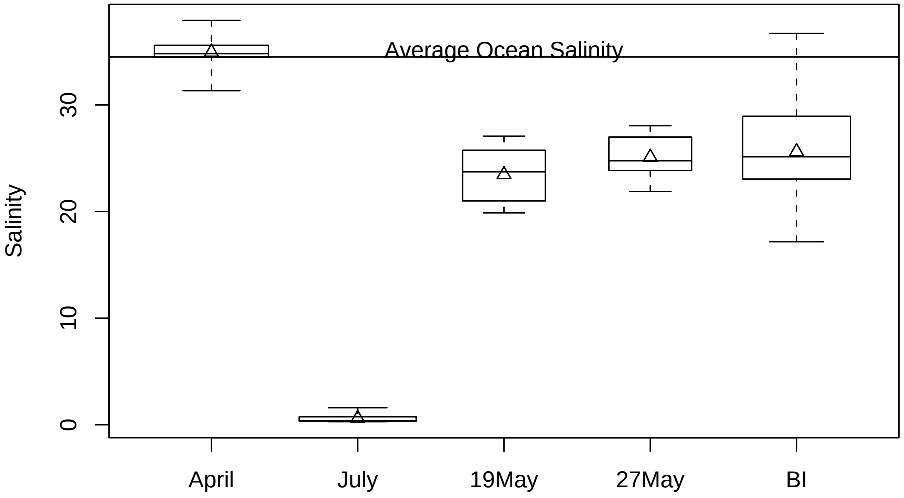

Figure 7: Measured bay salinities, shown as box plots with mean salinities as triangles. Starting at the left, the boxplots represent measurements of Nueces Bay water during April and July 2002, 19 and 27 May 2003, and Bird Island (BI) in the Upper Laguna Madre.

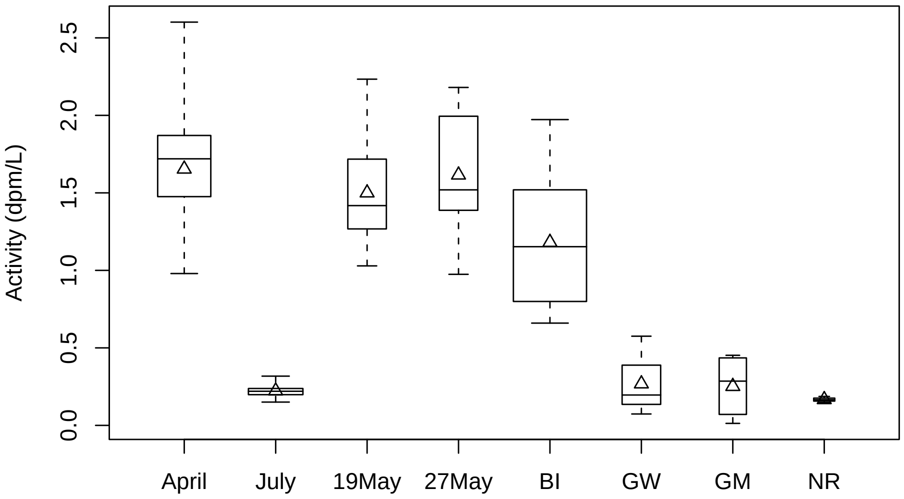

Figure 8: Measured ^{228}Ra activities, shown as box plots with mean activities as triangles. Starting at the left, the first four boxplots represent measurements of Nueces Bay water during April and July 2002 and 19 and 27 May 2003 followed by the measurements from Bird Island (BI) in the Upper Laguna, groundwater (GW) samples, Gulf of Mexico (GM) waters, and the Nueces River (NR).

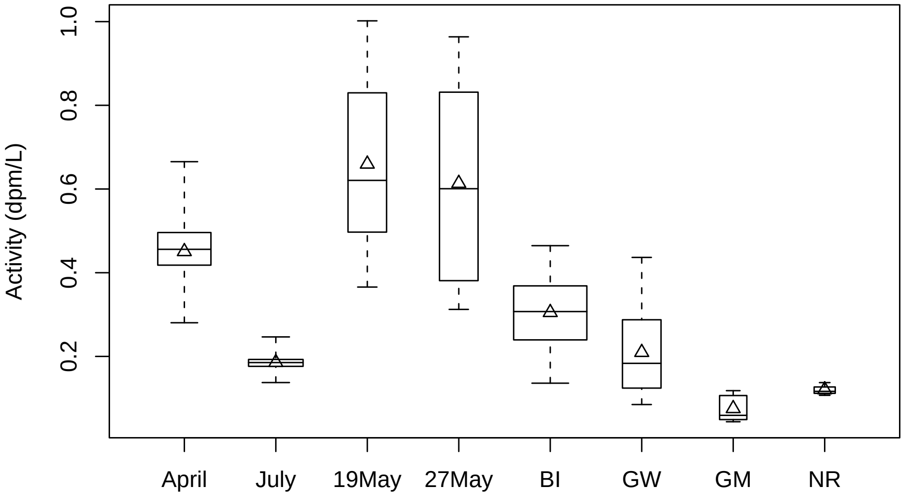

Figure 9: Measured ^{226}Ra activities as in Figure 8.

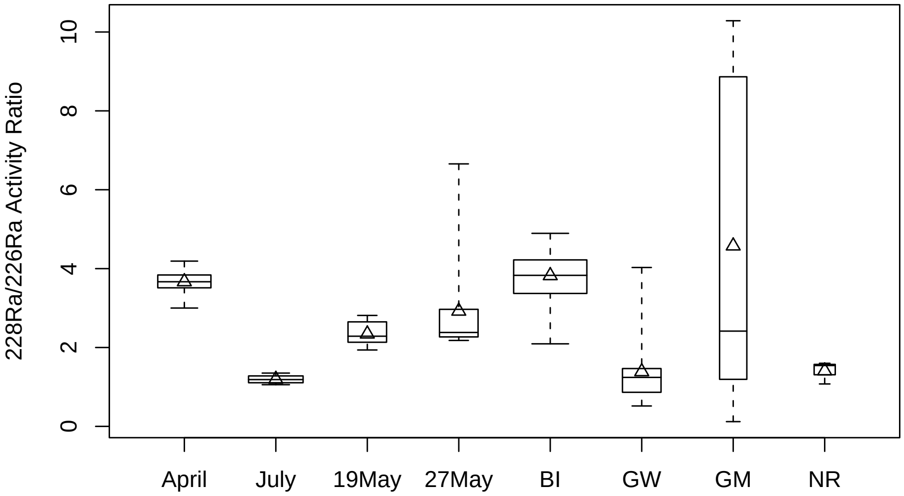

Figure 10: The activity ratio of ^{228}Ra to ^{226}Ra, shown as in Figure 8 and 9. The 27 May 2003 and groundwater sample sets each contain an exceptional outlier. Station 17 from the 27 May 2003 sample set has an activity ratio of 6.66 and groundwater sample 4 has an activity ratio of 4.03.

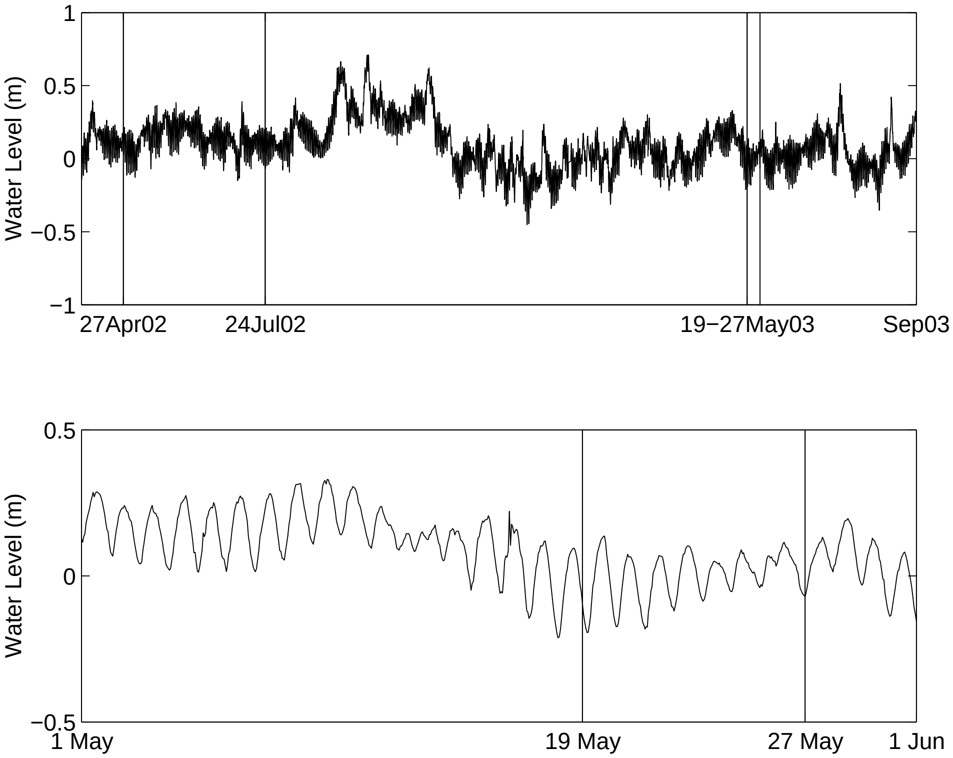

Figure 11: Time series plots showing the variation of tidal height with respect to mean sea level recorded at the Texas State Aquarium TCOON station (*TCOON*, 2003). This station is adjacent to the shipping channel and within several kilometers of the mouth of Nueces Bay, and for this study is considered representative of Nueces Bay water level. The sampling dates for Nueces Bay are shown as vertical lines with the upper graph encompassing all four sample periods and the lower graph focusing on the 19 and 27 May periods.

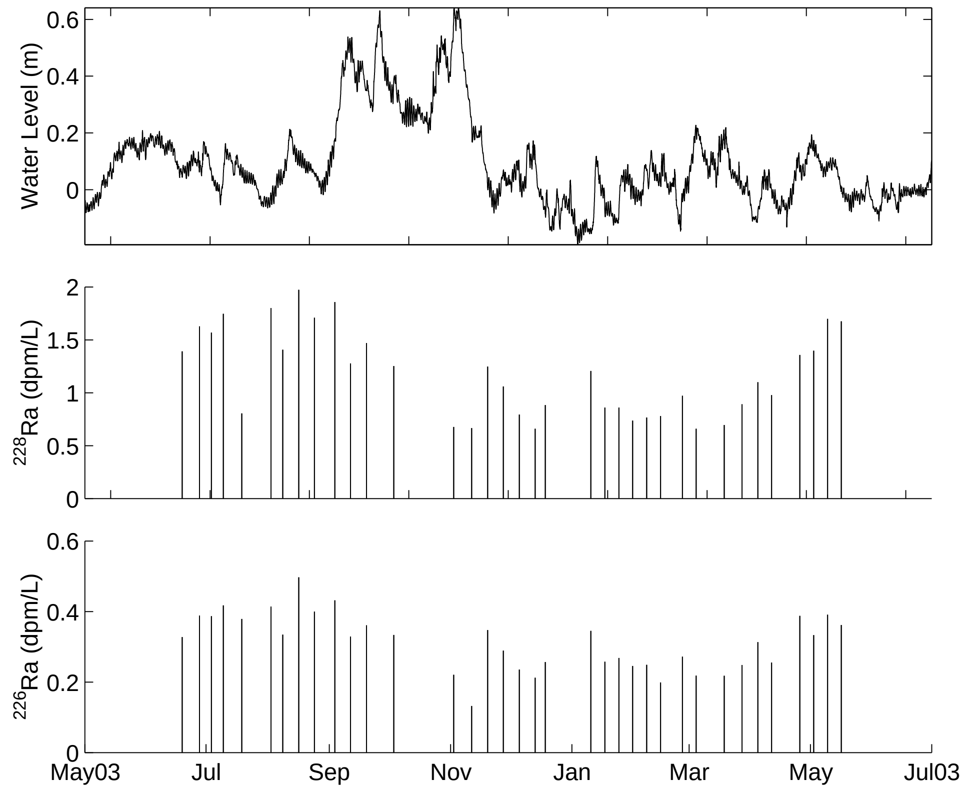

Figure 12: Time series plots indicating the variation of tidal height with respect to mean sea level recorded at the Bird Island TCOON station (*TCOON*, 2003) as well as the ^{228}Ra and ^{226}Ra activities measured through the same period.

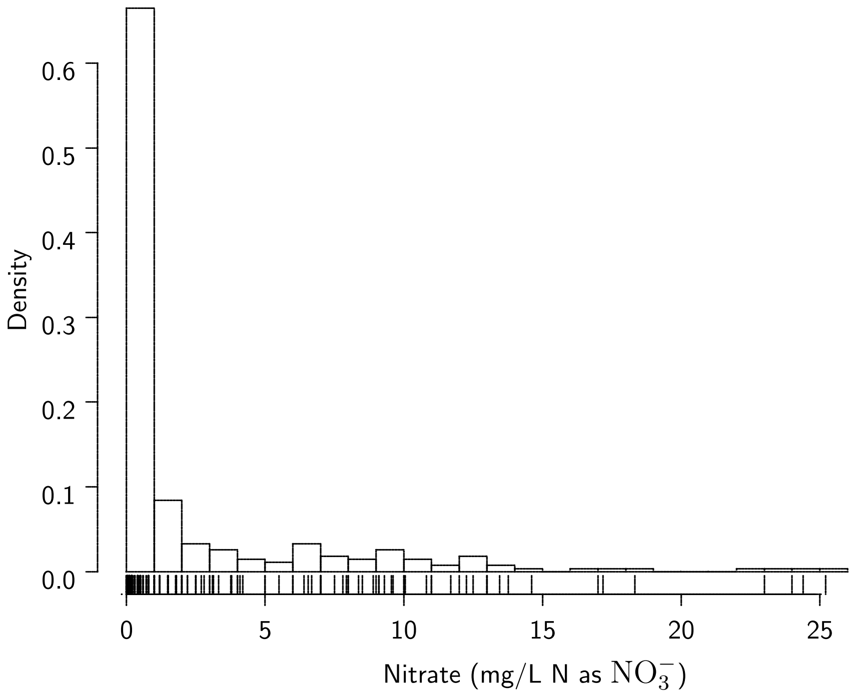

Figure 13: Histogram of nitrate levels in Nueces and San Patricio county wells based on data from the Texas Water Development Board groundwater database. The data consists of 274 samples collected from 176 wells during the period of 1950 to 2001. Well water nitrate levels range between a maximum of 25.21 mg/L N as NO_3^- (1800 μM) to below detection. The average nitrate concentration of this set is 2.56 mg/L N as NO_3^- (182 μM).

Table 1: Results of sampling in Nueces Bay, April 2002

Station	Temp.* (Celsius)	Sal.* (ppt)	PO_4^{3-} (μM)	SiO_2 (μM)	$NO_3^- + NO_2^-$ † (μM)	Activity (dpm/L)		$\frac{^{228}Ra}{^{226}Ra}$
						^{228}Ra	^{226}Ra	
1	26.31	33.67	0.59	76.91	0.54	0.98±0.07	0.28±0.02	3.49±0.36
2	26.04	34.67	0.26	185.58	0.90	1.23±0.09	0.33±0.03	3.67±0.39
3	25.59	33.67	0.12	104.01	0.68	1.02±0.08	0.29±0.02	3.58±0.37
4	25.96	34.25	0.52	129.95	1.48	1.30±0.10	0.33±0.03	3.95±0.45
5	26.40	34.36	0.23	177.39	0.59	1.57±0.12	0.45±0.03	3.47±0.37
6	26.25	34.81	0.12	167.16	0.84	1.51±0.12	0.43±0.04	3.47±0.40
7	26.06	34.61	0.01	221.56	0.64	1.64±0.13	0.45±0.04	3.64±0.42
8	26.66	35.12	0.42	280.80	1.17	1.72±0.13	0.46±0.03	3.78±0.40
9	26.89	34.80	0.18	190.91	0.43	1.72±0.14	0.46±0.04	3.76±0.44
10	26.86	35.48	0.29	300.70	0.68	1.95±0.16	0.58±0.05	3.33±0.39
11	26.67	35.54	1.29	301.79	6.56	1.96±0.15	0.51±0.04	3.85±0.41
12	26.02	36.14	0.07	275.39	0.70	1.50±0.12	0.50±0.04	3.00±0.34
13	26.66	34.54	1.18	272.52	5.06	1.87±0.16	0.49±0.04	3.83±0.47
14	26.88	35.65	1.22	326.05	7.00	1.73±0.13	0.46±0.03	3.78±0.40
15	26.82	31.34	1.30	268.56	5.78	1.87±0.15	0.53±0.04	3.53±0.41
16	26.86	37.93	0.95	280.03	0.26	2.60±0.21	0.67±0.06	3.91±0.46
17	27.10	35.42	1.46	297.84	6.19	1.45±0.12	0.40±0.03	3.61±0.43
18	27.09	36.29	1.24	260.60	0.23	1.76±0.13	0.46±0.03	3.85±0.41
19	27.12	35.70	0.51	280.25	0.25	2.06±0.17	0.49±0.04	4.19±0.50

* Temperature and salinity were determined using a YSI Model 6000 Sonde.

† Nutrient analysis for ammnonium not reported due to measurement difficulties.

Table 2: Results of sampling in Nueces Bay, July 2002

Station	Temp.[*]	Sal.[*]	PO_4^{3-}	$\mathrm{SiO_2}$	$\mathrm{NO_3^-} + \mathrm{NO_2^-}$[†]	Activity (dpm/L)		$\frac{^{228}\mathrm{Ra}}{^{226}\mathrm{Ra}}$
	(Celsius)	(ppt)	(μM)	(μM)	(μM)	^{228}Ra	^{226}Ra	
1	29.53	0.36	3.70	313.02	3.88	0.20±0.02	0.17±0.01	1.15±0.13
2	29.59	0.40	2.92	377.95	2.54	0.15±0.01	0.14±0.01	1.09±0.14
3	30.04	0.56	3.49	363.14	0.73	0.22±0.02	0.18±0.01	1.20±0.15
4	32.49	1.24	2.31	678.12	1.03	0.24±0.02	0.19±0.02	1.27±0.17
5	29.83	0.90	2.71	457.77	0.48	0.32±0.03	0.25±0.02	1.29±0.17
6	30.19	0.40	2.28	395.68	1.14	0.24±0.02	0.19±0.02	1.21±0.14
7	31.77	1.25	3.33	418.33	0.75	0.22±0.02	0.17±0.01	1.31±0.16
8	31.08	0.32	2.49	324.10	1.53	0.19±0.02	0.16±0.01	1.18±0.16
9	31.51	0.60	2.40	394.59	1.13	0.19±0.02	0.18±0.02	1.06±0.15
10	31.65	0.90	2.57	289.56	1.82	0.27±0.02	0.21±0.02	1.32±0.16
11	30.72	0.35	2.72	377.21	4.74	0.20±0.02	0.18±0.01	1.12±0.14
12	31.43	1.60	2.65	510.67	0.49	0.24±0.02	0.19±0.01	1.27±0.15
13	30.88	0.36	2.11	639.65	6.64	0.23±0.02	0.19±0.01	1.18±0.14
14	31.45	0.59	1.79	344.94	16.30	0.19±0.02	0.18±0.01	1.07±0.13
15	30.48	0.36	2.22	474.59	6.57	0.24±0.02	0.18±0.01	1.35±0.16
17	30.18	0.34	2.26	638.72	4.63	0.19±0.02	0.16±0.01	1.19±0.17
18	29.60	0.42	2.57	338.71	6.37	0.21±0.02	0.19±0.01	1.12±0.12
19	32.56	0.29	2.64	536.99	5.28	0.22±0.02	0.20±0.02	1.09±0.13
20	30.03	0.29	3.50	445.99	7.26	0.22±0.02	0.20±0.01	1.07±0.12
21	31.30	0.33	3.24	253.66	2.23	0.26±0.02	0.19±0.02	1.35±0.17

[*] Temperature and salinity were determined using a YSI Model 6000 Sonde.

[†] Nutrient analysis for ammonium not reported due to measurement difficulties.

Table 3: Results of sampling in Nueces Bay, 19 May 2003

Station	Temp.[*]	Sal.[*]	PO_4^{3-}	$\mathrm{SiO_2}$	$\mathrm{NH_4^+}$[†]	Activity (dpm/L)			$\frac{^{228}\mathrm{Ra}}{^{226}\mathrm{Ra}}$
	(Celsius)	(ppt)	(μM)	(μM)	(μM)	^{224}Ra	^{228}Ra	^{226}Ra	
1	29.08	27.070	0.15	56.16	3.37	0.56±0.07	1.03±0.08	0.37±0.03	2.81±0.29
4	30.31	20.998	0.37	169.46	0.27	1.34±0.39	1.32±0.11	0.50±0.04	2.65±0.30
8	28.64	25.858	0.41	75.85	0.38	1.06±0.16	1.21±0.09	0.50±0.04	2.43±0.26
9	31.11	21.183	0.74	181.43	0.08	1.23±0.35	1.29±0.10	0.49±0.04	2.65±0.29
10	29.66	20.910	0.49	102.52	0.12	0.66±0.21	1.27±0.10	0.54±0.04	2.34±0.25
13	30.37	19.878	0.62	131.39	0.84	5.14±1.51	1.52±0.11	0.70±0.05	2.17±0.23
16	28.74	25.754	0.53	70.94	1.77	2.37±0.41	2.23±0.18	1.00±0.08	2.23±0.25
17	29.99	22.855	0.44	78.37	0.15	4.43±1.59	1.82±0.14	0.86±0.06	2.13±0.22
18	29.20	25.610	0.46	70.25	0.06	1.92±0.30	1.59±0.13	0.82±0.06	1.94±0.21
21	29.47	24.600	0.24	58.41	0.13	1.06±0.19	1.72±0.13	0.83±0.06	2.07±0.22

[*] Temperature and salinity were determined using a SeaBird Electronics SeaCat CTD profiler.

[†] Nutrient analysis for $\mathrm{NO_3^-} + \mathrm{NO_2^-}$ not reported due to measurement difficulties.

Table 4: Results of sampling in Nueces Bay, 27 May 2003

Station	Sal.* (ppt)	PO_4^{3-} (μM)	SiO_2 (μM)	NH_4^+† (μM)	Activity (dpm/L) ^{224}Ra	^{228}Ra	^{226}Ra	$\frac{^{228}Ra}{^{226}Ra}$
1	27.847	0.11	43.72	0.15	0.43±0.10	0.97±0.07	0.31±0.02	3.12±0.34
4	27.869	0.54	157.43	0.20	0.75±0.21	1.13±0.09	0.38±0.03	2.97±0.32
8	27.849	0.18	64.61	0.54	0.44±0.12	1.46±0.11	0.61±0.05	2.39±0.26
9	27.868	0.65	79.74	0.81	-	1.39±0.10	0.52±0.04	2.67±0.28
10	27.831	0.48	118.64	0.10	-	1.40±0.11	0.59±0.04	2.37±0.25
13	27.852	0.77	118.12	68.60	1.16±0.18	1.58±0.12	0.70±0.05	2.27±0.25
16	27.859	0.26	76.47	22.97	1.30±0.40	1.95±0.15	0.83±0.06	2.34±0.25
17	27.871	0.55	78.84	1.00	-	2.10±0.16	0.32±0.02	6.66±0.73
18	27.851	0.53	106.08	5.47	1.25±0.33	2.18±0.16	0.96±0.07	2.26±0.23
21	27.836	0.58	84.60	0.52	-	1.99±0.15	0.92±0.07	2.18±0.23
CCB	28.109	0.27	50.53	0.42	-	1.03±0.08	0.33±0.02	3.15±0.33

* All data were determined using a YSI Model 6000 Sonde.Salinity was determined using a Guildline Autosal salinometer (no temperature data).

† Nutrient analysis for $NO_3^- + NO_2^-$ not reported due to measurement difficulties.

Table 5: Bird Island Nutrient and Radium Data, June 2002 - May 2003

Sample	Collection Date	PO_4^{3-} (μM)	SiO_2 (μM)	$NH_4^{+\dagger}$ (μM)	Activity (dpm/L)		$\frac{^{228}Ra}{^{226}Ra}$
					^{228}Ra	^{226}Ra	
1	19-Jun-2002	-	-	-	1.39±0.10	0.33±0.02	4.16±0.44
2	27-Jun-2002	-	-	-	1.63±0.12	0.39±0.03	4.22±0.44
3	3-Jul-2002	-	-	-	1.57±0.12	0.37±0.03	4.20±0.44
4	9-Jul-2002	-	-	-	1.75±0.13	0.40±0.03	4.35±0.46
5	19-Jul-2002	-	-	-	0.81±0.06	0.38±0.03	2.09±0.22
6	2-Aug-2002	-	-	-	1.80±0.13	0.41±0.03	4.44±0.47
7	8-Aug-2002	-	-	-	1.41±0.11	0.32±0.02	4.34±0.46
8	16-Aug-2002	0.33	-	-	1.97±0.15	0.46±0.03	4.25±0.45
9	24-Aug-2002	0.08	81.42	0.00	1.71±0.13	0.38±0.03	4.47±0.47
10	3-Sep-2002	0.00	76.26	0.00	1.86±0.14	0.44±0.03	4.22±0.44
11	11-Sep-2002	0.04	53.87	1.25	1.28±0.10	0.30±0.02	4.21±0.45
12	19-Sep-2002	0.37	-	-	1.47±0.11	0.33±0.02	4.49±0.48
13	3-Oct-2002	0.00	16.71	0.00	1.25±0.09	0.31±0.02	4.03±0.42
14	2-Nov-2002	0.07	68.87	0.36	0.68±0.05	0.21±0.02	3.20±0.34
15	11-Nov-2002	0.00	43.69	0.00	0.67±0.05	0.14±0.01	4.89±0.52
16	19-Nov-2002	0.12	5.29	0.48	1.25±0.09	0.35±0.03	3.58±0.37
17	27-Nov-2002	0.18	31.78	1.25	1.06±0.08	0.28±0.02	3.77±0.40
18	5-Dec-2002	0.13	33.90	0.41	0.79±0.06	0.24±0.02	3.37±0.35
19	13-Dec-2002	0.20	50.06	2.72	0.66±0.05	0.21±0.02	3.12±0.33
20	18-Dec-2002	0.20	4.09	0.32	0.88±0.07	0.24±0.02	3.63±0.39
21	10-Jan-2003	0.17	52.81	0.57	1.21±0.09	0.34±0.03	3.50±0.37
22	17-Jan-2003	0.25	46.99	1.63	0.86±0.07	0.27±0.02	3.16±0.35
23	24-Jan-2003	0.23	37.34	2.25	0.86±0.07	0.26±0.02	3.31±0.36
24	31-Jan-2003	0.25	77.36	7.51	0.74±0.05	0.23±0.02	3.17±0.33
25	7-Feb-2003	0.21	30.18	1.59	0.77±0.06	0.23±0.02	3.37±0.36
26	14-Feb-2003	0.47	45.32	0.66	0.78±0.06	0.20±0.02	3.89±0.42
27	25-Feb-2003	0.59	59.07	5.90	0.97±0.07	0.26±0.02	3.70±0.40
28	4-Mar-2003	0.32	39.02	5.08	0.66±0.05	0.21±0.02	3.09±0.32
29	18-Mar-2003	0.27	70.96	3.07	0.70±0.05	0.21±0.02	3.33±0.36
30	27-Mar-2003	0.30	14.53	0.98	0.89±0.07	0.26±0.02	3.49±0.38
31	4-Apr-2003	0.52	78.69	7.43	1.10±0.09	0.26±0.02	4.19±0.50
32	11-Apr-2003	0.30	77.24	2.87	0.98±0.08	0.28±0.02	3.52±0.40
33	25-Apr-2003	0.36	131.79	6.80	1.36±0.10	0.36±0.03	3.74±0.40
34	2-May-2003	0.02	149.57	5.31	1.40±0.10	0.33±0.02	4.22±0.45
35	9-May-2003	0.00	167.85	11.55	1.70±0.13	0.41±0.03	4.16±0.46
36	16-May-2003	0.00	163.70	18.22	1.68±0.13	0.35±0.03	4.73±0.50

[†] Nutrient analysis for $NO_3^- + NO_2^-$ not reported due to measurement difficulties. Also note, nutrient samples were not collected prior to 16 Aug. 2002.

Table 6: Bird Island Ancillary Sample Station Parameters, June 2002 - May 2003

ID	Date	Temp. (Celsius)	Cond. (mS/cm)	%DO	DO (mg/L)	pH	Sal. (ppt)
1	19-Jun-3902	-	-	-	-	-	-
2	27-Jun-3902	-	-	-	-	-	-
3	3-Jul-3902	-	-	-	-	-	-
4	9-Jul-3902	-	-	-	-	-	-
5	19-Jul-3902	-	-	-	-	-	-
6	2-Aug-3902	-	-	-	-	-	-
7	8-Aug-3902	-	-	-	-	-	-
8	16-Aug-3902	-	-	-	-	-	-
9	24-Aug-3902	-	-	-	-	-	-
10	3-Sep-3902	-	-	-	-	-	-
11	11-Sep-3902	-	-	-	-	-	-
12	19-Sep-3902	-	-	-	-	-	-
13	3-Oct-3902	-	-	-	-	-	-
14	2-Nov-3902	-	-	-	-	-	-
15	11-Nov-3902	-	-	-	-	-	-
16	19-Nov-3902	22.10	44.81	128.0	9.45	8.34	29.01
17	27-Nov-3902	-	-	-	-	-	-
18	5-Dec-3902	9.53	31.95	105.6	10.61	8.29	19.85
19	13-Dec-3902	15.48	27.83	115.1	10.34	8.13	17.17
20	18-Dec-3902	23.63	36.45	114.2	8.48	8.48	23.05
21	10-Jan-3903	15.62	35.90	110.1	9.54	7.86	22.71
22	17-Jan-3903	10.18	33.49	109.3	10.75	8.18	20.92
23	24-Jan-3903	9.39	36.88	113.7	11.21	7.97	23.23
24	31-Jan-3903	16.82	37.20	102.3	8.60	7.99	23.62
25	7-Feb-3903	9.00	-	-	-	-	-
26	14-Feb-3903	20.70	39.40	116.5	9.01	8.20	25.16
27	25-Feb-3903	7.70	38.62	102.3	10.42	8.16	24.33
28	4-Mar-3903	14.68	39.40	97.8	8.51	8.10	25.14
29	18-Mar-3903	-	-	-	-	-	-
30	27-Mar-3903	-	-	-	-	-	-
31	4-Apr-3903	23.67	40.92	-	-	8.00	26.20
32	11-Apr-3903	17.39	40.89	-	-	8.11	26.23
33	25-Apr-3903	28.54	44.91	112.3	7.41	8.15	28.94
34	2-May-3903	28.99	45.58	117.2	7.76	8.35	29.42
35	9-May-3903	30.27	51.73	-	-	8.40	33.86
36	16-May-3903	29.30	55.53	125.8	7.86	8.04	36.71

Table 7: Lake Corpus Christi and Nueces River Nutrient and Radium Data

Sample	Collection Date	PO_4^{3-}	SiO_2	$\mathrm{NH}_4^{+\dagger}$	Activity (dpm/L)		$\frac{^{228}\mathrm{Ra}}{^{226}\mathrm{Ra}}$
		(μM)	(μM)	(μM)	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	
LCC	12-Dec-2003	0.39	229.97	0.85	0.19±0.02	0.12±0.01	1.60±0.19
NR	13-Dec-2003	0.67	227.81	0.55	0.15±0.01	0.14±0.01	1.08±0.12
NR	14-Dec-2003	0.66	149.56	0.68	0.17±0.01	0.11±0.01	1.54±0.17

† Nutrient analysis for $\mathrm{NO}_3^- + \mathrm{NO}_2^-$ not reported due to measurement difficulties.

Table 8: Groundwater Nutrient and Radium Data

Sample	Collection Date	PO_4^{3-}	SiO_2	$\mathrm{NH}_4^{+\dagger}$	Activity (dpm/L)			$\frac{^{228}\mathrm{Ra}}{^{226}\mathrm{Ra}}$
		(μM)	(μM)	(μM)	$^{224}\mathrm{Ra}$	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	
1	03-June-2003	2.50	275.40	11.56	0.23±0.05	0.22±0.02	0.15±0.01	1.47±0.17
2	03-June-2003	0.32	347.85	4.62	0.15±0.05	0.14±0.01	0.10±0.01	1.50±0.19
3	03-June-2003	0.57	355.42	4.12	0.40±0.09	0.58±0.04	0.44±0.03	1.32±0.14
4	09-Oct-2002	0.00	196.90	7.67	0.96±0.19	0.50±0.04	0.12±0.01	4.03±0.47
5	09-Oct-2002	0.04	346.08	1.22	-	0.39±0.03	0.29±0.02	1.34±0.15
6	09-Oct-2002	0.07	173.32	1.21	0.16±0.06	0.34±0.03	0.29±0.02	1.17±0.12
7	09-Oct-2002	0.23	296.41	1.03	-	0.13±0.01	0.26±0.02	0.52±0.06
8	15-May-2003	0.17	310.77	1.38	-	0.17±0.01	0.18±0.01	0.94±0.10
9	15-May-2003	0.23	309.47	0.27	-	0.07±0.01	0.09±0.01	0.86±0.11
10	16-May-2003	-	311.49	0.94	-	0.14±0.01	0.19±0.01	0.73±0.08

† Nutrient analysis for $\mathrm{NO}_3^- + \mathrm{NO}_2^-$ not reported due to measurement difficulties.

Table 9: Information on Wells Sampled

Sample	Name	TWDB Well ID	Long.	Lat.	Depth (ft)	Well Dia. (in)	Screen (ft)	Comments
1	Garrett home	-	-97.05167	27.83833	20	3×2	17-20	Three wells 20 ft apart sampled at common header.
2	UTMSI	-	-97.05167	27.83833	-	-	-	Pumped well.
3	Moorehead home	-	-97.31995	27.65397	-	-	-	Pumped well.
4	Koonce pasture	-	-97.42200	27.87527	28	36	none	Large diameter dug well pumped by windmill, sampled at discharge.
5	San Patricio Church	-	-97.77172	27.95473	-	-	-	Pumped well used for lawn.
6	Sinton Golf Course	-	-97.52894	27.07324	275	3×4	-	Three 4 in. wells sampled at common header.
7	Welder Wildlife Refuge 1	7961305	-97.40350	28.10463	-	-	-	Windmill, sampled collected at discharge.
8	Welder Wildlife Refuge 2	7961304	-97.39651	28.12323	-	-	-	Windmill, sampled collected at discharge.
9	Welder Wildlife Refuge 3	7962111	-97.33675	28.10066	-	-	-	Windmill, sampled collected at discharge.
10	Welder Wildlife Refuge 4	-	-97.37389	28.11583	-	4	-	Pumped well.

Table 10: Gulf of Mexico Radium Data, September 2002

Sample	Activity (dpm/L)		$\frac{^{228}\mathrm{Ra}}{^{226}\mathrm{Ra}}$
	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	
1	0.45±0.03	0.04±0.00	10.28±1.16
2	0.44±0.03	0.05±0.00	8.86±1.01
5	0.29±0.02	0.12±0.01	2.42±0.26
7	0.07±0.01	0.06±0.01	1.19±0.16
7(500m)	0.01±0.00	0.11±0.01	0.12±0.03

Table 11: Results of Model Calculations of Submarine Groundwater Discharge to Nueces Bay

		April 2002		July 2002		19 May 2003		27 May 2003	
		$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$	$^{228}\mathrm{Ra}$	$^{226}\mathrm{Ra}$
$\mathrm{Ra_{NB}}$	(dpm/L)	1.65±0.16	0.45±0.04	0.22±0.01	0.19±0.01	1.50±0.21	0.66±0.12	1.62±0.25	0.61±0.14
$\mathrm{Ra_{GM}}$	(dpm/L)	0.45	0.04	0.45	0.04	0.45	0.04	0.45	0.04
$\mathrm{Ra_{GW}}$	(dpm/L)	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1
$\mathrm{Ra_{NR}}$	(dpm/L)	0.17±0.02	0.12±0.02	0.17±0.02	0.12±0.02	0.17±0.02	0.12±0.02	0.17±0.02	0.12±0.02
$\mathrm{Ra_{sed}}$	(dpm/L/$\mathrm{m^2}$)	0.19	0.05	0.10	0.02	0.19	0.05	0.19	0.05
$\mathrm{Ra_{ex}}$	(dpm/L)	0.27	0.14	N/A[†]	N/A[†]	-[‡]	0.07	-[‡]	0.07
$\mathrm{Q_{NR}}$	($10^6\mathrm{m^3}$/month)	2.3	2.3	16.9	16.9	0.6	0.6	0.6	0.6
Precip.	($10^6\mathrm{m^3}$/month)	7.8	7.8	190.4	190.4	5.7	5.7	5.7	5.7
Evap.	($10^6\mathrm{m^3}$/month)	13.6	13.6	13.1	13.1	14.5	14.5	14.5	14.5
τ	(days)	250	250	14	14	250	250	250	250
$\mathrm{A_{NB}}$	($10^6\mathrm{m^2}$)	74.9	74.9	74.9	74.9	74.9	74.9	74.9	74.9
$\mathrm{V_{NB}}$	($10^6\mathrm{m^3}$)	91.2	91.2	91.2	91.2	91.2	91.2	91.2	91.2
SGWD	($10^6\mathrm{m^3}$/month)	6.0	15.4	N/A[†]	N/A[†]	-[‡]	8.2	-[‡]	7.2
SGWD*	($10^6\mathrm{m^3}$/month)	6.9	16.4	N/A[†]	N/A[†]	-[‡]	9.3	-[‡]	8.3

[†] For the July 2002 flood period, there is little or no discernible excess Ra in the bay, and so no calculation of SGWD is possible.

[‡] For 19 and 27 May 2003 there was no excess of $^{228}\mathrm{Ra}$ that could not be accounted for by sources other than SGWD.

[*] This row of estimates of SGWD is calculated assuming there is no diffusive flux of radium from the sediments.

B Comments from TWDB on Draft Report

Attached in this appendix are specific comments from TWDB reviewers on the first draft submitted in June 2003 prior to the completion of the analyses. All of these comments were incorporated in a revised draft report submitted on October 1, 2003.

Henrietta Edwards

TEXAS WATER DEVELOPMENT BOARD

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RECEIVED
DEC 15 2003
Office of Sponsored Projects

December 2, 2003

Mr. Bobby McQuiston, Director
University of Texas at Austin
Office of Sponsored Projects
Austin, TX 78713-7726

Re: Water Research Contract Between the University of Texas Marine Science Institute (UTMSI) and the Texas Water Development Board (Board), TWDB Contract No. 2002-483-416, Revised Draft Report Entitled "TWDB Report"

Dear Mr. McQuiston:

Staff members of the Texas Water Development Board have completed a review of the revised draft report under TWDB Contract No. 2002-483-416. As stated in the above referenced contract, UTMSI will consider incorporating comments from the EXECUTIVE ADMINISTRATOR shown in Attachment 1 and other commentors on the draft final report into the final report. A written explanation on comments not incorporated into the Final Report must be submitted to the Board for approval.

The revised draft report is acceptable to the Board. Please forward to the Board one (1) electronic copy, one (1) unbound single-sided camera-ready original, and nine (9) bound double-sided copies of the final report on this project, to the attention of Phyllis Thomas at the address listed below.

Please contact Dr. David Brock at (512) 936-0819 if you have any questions about this contract.

Sincerely,

William F. Mullican, III
Deputy Executive Administrator
Office of Planning

c: David Brock, TWDB

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ATTACHMENT 1

Texas Water Development Board Comments on Draft Final Report entitled "TWDB Report" Contract Number 2002-483-416

This report is incomplete due to required information dealing with: 1) analysis results, 2) calculations of groundwater discharge and nutrient fluxes, and 3) evaluation of the importance of groundwater inputs are missing. Consequently, this report does not adequately address the three objectives outlined in the Scope of Work.

Please address each of the following items in the revised draft plan:

1. Add a location map of the study area.
2. It appears that the period of high inflows to the estuary disrupted sampling plans such that sampling was not done quarterly. Please state and explain why the sample plan was not followed.
3. Page 2, paragraph 1: It is unlikely that trawling can breach a layer of sediment that is thick enough to be an effective confining unit. State and explain the effects of reduced groundwater discharge.
4. Page 3, paragraph 1: The sentence "...where the groundwater table lie above seawater" should be changed to "...where the water table lies above sea level"
5. Page 3, paragraph 2: Change "...coastal lowlands aquifer system..." to "...Gulf Coast aquifer system..." Delete "...and to shallow surface aquifers"
6. Page 5, Hydrogeology section, 4th sentence: "there" should be "their".
7. Page 5, paragraph 2: Change "...deposits from fluvial..." to "...deposited in...". Change word "tilt" to "dip". Delete the sentences "During the Pleistocene..." and "In addition the coastal..."
8. Page 5, paragraph 3: Delete the sentence "Sedimentation continues..."
9. Page 6, paragraph 1: Change "...only stream that does..." to "...only stream in the study area that does...". Change "...the deposits tend towards sand at the shoreline and mud in the central areas..." to "...the sediments grade from sand at the shoreline to clay offshore..."
10. Page 6, paragraph 2: Change "...both water table and ..." to "...both unconfined and ...". Change "...mainly artesian wells." To "...mainly from artesian wells."
11. Page 6, paragraph 3: Change "Recharge of ..." to "Recharge to...". "...Drought, drench" is not terminology to be used in a professional report. Change "...groundwater moves towards..." to "...groundwater flows towards..."
12. Page 7, paragraph 1: "would be" should be "are"
13. Page 7, paragraph 2: Change "exchange with" to "discharge to". Delete "through the submerged sediment...fractures.". Fracture flow is not applicable to unconsolidated

ATTACHMENT 1

Texas Water Development Board Comments on
Draft Final Report entitled
"TWDB Report"
Contract Number 2002-483-416

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aquifers. Change "zone of transition" to "mixing zone" or "freshwater-saltwater interface". Need to state how does urbanization alters groundwater flow rates

14. Page 9, in discussion of seepage meters, superscript needed for m2. In last sentence of paragraph, separate two words.

15. Page 10, Sampling section: change endmember to end-member.

16. In results, some tables do not show salinities or nutrient data. Text should explain if data were not analyzed or if samples/measurements were not performed. Salinities may be/or are available from other sources (CBI Salt01, TCEQ sites)

17. The nutrient data and implications for nutrients associated with groundwater seepage are not discussed. If the information was more difficult to assess than anticipated, please state and discuss what was attempted in that area.

18. There are a number of stations in Nueces Bay; Table 9 should show confidence bounds for Nueces Bay Ra data.

19. Conclusions are needed before the draft report can be appraised. Without the final conclusions and with the analysis focusing on Nueces Bay, it is hard to judge the report as a final product. A new draft, including conclusions, is needed before the Board can review the document for finalization.