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Characterizing sources of groundwater to a tropical coastal lagoon in a karstic area using radium isotopes and water chemistry

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Abstract

Radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) and water chemistry were used to identify two chemically distinct sources of submarine groundwater discharge (SGD) in Celestún Lagoon, Yucatán, Mexico. Low salinity groundwater discharging from springs within the lagoon has previously been identified and extensively sampled for nutrient concentrations. However, a second type of groundwater discharging into the lagoon was detected during this study using radium isotope activity measurements. This second type of groundwater is characterized by moderate salinities (within the range of lagoon salinities) and very elevated radium activities in comparison to the low salinity groundwater, mixed lagoon water, and seawater. Further analysis showed that the two types of groundwater also have distinct chloride, strontium, and sulfate ratios, along with slightly different nutrient concentrations. Groundwater discharge occurs through large and small springs scattered throughout the lagoon, and both types of groundwater were detected discharging from one of the larger springs. The relative proportions of low salinity groundwater and brackish high radium groundwater varied over the tidal cycle. In order to better understand the relative contributions of each type of groundwater to the lagoon, a three end-member mixing model based on the distinct chemical and isotopic compositions of both types of groundwater and of seawater was used to estimate the distribution of each water type throughout the lagoon in different seasons. This study suggests that substantial groundwater discharge to the lagoon can occur during both dry and rainy seasons. The presence of two groundwater sources has implications for monitoring and protection of the Celestún Lagoon Biosphere Reserve, since the two sources may have different susceptibilities to anthropogenic contamination depending on their respective recharge area and recharge rates.

Keywords: Submarine groundwater discharge; Radium; Lagoons; Nutrients; Coastal waters

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1. Introduction

Groundwater discharge can be an important source of nutrients, contaminants, and low salinity water to many types of coastal ecosystems (Moore, 1996, 1999; Corbett et al., 2000; Kelly and Moran, 2002; Garrison and Glenn,

2003; Boehm et al., 2004; Paytan et al., 2006). This may be particularly important in karstic areas such as the Yucatán Peninsula, Mexico, where the high permeability of the bedrock prevents the formation of rivers and reduces the amount of surface runoff (Perry et al., 2002). Although many studies have shown that coastal groundwater discharge may be spatially and temporally variable (i.e. Rama and Moore, 1996, Hussain et al., 1999; Krest et al., 1999), fewer studies have addressed either seasonal changes in discharge and associated nutrient fluxes (Bollinger and Moore, 1993; Top et al., 2001; Kelly and Moran, 2002), or the contribution of more than one groundwater source to a coastal site (Moore, 2003; Charette, 2007). Variations in groundwater sources as well as overall discharge rates could contribute to seasonal differences in nutrient and/or pollutant input to coastal areas. Accordingly, it is important to characterize each distinct source of groundwater and determine its contribution to the coastal ecosystem. This knowledge may also be useful for designing the best management plans for coastal ecosystems restoration and protection efforts.

In many coastal areas, including the northern Yucatán Peninsula, water discharging from coastal aquifers consists of a mixture of meteoric fresh water, recycled seawater, and possibly wastewater (Corbett et al., 2000; Top et al., 2001). Moore (1999) defined the underground mixing zone for these waters as the "subterranean estuary", and described how chemical mixing and various dissolution/precipitation reactions may result in water with a distinct chemical composition different from that of the original sources. The subterranean mixing of freshwater and seawater results in brackish groundwater that is often enriched in nutrients and other elements compared to the coastal waters. This brackish water, along with fresh groundwater, is generally referred to as submarine groundwater discharge (SGD) (Johannes, 1980; Church, 1996; Burnett et al., 2003; Moore, 2003). Nutrient fluxes from SGD to coastal waters have been calculated using estimates of total SGD and the nutrient content of this water at locations around the world (Kelly and Moran, 2002; reviewed in Burnett et al., 2003; Garrison and Glenn, 2003; Boehm et al., 2004).

Various groundwater sources can be identified and characterized using natural chemical and isotopic tracers (e.g. Swarzenski et al., 2001; Top et al., 2001; Vengosh et al., 2002). These signatures could be used to distinguish between different groundwater reservoirs that discharge to the same coastal area and to quantify the contribution from each source. Using multiple chemical parameters (major and minor elements, nutrients, isotope signatures) allows for greater distinction between potential sources. Moore (2003) used Ra isotope ratios to identify two separate sources of SGD for a section of coastline along the northeast Gulf of Mexico, a surficial aquifer and a deeper aquifer, both discharging in close proximity to each other. However, this approach has not been widely applied and to our knowledge very few studies of SGD have evaluated temporal changes in contribution of multiple sources of SGD to a single coastal area (Charette, 2007). In this study we use Ra isotopes along with other chemical tracers to distinguish between groundwater types discharging into a single lagoon on the Yucatán Peninsula and assess the temporal fluctuation in the relative contribution to the lagoon from these distinct sources.

The radium isotope quartet, consisting of two long-lived isotopes (^{226}Ra and ^{228}Ra) and two short-lived isotopes (^{223}Ra and ^{224}Ra), has been identified as a powerful set of natural isotopic tracers for quantifying discharge of brackish SGD (Rama and Moore, 1996; Moore, 1999). Radium isotopes are decay products of naturally occurring uranium and thorium. All three elements are tightly bound to particles in freshwater environments, and as the ionic strength of the groundwater increases with increasing salinity, the radium isotopes desorb from the particles and are released into the brackish water (Li et al., 1977; Webster et al., 1995). Radium isotope activities in brackish groundwater are often several orders of magnitude higher than in either fresh surface water or ocean water. Once the contribution of radium isotopes from river inflow, open ocean water, and regeneration within sediments to any system has been determined, total SGD input to the system can be quantified using the measurements of the excess radium isotope activities within the system (following Moore, 1996).

The northwestern Yucatán aquifer consists of a freshwater lens 15–100 m thick underlain by a saline intrusion that extends more than 40 km inland (Marin, 1990; Steinich and Marin, 1997; Perry et al., 1995, 2002). The upper part of the Yucatán aquifer developed in a highly permeable, flat-lying Tertiary limestone and dolomite, and it overlies the terminal Cretaceous Chicxulub bolide impact crater and its surrounding breccia blanket (Hildebrand et al., 1991, 1995; Sharpton et al., 1993). Most of the Yucatán aquifer is unconfined and responds rapidly to precipitation events. However, there is a thin, partially confining layer of nearly impermeable calcium-carbonate present along the northern coastline of the Peninsula (Perry et al., 1995). The presence of this aquitard results in a chemically active mixing zone along the coast, where the water from the underlying saline intrusion mixes with the freshwater lens, as indicated by the brackish salinities of the springs

discharging along the coast and into the coastal lagoons (Perry et al., 1989, 1995, 2002).

2. Materials and methods

2.1. Study area

Celestún Lagoon (Fig. 1) is a long (22 km), shallow (average depth 1.2 m) coastal lagoon located on the Yucatán Peninsula, Mexico. The lagoon bottom is fairly flat except for a 100 m wide tidal channel which extends about 15 km from the mouth of the lagoon towards the northern part of the lagoon (Herrera-Silveira, 1994c). The semidiurnal tidal range is approximately 0.5 m. The lagoon and surrounding mangrove forests are part of a designated U. N. Biosphere Reserve, and provide important habitat for many species of wildlife, including economically important fish and crustaceans.

The climate of the northern Yucatán Peninsula consists of a dry season from March through May during which rainfall is typically less than 50 mm, a rainy season from June through October during which the majority of the annual rainfall (>500 mm) occurs, and the "nortes" season from November through February, characterized by moderate rainfall (20–60 mm) and intermittent high wind speeds greater than 80 km hr^{-1} (Herrera-Silveira, 1994c). Mean annual rainfall in the Celestún area is 750 mm, and the evaporation rate is approximately 1400 mm (Herrera-Silveira et al., 1999).

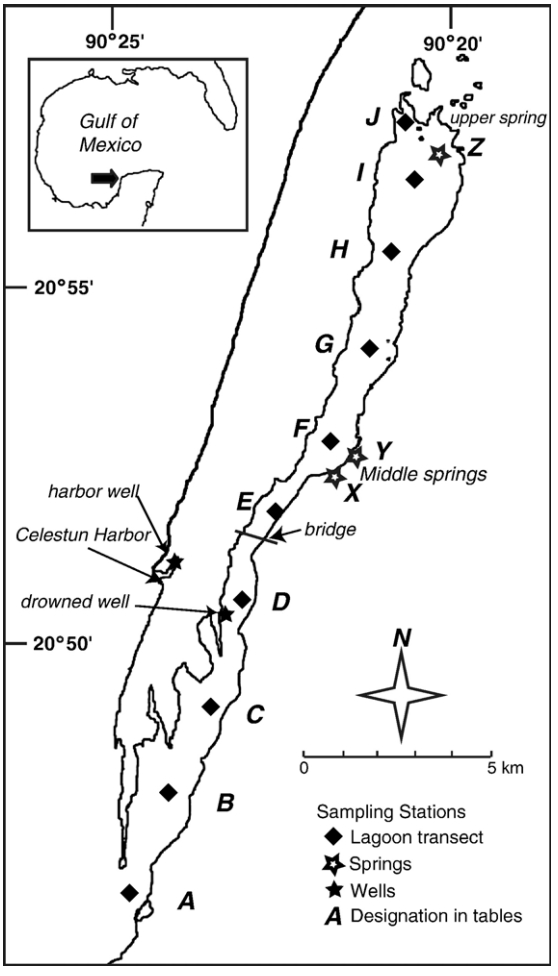

Fig. 1. Map of Celestún Lagoon, Yucatán, Mexico. Lagoon transect stations and groundwater sampling locations are shown on the map.

Due to the karstic nature of the Yucatán Peninsula precipitation rapidly penetrates the ground resulting in negligible surface runoff and no rivers in the area. Groundwater discharge from the Yucatán aquifer has been detected in many places along the coast (Back et al., 1979; Stoessell et al., 1989; Merino et al., 1990; Herrera-Silveira, 1994a; Herrera-Silveira et al., 1999). At least 30 different submarine springs are present throughout Celestún Lagoon, with the majority concentrated in the middle and northern parts of the lagoon (Alonzo Parra, personal communication). The discharge of water from these springs results in a year-round salinity gradient with fresher water in the northern section grading out to seawater salinities near the mouth of the lagoon (Fig. 2). Most of the discharge points are small, and no published maps of these springs currently exist, due in part to the seasonal nature of some of the springs, and the difficulty in finding the smaller discharge points. Relatively large submarine springs are located near the northern end of the lagoon and near the middle of the lagoon (Fig. 1).

Nutrient and basic water quality monitoring within the lagoon and at submarine springs in the northern lagoon has been conducted during various time periods from 1987 through 2002 (Herrera-Silveira, 1994a,b, 1995, 1996; Herrera-Silveira and Comin, 1995; Herrera-Silveira et al., 1998, submitted for publication). During the course of these studies, groundwater samples were collected from the submarine springs in the northern lagoon only, and did not include analyses for potential conservative tracers of groundwater other than salinity and silica. Therefore, only the presence of the low salinity groundwater was detected, and the second groundwater type, the brackish high radium groundwater, was not identified. The results of this long-term nutrient monitoring of the lagoon and low salinity groundwater indicate that Celestún has not yet shown evidence of considerable eutrophication; however, moderate increases in nitrate and ammonia concentrations have been observed in the northern submarine springs over this time interval, possibly resulting from enhanced agricultural or sewage infiltration into the groundwater at the recharge zone (Herrera-Silveira et al., submitted for publication).

2.2. Sampling plan

Water samples were collected during three sampling trips occurring in October 2001, July 2002, and March–April 2003. The majority of annual groundwater discharge to the lagoon is thought to occur during the 5 months of the rainy season (June–October) (Herrera-Silveira and Comin, 1995; Herrera-Silveira, 1996), and therefore one sampling trip was conducted during the late part of the rainy season (October 2001), while another

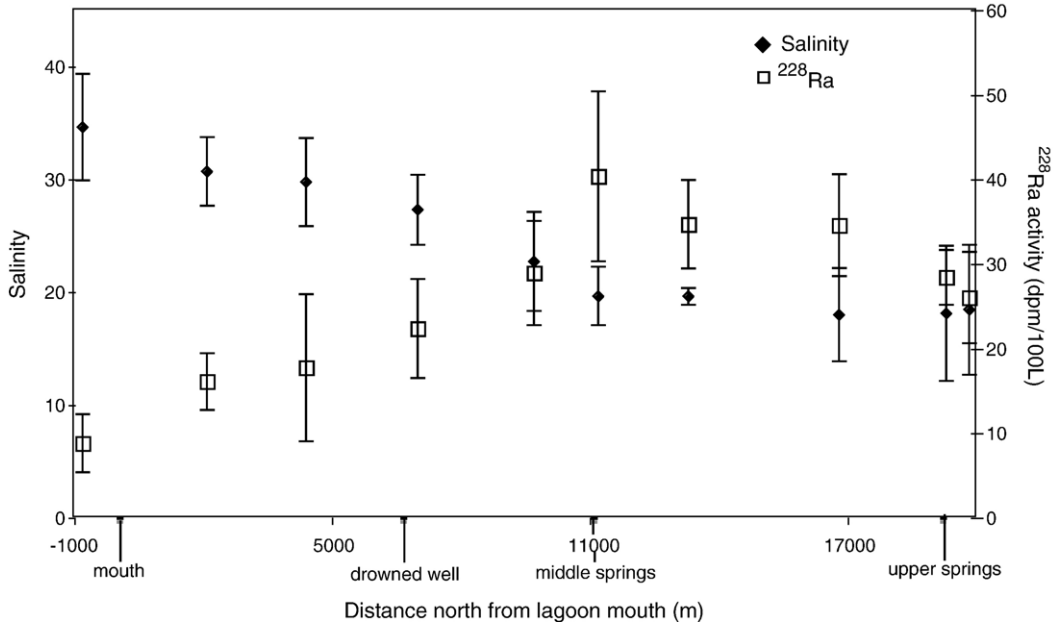

Fig. 2. Average salinity and ^{228}Ra activity along the length of Celestún Lagoon, compiled from all sampling trips. Locations of groundwater sampling points and lagoon mouth are marked for reference.

trip was conducted during the early part of the rainy season (July 2002). For comparison, samples were collected during the middle of the dry season (March–April 2003), when groundwater discharge was expected to be at its lowest. During each sampling trip, water samples were collected along a lengthwise transect of the lagoon, and from two large springs located near the midpoint of the lagoon on the east side. During the March–April 2003 sampling trip, a series of samples was collected from one of the middle springs over different stages of a tidal cycle in order to better characterize mixing between the lagoon water and discharging groundwater over the course of a tidal cycle.

All water samples were collected using a battery-operated bilge pump or by direct filling of the sample containers. Samples were collected from the groundwater discharge points by lowering the sampling pump into the depression in the lagoon sediments created by the groundwater discharge at the center of the discharge point (i.e. these samples included some lagoon water). At each sampling station, 80–100 L of water were collected in 20 L polypropylene containers for radium analysis, and 1 L of water was collected in amber high density polyethylene (HDPE) bottles for chemical and nutrient analysis. Water collected in the 1 L sample bottles was filtered and split into appropriate sample containers on the day of collection and frozen immediately after splitting for future analysis.

2.3. Radium analysis

Water for radium analysis was transferred into 100 L containers and gravity filtered through a column containing manganese coated acrylic fiber (Mn fiber) at a flow rate of approximately 1 L per minute to quantitatively remove Ra (Moore, 1976), and the total volume of filtered water was recorded. The fibers were returned to the laboratory within 5 to 10 days, rinsed with Ra-free Milli-Q water, and partially dried. The fiber was then placed in a closed loop air circulation system described by Moore and Arnold (1996) and the system was flushed with helium. The helium was circulated through the system, carrying ^{219}Rn and ^{220}Rn, the daughter products of ^{223}Ra and ^{224}Ra respectively, into a 1.1 L scintillation cell attached to a photomultiplier tube. The activities of ^{223}Ra and ^{224}Ra were calculated from the measured decay of their daughter products using a delayed coincidence counter developed by Moore and Arnold (1996). The expected analytical error for these measurements is approximately 10% (Rama et al., 1987). The samples were re-analyzed after 3 weeks in order to correct for ^{224}Ra activity supported by ^{228}Th bound to the fibers (Moore and Arnold, 1996). The average ^{228}Th correction was 7% of the total ^{224}Ra activity, and the range for all samples was 2–15% (n=85).

^{228}Ra activity was measured in the same alpha scintillation cell delayed coincidence counter used to measure activities of the short-lived radium isotopes. This method requires that the samples be aged for at least 0.5 years to allow for the partial decay of ^{228}Th bound to the fibers during the sampling, and in-growth of new ^{228}Th from the ^{228}Ra also bound to the fibers during sample filtration. Sample ^{228}Ra activity was calculated using the ^{220}Rn activity of the sample measured on the alpha scintillation cell-delayed coincidence counter, subtracting the ^{220}Rn activity supported by ^{228}Th (taken from the original sample analysis), and correcting for the percent of secular equilibrium reached and the decay of ^{228}Ra since sample collection.

^{226}Ra activity on the fibers was measured using a Durridge Co. RAD7 radon-in-air monitor following the method of Kim et al. (2001). Briefly, after analysis for activities of the short-lived radium isotopes, the fibers were moistened and hand squeezed to a

water/fiber weight ratio between 1 and 2.5 in order to achieve constant recoil efficiency for Rn. The fibers were placed in individual glass tubes which were flushed with helium, sealed, and incubated for approximately 3 weeks to allow the ^{222}Rn inside the tubes to approach secular equilibrium with the ^{226}Ra bound to the fibers. The incubation tube was then attached through a loop to the RAD7, which pumped the gas from the tube into the instrument chamber. The RAD7 was set to report alpha decays of ^{218}Po, a daughter product of ^{222}Rn, and the initial ^{226}Ra activity on the fiber was calculated using the measured ^{218}Po activity, correcting for counting efficiency using calibrated standards. The error associated with this method was found to be approximately 7%, as determined by repeated measurements of standards.

2.4. Water chemistry

Concentrations of dissolved elements (Li, B, Mg, Si, K, Ca, Mn, Rb, Sr) were measured using a Perkin Elmer Elan 6000 quadra pole inductively coupled mass spectrometer (ICP-MS) at the United States Geological Survey in Menlo Park, CA. Concentrations were based on the analysis of a series of synthetic standards made gravimetrically from pure element solutions of known concentration and included all elements of interest. The standards used were in the range of concentrations of elements in the samples. Be, Ge, and Tl were used as internal standards. Analytical error was less than 5% for all elements. Samples for [Cl^-] and [SO_4^{2-}] analysis were diluted 50-fold with Milli-Q water, then analyzed with a Dionex DX-500 ion chromatograph with a CD25 conductivity detector, an Ionpac AS9-HC column (4 mm), and AG9-HC (4 mm) guard column.

2.5. Nutrients

During the October 2001 and July 2002 trips samples were analyzed for dissolved inorganic nutrients at the Laboratorio

Table 1
Salinity and radium activity data for Celestún Lagoon

Station	Distance from mouth (m)	Salinity	^{223}Ra (dpm/100 L)	^{224}Ra (dpm/100 L)	^{226}Ra (dpm/100 L)	^{228}Ra (dpm/100 L)
October 13, 2001						
A	−800	38.5	4.0	7.7	51.9	5.6
B	2100	30	7.1	9.9	222	18.8
C	4400	32	4.7	10.3	170	11.7
D	7000	30	6.1	11.3	262	17.0
E	9700	25.5	8.5	16.5	375	23.8
F	11,200	21.5	8.4	19.0	591	33.2
G	13,300	20	6.4	18.2	539	35.1
H	16,800	14.1	7.7	17.2	610	33.3
I	19,300	14	3.8	12.6	694	31.8
July 16, 2002						
A	−800	36	6.6	11.8	82.3	8.3
B	2100	34	6.0	12.9	167	12.4
C	4400	32	9.6	15.4	189	13.7
D	7000	28	13.4	28.2	323	21.5
E	9700	25	17.8	34.6	484	27.2
F	11,200	17.8	26.5	48.4	655	47.5
G	13,300	18.8	10.1	42.9	631	29.3
H	16,800	22.4	5.4	30.3	767	29.3
I	19,300	25.0	4.3	14.9	723	28.2
J	19,833	22.5	4.0	10.8	743	29.8
Near mid. springs	11,780	16.6	72.7	134	1030	39.7
April 8, 2003[a]						
A	−800	29.3 (32.2, 26.5)	4.9 (7.7, 2.0)	15.2 (19.3, 11.1)	214 (308, 120)	12.4 (17.7, 7.1)
B	2100	28.1(26.2, 30.0)	5.4 (5.2, 5.7)	12.6 (9.4, 15.8)	239 (321, 157)	17.1 (23.3, 10.8)
C	4400	25.2 (20.0, 30.5)	10.9 (10.3, 11.4)	24.8 (24.6, 25.0)	392 (427, 357)	27.7 (29.5, 25.9)
D	7000	23.9 (21.0, 26.8)	5.2 (5.9, 4.6)	21.3 (21.6, 21.0)	483 (616, 351)	28.6 (33.1, 24.2)
E	9700	17.7 (16.8, 18.5)	11.0 (11.0, 11.1)	31.6 (31.2, 32.1)	635 (767, 503)	35.7 (38.0, 33.4)
G (low slack only)	13,300	20.1	10.4	24.9	709	39.7
H	16,800	17.2 (15.5, 18.7)	5.3 (2.9, 7.71)	24.9 (31.9, 17.9)	662 (631, 693)	58.1 (56.3, 60.0)
I	19,300	17.8 (16.4, 19.3)	3.4 (3.8, 3.0)	11.2 (8.4, 14.1)	608 (594, 623)	27.2 (28.4, 25.9)
J (flood only)	20,900	14.4	4.1	16.1	650	22.2

dpm/100 L disintegration per minute per 100 L.
[a] Data presented as average (ebb tide or low slack tide, flood tide).

de Produccion Primaria, CINVESTAV, in Mérida, Mexico. Samples were analyzed for nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), soluble reactive silica (SRSi), and soluble reactive phosphate (SRP) according to the methods described in Herrera-Silveira et al., (1998). Samples taken during the March–April 2003 trip were filtered directly into 50 mL

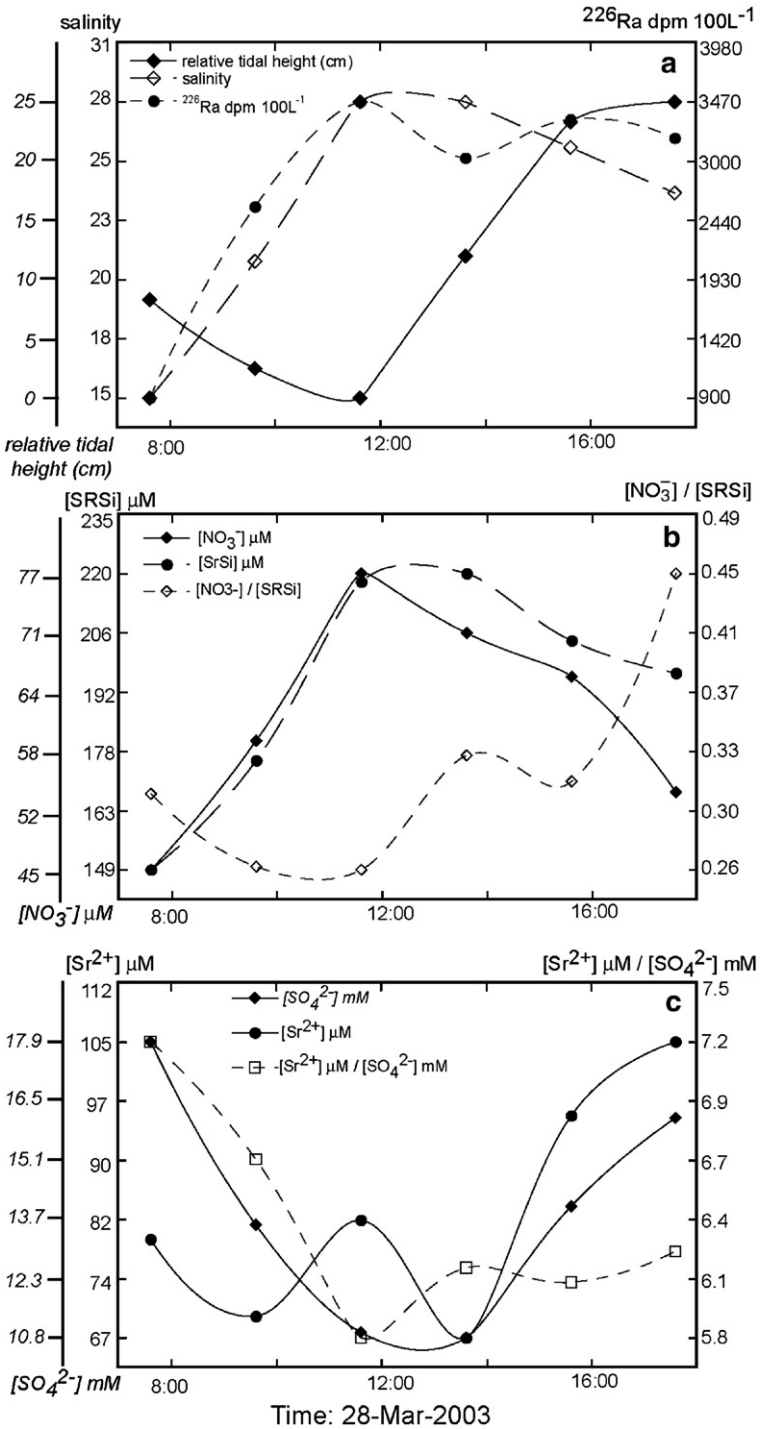

Fig. 3. Variations in the chemical composition of water discharging from middle spring *X* over the course of a partial tidal cycle. Discharge of low salinity, low radium water was detected during ebb tide, while discharge of brackish high radium groundwater increased just before low slack tide and remained high during flood tide.

opaque plastic bottles, frozen, and sent to Oregon State University for analysis of NO_3^-, NO_2^- SRSi, and SRP.

2.6. Hydrodynamic measurements

In July 2002, hydrographic measurements of tidal height, water flow velocity and direction, water temperature, and salinity were collected every five minutes over a five day sampling period. The measurements were made by deploying a Nortek Vector acoustic Doppler velocimeter and an Ocean Sensors OS2000 CTD (Conductivity, Temperature, and Depth) in the boat channel near the midpoint of the lagoon about 420 m north of the Celestún bridge (Fig. 1). These measurements were used to determine the tidal conditions during sample collection since no tidal monitoring stations are present in the lagoon or along the nearby coast. Tidal conditions for samples collected during the October 2001 and March–April 2003 trips were determined by measuring relative tidal height at the DUMAC field station dock every 1–2 h during the sampling trips.

2.7. Three end-member mixing model

Direct measurement of groundwater discharge into Celestún Lagoon is extremely difficult due to the numerous discharge points distributed throughout the lagoon. Both types of groundwater appear to discharge simultaneously from at least one of the major springs located near the middle of the lagoon, while only the low salinity groundwater discharges from springs in the upper lagoon. Therefore, physical measurements of discharge rates will not be able to distinguish the contributions of each type of groundwater. Radium activity and trace chemistry results show three distinct water types entering the lagoon: low salinity groundwater, brackish high radium groundwater, and seawater entering from the lagoon mouth. In order to determine the relative contribution of these distinct water sources (identified by their chemistry) to the lagoon water at any given location or sampling time period, we used a set of three equations modified from Moore (2003) and Moore et al. (2006).

$$f_{sw} + f_{gw1} + f_{gw2} = 1$$
$$f_{sw}[X]\mathrm{sw} + f_{gw1}[X]\mathrm{gw1} + f_{gw2}[X]\mathrm{gw2} = [X]\mathrm{L}$$
$$f_{sw}[Y]\mathrm{sw} + f_{gw1}[Y]\mathrm{gw1} + f_{gw2}[Y]\mathrm{gw2} = [Y]\mathrm{L}$$

where f_{sw} is the fraction of seawater, f_{gw1} is the fraction of groundwater type 1, and f_{gw2} is the fraction of groundwater type 2. $[X]$ and $[Y]$ are the concentrations of selected natural tracers within the end-members (SW, GW1, GW2) and lagoon transect (L) samples. The above equations were solved by

Table 2
Salinity and radium activity data for potential water input sources to Celestún Lagoon

Sample description	Sampling date	Salinity	^{223}Ra (dpm/100 L)	^{224}Ra (dpm/100 L)	^{226}Ra (dpm/100 L)	^{228}Ra (dpm/100 L)
October 2001						
Coastal transect 0–3.5 km offshore (n=6)	6-Oct-01	31.3±1.3	2.9±0.68	6.9±1.7	56.3±15.2	6.0±1.3
Middle spring *X*	13-Oct-01	20	133.4	199	2570	97.6
Middle spring *Y*	13-Oct-01	20	175.5	191	3080	128
Upper spring *Z*	13-Oct-01	3.8	14.5	27.2	592	32.7
July 2002						
Coastal transect 0–6 km offshore (n=6)	14-Jul-02	36.8±1.8	3.2±0.82	4.4±0.45	37.5±11.4	4.9±0.99
Middle spring *X*	16-Jul-02	17.0	291	260	2390	96.6
Middle spring *Y*	16-Jul-02	15.0	258	161	2720	121
March–April 2003						
Middle spring X						
Ebb tide 1	28-Mar-03 7:37 am	15	22.4	87.7	904	56.7
Ebb tide 2	28-Mar-03 9:40 am	21	130	212	2561	106.3
Low slack tide	28-Mar-03 11:40 am	28	98.0	365	3468	110.1
Flood tide 1	28-Mar-03 1:40 pm	28	144	312	2983	116.2
Flood tide 2	28-Mar-03 3:40 pm	26	118	362	3318	136.1
Flood tide 3	28-Mar-03 5:40 pm	24	133	283	3155	110.1
Ebb tide	8-Apr-03 10:00 am	22.4	282	279	3660	130
Flood tide	8-Apr-03 4:30 pm	20.2	121	271	2702	118
Middle spring Y (lagoon transects)						
Ebb tide	8-Apr-03 10:30 am	30.5	163	414	4134	167
Flood tide	8-Apr-03 4:00 pm	22.3	97.3	300	2857	96.1
Upper spring Z						
Ebb tide	28-Mar-03 9:05 am	10	6.8	28.7	509	25.4
Flood tide	28-Mar-03 4:15 pm	12	11.6	36.7	491	31.0

Where given, errors represent standard deviation of multiple samples.
dpm/100 L disintegration per minute per 100 L.

substitution to calculate the fraction of each end-member in any given lagoon transect sample (Moore, 2003).

$$f_{GW1} = [(Y_L - Y_{SW}/Y_{GW2} - Y_{SW}) - (X_L - X_{SW}/X_{GW2} - X_{SW})] \div (Y_{GW1} - Y_{SW})/(Y_{GW2} - Y_{SW}) - (Y_{GW1} - Y_{SW})/(Y_{GW2} - Y_{SW})$$

$$f_{GW2} = Y_L - Y_{SW} - f_{GW1}[Y_{GW1} - Y_{SW}]/(Y_{GW2} - Y_{SW})$$

$$f_{SW} = 1.00 - f_{GW1} - f_{GW2}$$

3. Results and discussion

3.1. Salinity and radium isotope activity

Salinity and radium isotope activities for Celestún Lagoon transects are presented in Table 1. A salinity gradient along the length of the lagoon was observed during all sampling trips, with lower salinity in the upper (northern) part of the lagoon and increasing salinity towards the mouth of the lagoon (Fig. 2). This pattern is consistent with the discharge of low salinity groundwater in the upper lagoon observed in previous studies (Herrera-Silveira, 1994b; Herrera-Silveira and Comin, 1995; Medina-Gomez and Herrera-Silveira, 2002). Radium activity did not follow the same pattern as salinity. Instead, the activity of ^{223}Ra, ^{224}Ra, and ^{228}Ra was highest near the middle of the lagoon, where two large springs discharge groundwater, and decreased towards both the upper and lower lagoon (Fig. 2). ^{226}Ra activity was the same (within analytical error) in the middle and upper lagoon, and showed a decrease from the middle lagoon towards the mouth. The pattern of salinity and radium activity throughout the lagoon suggests the presence of at least three distinct water sources to the lagoon. Seawater entering the mouth of the lagoon has high salinity and low radium activity, groundwater discharging in the upper lagoon has low salinity and low radium activity, and a second groundwater source characterized by moderate salinity and very high radium isotope activity is present in the middle springs. For clarity, these three end-members will be referred to as seawater (coastal water entering the mouth of the lagoon), low salinity groundwater (not enriched in radium compared to the lagoon water), and brackish high radium groundwater.

Samples collected at two-hour intervals over a partial tidal cycle at middle spring X during the March–April 2003 trip reveal an additional complication to distinguishing the different water sources to the lagoon. The enrichment in radium isotope activity in the middle spring water varied during the tidal cycle (Fig. 3). Over the course of a partial tidal cycle, radium activity in the middle spring water increased at low slack tide, then remained relatively constant as the tide began to rise. The increase in radium activity corresponded to an increase in salinity. Increased mixing of lagoon water with spring water could explain the salinity increase, but this would result in a decrease in radium activity, not the observed increase. Therefore, it appears that the mixture of water discharging from the middle spring varies over the tidal cycle. Both low salinity, low radium groundwater and brackish high radium groundwater discharge at this point in the lagoon, and the relative input from these distinct sources is tidally modulated.

Salinity and radium activities for potential end-members are given in Table 2. The seawater end-member is represented by samples taken along coastal transects outside the lagoon. Since groundwater discharge in the lagoon occurs only through submarine springs, it was not possible to obtain an entirely pure groundwater sample: all samples have undergone some degree of mixing with lagoon water. In order to obtain a representative end-member value for the brackish high radium groundwater, samples were collected at each of the two large middle springs during every sampling trip. Additionally, samples were collected at two-hour intervals over a partial tidal cycle at middle spring X during the March–April 2003 trip. Since it appears that both low salinity groundwater and brackish high radium groundwater discharge from this spring, the sample with the highest radium activity was taken as the best representation of the brackish groundwater end-member, although it is possible that the true end-member radium activity may be even higher than what was measured.

During each sampling trip, ^{223}Ra and ^{224}Ra activities in the middle springs were 10 to 30 times higher than the average activity measured along the lagoon transect, while ^{226}Ra and ^{228}Ra activities in the middle springs were 5 to 8 times higher than average activity along the lagoon transect. These results

Table 3
Salinity and radium activity data for various wells within and around Celestún Lagoon

Station	Salinity	^{223}Ra (dpm/100 L)	^{224}Ra (dpm/100 L)	^{226}Ra (dpm/100 L)	^{228}Ra (dpm/100 L)
Drowned lagoon well					
July 02	4	38.6	111	573	59.9
Mar 03 ebb tide	3.5	12.7	92.6	497	58.4
Mar 03 flood tide	2.6	17.0	105	670	71.6
Harbor Packing Plant well					
Oct 01	4.9	58.5	168	738	122
July 02	5	58.0	207	720	91.3
Mar 03	3.1	21.1	124	531	75.1
Well in Celestún graveyard					
Oct 01	4.6	1.23	7.75	98.2	11.7
July 02	3	1.68	9.61	73.7	7.07
Other town wells					
Oct 01-private well 1	1.8	1.72	3.93	[a]	3.83
Oct 01-private well 2	4.1	0.96	5.77	57.3	5.43
Oct 01-private well 4	4.6	1.04	2.61	48	1.51
Oct 01-private well 5	2.1	3.61	7.36	50.9	3.40
Oct 01-private well 7	1.6	4.36	4.07	[a]	2.80
July 02 drinking water well	0	4.22	6.17	38.4	2.52

dpm/100 L disintegration per minute per 100 L.
[a] Samples lost prior to ^{226}Ra measurements.

show that the water discharging at the middle springs is highly enriched in all radium isotopes compared to lagoon water during all seasons. Activities of the short lived isotopes in the lagoon water decrease (relative to the input signatures) due to both mixing with low radium water and isotopic decay, while the activities of the long lived isotopes will only decrease due to mixing. This may explain why the short lived isotopes are many times more enriched in the middle spring water compared to the lagoon water than the longer lived isotopes. In addition, the spring water may be more enriched in short lived Ra relative to long lived Ra due to the regeneration rates within the aquifer sediments, which are a function of how often the sediment is inundated with saline water and the half-life of the isotope of interest (days for the short lived to years for the long lived).

In October 2001, water discharging from the upper spring Z was slightly elevated in ^{223}Ra and ^{224}Ra compared to the surrounding lagoon water, but no detectable differences in ^{226}Ra and ^{228}Ra activities were observed. During the March–April 2003 trip, there were no detectable differences between the upper spring water and the lagoon water for any of the four individual radium isotope activities. These results indicate that the groundwater discharging at this site is low in radium most likely as a result of its low ionic strength (low salinity) and thus lack of desorption from aquifer sediments (Webster et al., 1995). However, in both 2001 and 2003, the ratios of the short lived radium isotopes to the long lived radium isotopes were higher in the upper spring low salinity groundwater than in the surrounding lagoon water, although overall activities were still much lower than those measured in the middle springs. Therefore, the ratios of the short lived to long lived radium isotopes throughout the lagoon are not only controlled by radioactive decay during the residence time of the water, but are also a function of relative amounts of groundwater discharge from the low salinity groundwater and the brackish high radium groundwater.

Sampling of radium in seawater along a coastal transect conducted north of the lagoon mouth in October 2001 showed no significant differences between average radium activity in the coastal waters and the sampling station at the mouth of the lagoon, while coastal water radium activity measured in July 2002 was somewhat lower than that measured at the mouth of the lagoon. These results suggest that samples collected at the mouth of the lagoon are a reasonable representation of the seawater end-member entering the lagoon, although the true seawater end-member may contain slightly lower radium activities. Samples collected during both a rising and falling tide on the same day in April 2003 show, as expected, that radium activity was higher at the mouth during the falling tide, when lagoon water was flowing out to the coast, and lower on the rising tide, as seawater entered the lagoon. Samples collected at the mouth of the lagoon during rising tides are therefore the best representation of the seawater end-member entering the lagoon.

Samples collected from a single well within the lagoon along with samples from other wells in the town of Celestún

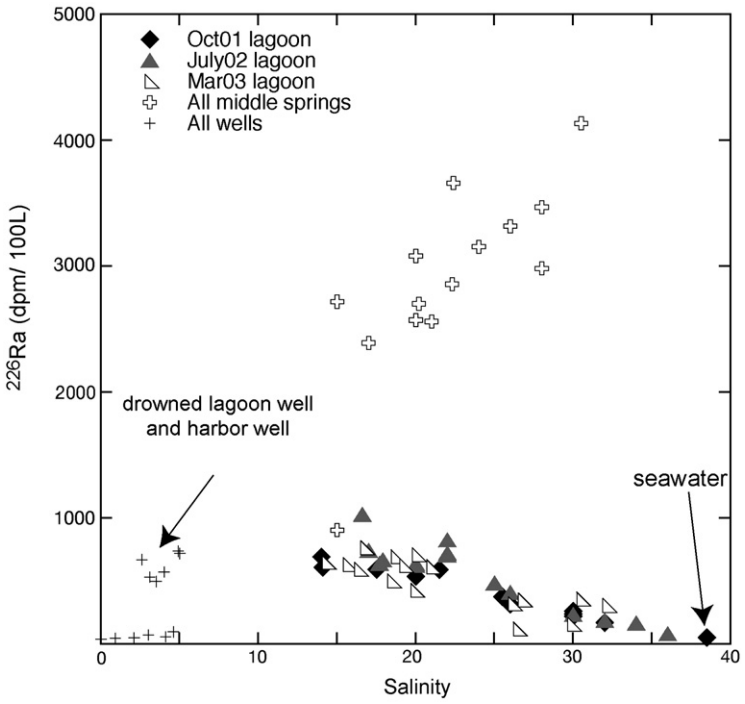

Fig. 4. Relationship between salinity and ^{226}Ra for all water samples. Activity of the other three radium isotopes followed a similar pattern. The brackish wells appear to fall on a mixing line between the low ^{226}Ra groundwater and the high ^{226}Ra middle spring water.

show the presence of both fresh and brackish groundwater in the area (Table 3). The wells fall into two groups based on radium activities: wells with very low radium activities, and wells with moderate radium activities which appear to fall along a mixing line between the low radium wells and the middle springs water (Fig. 4). Unlike the springs within the lagoon, the relationship between salinity and radium activity for the wells is not clear. The salinity of the moderate radium activity well samples ranged from 2.6 to 5, while the salinity of the low radium activity well samples ranged from 0 to 4.6. Because of the complicated nature of groundwater flow patterns within coastal karstic systems, it is possible that some of the low radium wells experience a small amount of seawater intrusion (increasing the salinity), but remain separate from the high radium brackish groundwater in the area.

3.2. Other chemical tracers

A strong linear relationship ($R^2=0.999$; $n=23$) between $[Cl^-]$ and $[SO_4^{2-}]$ was observed for most of the water samples collected in the lagoon from the October 2001 and July 2002 trips (Fig. 5a, Tables 4 and 5). This relationship corresponds to a mixing line between standard seawater ($[SO_4^{2-}]$ to $[Cl^-]$ ratio of 0.052 (Pilson, 1998) and groundwater enriched in SO_4^{2-} as defined by the sampled wells (e.g. with mean $[SO_4^{2-}]$:$[Cl^-]$ ratio of 0.164). No seasonal differences in the $[SO_4^{2-}]$:$[Cl^-]$ ratios were observed in the wells sampled during all three trips, suggesting that the composition of groundwater reaching each particular well is not changing seasonally (Table 6). Perry et al. (2002) identified dissolution of evaporites within the freshwater lens as the probable source of the excess SO_4^{2-} found in some Yucatán groundwater.

Samples collected in the northern section of the lagoon during July 2002 fall along a different mixing line. Samples falling along this line have more SO_4^{2-} than expected from mixing between seawater and the low salinity groundwater defined by the upper spring and well samples. Samples taken during the March–April 2003 lagoon transect showed more scatter than the lagoon samples from the other two trips, with some samples showing sulfate depletion and others showing sulfate enrichment. This suggests that during both the July 2002 and March–April 2003 sampling trips there was an additional source of water to the lagoon with a higher $[SO_4^{2-}]$:$[Cl^-]$ ratio than the measured low salinity groundwater, brackish high radium groundwater, or seawater. Extensive sulfate reduction occurs within the top 0 to 10 cm of the lagoon sediments, and is highly spatially variable (Young et al, in preparation). Porewater exchange and groundwater pumping through sulfate depleted sediments could result in low $[SO_4^{2-}]$:$[Cl^-]$ mixing into the lagoon. Water collected from the middle springs during the March–April 2003 trip also showed a different $[SO_4^{2-}]$:$[Cl^-]$ relationship than seen during the other trips. Four of the samples collected from the middle spring at different points in the tidal cycle fell along the same trendline (e.g. defined by mixing of sulfate rich groundwater and seawater) as the October 2001 and July 2002 middle springs, while the other four samples, collected during rising tide, fell below the trendline. The tidal cycle samples with lower $[SO_4^{2-}]$:$[Cl^-]$ ratios also had the highest radium activities, indicating that the lower $[SO_4^{2-}]$:$[Cl^-]$ ratios were associated with the brackish groundwater at this time. Sulfate reduction has been measured in many of the cenotes (deep sinkholes which provide direct access to the groundwater) throughout the Yucatán Peninsula (Socki et al., 2002), and this could explain the lower $[SO_4^{2-}]$:$[Cl^-]$ ratios found in the brackish groundwater. Although $[SO_4^{2-}]$:$[Cl^-]$ ratios can be potentially be used to distinguish the different types of groundwater, it is likely that sulfate does not behave entirely as a conservative tracer within the lagoon. Variations in rates of sulfate reduction and porewater exchange in the lagoon sediments, along with variations in sulfate reduction within the aquifer itself may result in errors if sulfate is used for mixing model calculations. The use of seasonally-specific groundwater sulfate chemistry to define the end-members could compensate for changes in sulfate reduction within the aquifer, but porewater exchange throughout the lagoon remains difficult to quantify.

Perry et al. (2002) demonstrated that strontium concentration $[Sr^{2+}]$ in Yucatán groundwater can be used with both SO_4^{2-} and Cl^- concentrations as a powerful tracer of groundwater types and chemical processes. $[Sr^{2+}]$:$[Cl^-]$ ratios and $[Sr^{2+}]$:$[SO_4^{2-}]$ ratios clearly show mixing between two different types of groundwater and seawater within Celestún Lagoon. All of the groundwater samples collected from the springs and wells had significantly higher $[Sr^{2+}]$:$[Cl^-]$ ratios than seawater, indicating the presence of an additional source of Sr^{2+} to Yucatán groundwater. Perry et al. (2002) identified celestite ($SrSO_4$) in evaporite layers as the most likely source of the excess Sr^{2+}, and aragonite as another contributor of Sr^{2+} to groundwater. The well and spring samples had higher $[Sr^{2+}]$:$[Cl^-]$ and $[SO_4^{2-}]$:$[Cl^-]$ ratios than seawater, reflecting the inputs of both SO_4^{2-} and Sr^{2+} from mineral dissolution processes within the aquifer. $[SO_4^{2-}]$ and $[Sr^{2+}]$ for all lagoon, spring, and well samples are shown in Fig. 6. All the samples fall within a three end-member mixing triangle defined by seawater, low salinity groundwater, and the brackish groundwater. Interestingly, only one of the lagoon spring samples falls directly along the Sr^{2+}:SO_4^{2-} relationship line found for Yucatán groundwater by Perry et al. (2002): all of the other spring samples show what could be either varying degrees of seawater influence or a reflection of more localized mineral dissolution processes. Both of these explanations are consistent with increased tidally-driven mixing of seawater and both brackish and low salinity groundwater near the coast in comparison to more inland wells sampled by Perry et al. (2002). Samples collected from the middle springs during the partial tidal cycle fall close to the Yucatán groundwater $[Sr^{2+}]$:$[SO_4^{2-}]$ mixing line and have a similar slope. Changes in the $[Sr^{2+}]$:$[SO_4^{2-}]$ of the middle spring water over the partial tidal cycle show the increasing contribution of brackish groundwater (higher Sr^{2+} and SO_4^{2-} concentrations, but lower $[Sr^{2+}]$:$[SO_4^{2-}]$ ratio than low salinity groundwater), reaching a minimum at low slack tide and then remaining low (Fig. 3c). The maximum in Sr^{2+} and SO_4^{2-}

concentration corresponds closely to the maximum seen in radium activity, and the $[Sr^{2+}]$:$[SO_4^{2-}]$ ratio follows a reverse pattern to radium activity, with the ratio dropping at low slack tide, then remaining low during the beginning of flood tide. More extensive tidal sampling at the major springs is needed to fully understand the relationship between tide and relative discharges of the two types of groundwater.

3.3. Nutrients

Previous studies have identified low salinity groundwater discharging into the northern lagoon as an important source of nutrients, particularly nitrate and soluble reactive silicate (SRSi), to Celestún Lagoon (Herrera-Silveira, 1994a,b,c; Herrera-Silveira and Comin, 1995; Herrera-Silveira et al., 1998; Medina-Gomez and Herrera-Silveira, 2002). Although nutrients do not behave conservatively within the lagoon, repeated measurements of nitrate and SRSi in the upper and middle lagoon springs, along with published data from the studies cited above, were used to estimate the nitrate and SRSi concentrations in the different groundwater types entering the lagoon. Measured nitrate concentrations in the low salinity (S=2 to 6) groundwater discharge from springs in the upper lagoon ranged from 49.7 to 138.8 μM, and SRSi concentrations ranged from 87.8 to 289.2 (Herrera-Silveira, 1994c; Herrera-Silveira et al., submitted for publication). Nitrate and SRSi concentrations measured in the upper springs during this study fell within the previously reported range. Nitrate concentrations in the brackish groundwater from the middle springs ranged from 27.5 to 107 μM over the course of this study, while SRSi concentrations ranged from 100 to 337 μM. No significant differences in concentrations were found between the trips, primarily due to the high variability between samples collected within each trip, and the relatively small number of samples analyzed. Average nitrate

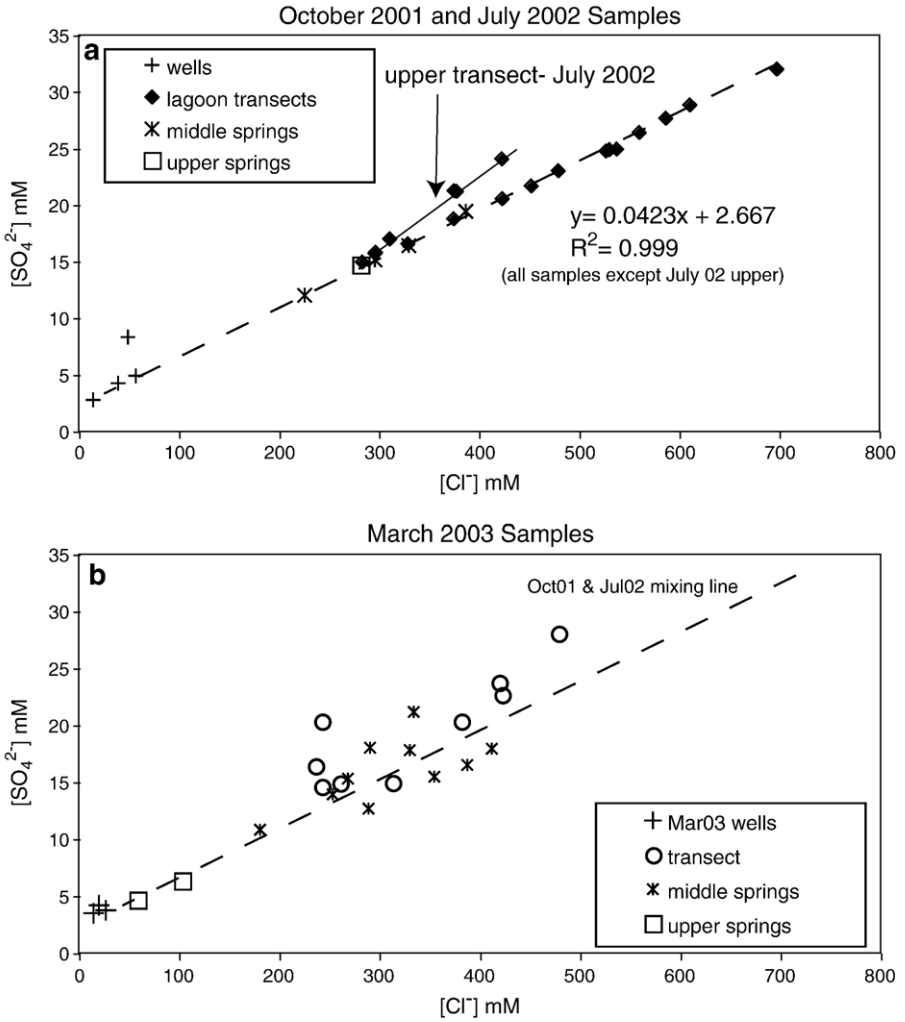

Fig. 5. a–b. Relationship between $[Cl^-]$ and $[SO_4^{2+}]$ in lagoon samples and potential end-members. The dotted line on both graphs represents the mixing line between standard seawater (from Pilson, 1998) and the well samples collected for this study. The solid line in (a) shows the trend line for the July 2002 upper lagoon samples.

Table 4
Trace chemistry and nutrient data for Celestún Lagoon transect samples

Station	Distance from mouth (m)	$[Cl^-]$ mM	$[SO_4^{2+}]$ mμ	$[Sr^{2+}]$ μM	$[SO_4^{2+}]$ μM/$[Cl^-]$ mM	$[Sr^{2+}]$ μM/$[Cl^-]$ mM	$[Sr^{2+}]$ μM/$[SO_4^{2+}]$ mM	$[NO_3^-]$ μM	[SRSi] μM	$[NO_3^-]$/[SRSi]
October 13, 2001										
A	−800	697	32.0	85.9	0.0459	0.123	2.68	4.9	13.7	0.360
B	2100	530	24.9	76.3	0.0469	0.144	3.07	1.7	78.9	0.022
C	4400	537	24.9	78.3	0.0464	0.146	3.14	8.0	185	0.043
D	7000	526	24.7	76.5	0.0470	0.145	3.09	4.1	37.1	0.112
E	9700	452	21.7	72.4	0.0479	0.160	3.34	0.6	14.3	0.040
F	11,200	375	18.8	68.9	0.0501	0.184	3.67	2.4	29.4	0.082
G	13,300	329	16.6	69.4	0.0504	0.211	4.18	16.7	157	0.106
H	16,800	226	[a]	[a]	[a]	[a]	[a]	5.8	105	0.055
I	19,300	224	[a]	[a]	[a]	[a]	[a]	1.4	44.4	0.031
July 16, 2002										
A	−800	610	28.8	85.9	0.0473	0.141	2.98	3.1	34.8	0.089
B	2100	586	27.7	85.2	0.0472	0.145	3.08	1.5	36.6	0.041
C	4400	560	26.4	83.9	0.0472	0.150	3.18	2.6	44.1	0.059
D	7000	479	23.0	84.9	0.0481	0.177	3.69	2.9	134	0.022
E	9700	423	20.6	87.3	0.0486	0.206	4.25	3.8	198	0.019
F	11,200	297	15.8	79.0	0.0533	0.266	4.99	0.6	260	0.002
G	13,300	310	17.0	86.4	0.0547	0.278	5.09	2.0	301	0.007
H	16,800	375	21.2	102.3	0.0566	0.273	4.82	1.3	397	0.003
I	19,300	422	24.1	106.2	0.0570	0.251	4.41	1.0	382	0.003
J	19,833	377	21.2	108.4	0.0562	0.287	5.11	0.9	405	0.002
Near mid. spring	11,780	283	14.9	76.6	0.0527	0.270	5.13	2.3	320	0.007
April 8, 2003										
A	−800	479	28.1	92.5	0.0602	0.197	3.30	8.2 (11.9, 4.5)	18.7 (26.6, 10.7)	0.440 (0.447, 0.421)
B	2100	422	22.7	93.1	0.0538	0.222	4.10	10.2(15.3, 5.0)	21.7(31.4, 11.9)	0.469 (0.487, 0.420)
C	4400	420	23.8	61.2	0.0581	0.155	2.58	13.5 (16.1, 10.9)	48.6 (60.8, 36.4)	0.278 (0.265, 0.299)
D	7000	382	20.3	87.3	0.0538	0.232	4.30	10.3 (8.9, 11.6)	82.3 (116.8, 47.7)	0.125 (0.076, 0.243)
E	9700	242	20.3	79.8	0.0834	0.332	3.93	11.2 (10.6, 11.8)	98.9 (131, 67.1)	0.113 (0.081, 0.176)
G (ebb only)	13,300	313	15.0	83.4	0.0479	0.267	5.57	5.7	164	0.035
H	16,800	236	16.4	88.8	0.0705	0.377	5.41	3.1 (2.8, 4.7)	265 (310, 219)	0.012 (0.009, 0.017)
I	19,300	260	14.9	88.8	0.0575	0.340	5.95	4.5 (4.2, 4.7)	246 (219, 274)	0.018 (0.019, 0.017)
J (flood only)	20,900	243	14.6	80.5	0.0602	0.332	5.51	3.9	298	0.019

[a] Samples not analyzed.

Table 5
Trace chemistry and nutrient data for potential water input sources to Celestún Lagoon

Sample description	Sampling date	$[Cl^-]$ mM	$[SO_4^{2+}]$ mM	$[Sr^{2+}]$ μM	$[SO_4^{2+}]$ μM/ $[Cl^-]$ mM	$[Sr^{2+}]$ μM/ $[Cl^-]$ mM	$[Sr^{2+}]$ μM/ $[SO_4^{2+}]$ mM	$[NO_3^-]$ μM	[SRSi] μM	$[NO_3^-]$/[SRSi]
October 2001										
Coastal transect 0–3.5 km offshore ($n=6$)	6-Oct-01	697	32.0	85.9	0.0459	0.1231	2.68	1.89±0.83	28.6±16.1	0.095±0.078
Middle spring *X*	13-Oct-01	330	16.4	77.3	0.0498	0.2345	4.71	107	135	0.788
Middle spring *Y*	13-Oct-01	387	19.5	86.7	0.0503	0.2243	4.46	60.4	105	0.577
Upper spring *Z*	13-Oct-01	282	14.7	65.2	0.0522	0.2314	4.43	6.85	26.1	0.262
July 2002										
Coastal transect 0–6 km offshore ($n=6$)	14-Jul-02	665±3.8	31.0±0.27	87.2±0.66	0.0467±0.0003	0.1312±0.0012	2.81±0.0155	1.3±0.9	112±11.4	0.011±0.007
Middle spring *X*	16-Jul-02	296	15.1	70.3	0.0511	0.237	4.65	90.3	315	0.287
Middle spring *Y*	16-Jul-02	226	12.0	71.0	0.0532	0.314	5.91	107	337	0.316
March–April 2003										
Middle spring X-partial tidal cycle										
Ebb tide 1	28-Mar-03 7:37 am	181	10.8	66.6	0.0599	0.368	6.15	77.3	173	0.447
Ebb tide 2	28-Mar-03 9:40 am	253	13.9	80.7	0.0550	0.318	5.79	57.4	154	0.372
Low slack tide	28-Mar-03 11:40 am	412	17.9	104	0.0435	0.252	5.78	45.7	177	0.258
Flood tide 1	28-Mar-03 1:40 pm	388	16.5	105	0.0426	0.270	6.34	45.1	149	0.302
Flood tide 2	28-Mar-03 3:40 pm	355	15.5	96.1	0.0436	0.271	6.21	59.4	203	0.293
Flood tide 3	28-Mar-03 5:40 pm	289	12.7	91.9	0.0439	0.318	7.24	69.0	220	0.313
Middle spring X—lagoon transects										
Ebb tide	8-Apr-03 10:00 am	330	17.8	106	0.0539	0.321	5.96	30.0	138	0.217
Flood tide	8-Apr-03 4:30 pm	269	15.3	93.0	0.0570	0.346	6.07	56.0	184	0.304
Middle spring Y—lagoon transects										
Ebb tide	8-Apr-03 10:30 am	291	18.0	117	0.0619	0.404	6.53	21.6	100	0.216
Flood tide	8-Apr-03 4:00 pm	334.3	21.1	24.3	0.0633	0.073	1.15	33.4	118	0.283
Upper spring Z										
Ebb tide	28-Mar-03 9:05 am	103	6.36	34.1	0.0615	0.330	5.37	45.7	206	0.222
Flood tide	28-Mar-03 4:15 pm	58.9	4.66	46.8	0.0791	0.795	10.0	56.3	180	0.313

Where given, errors represent standard deviation of multiple samples.

Table 6
Trace chemistry and nutrient data for various wells within and around Celestún Lagoon

Station	$[Cl^-]$ mM	$[SO_4^{2+}]$ mM	$[Sr^{2+}]$ μM	$[SO_4^{2+}]$ μM/ $[Cl^-]$ mM	$[Sr^{2+}]$ μM/ $[Cl^-]$ mM	$[Sr^{2+}]$ μM/ $[SO_4^{2+}]$ mM	$[NO_3^-]$ μM	[SRSi] μM	$[NO_3^-]$/ [SRSi]
Drowned lagoon well									
July 02	39.1	4.23	33.1	0.108	0.85	7.82	177	352	0.504
Mar 03 am	26.9	3.77	39.3	0.140	1.46	10.43	125	294	0.427
Mar 03 pm	14.7	3.51	28.2	0.239	1.92	8.04	114	244	0.465
Harbor Packing Plant well									
July 02	56.7	4.89	35.5	0.086	0.63	7.26	215	395	0.544
Mar 03	20.1	4.18	22.0	0.208	1.09	5.26	45.8	228	0.201
Well in Celestun graveyard									
July 02	49.0	8.32	35.7	0.170	0.73	4.29	103	44.9	2.30
Other town wells									
July 02 drinking water well	14.3	2.77	21.6	0.194	1.51	7.81	43.5	455	0.096

and SRSi concentrations for the middle springs from all trips were 55.2±23.0 μM, and 155±37.9 μM, respectively. These values were not significantly different from the nitrate and SRSi concentrations measured in the upper springs during this study, and fall within the range of concentrations reported for fresh groundwater from the upper springs in previous studies (Herrera-Silveira, 1994c; Herrera-Silveira and Comin, 1995; Herrera-Silveira et al., 1998, submitted for publication; Medina-Gomez and Herrera-Silveira, 2002). Data collected at middle spring *X* over a partial tidal cycle suggests that the high radium brackish groundwater contains less nitrate than the fresh groundwater. Nitrate concentrations were highest prior to low tide, corresponding to low salinity and low radium activity (Fig. 3). Nitrate concentrations dropped at low slack tide, corresponding to a sharp increase in salinity and radium activity. A comparison of all the data from the middle springs collected during the sampling trips shows no significant correlation between nitrate concentrations and radium activity, and much greater variation was observed in the nitrate concentrations than in the radium activity. Large variations in nitrate concentrations were also observed in the town wells sampled at the same time, and in the same town wells sampled in different seasons. This degree of variation is consistent with the karstic nature of the area, where complex flow patterns may result in spatial and temporal variability in both natural and anthropogenic nutrient supplies to the groundwater. Additional nutrient concentration monitoring

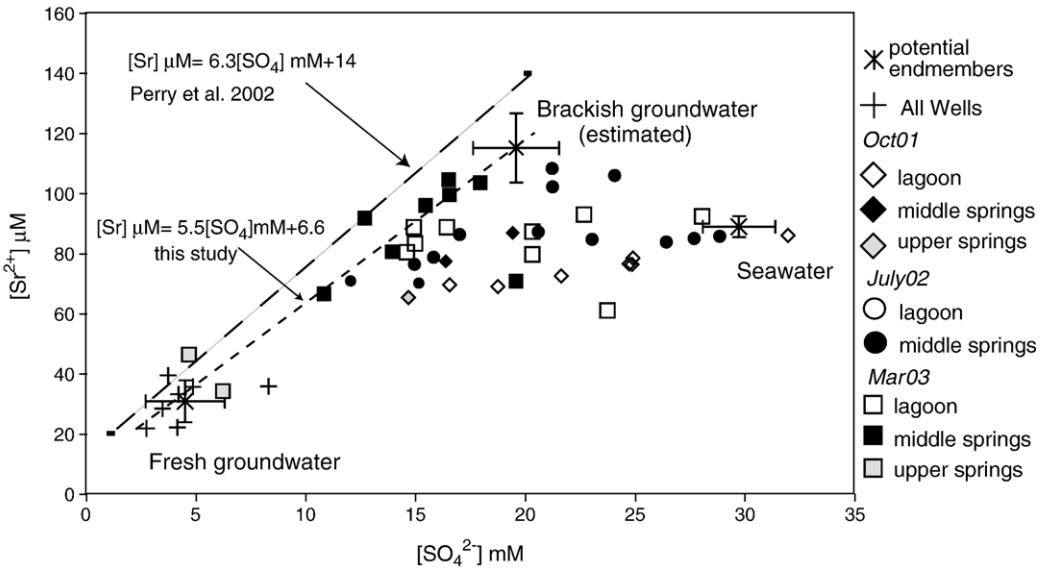

Fig. 6. Relationship between $[SO_4^{2-}]$ and $[Sr^{2+}]$ for all samples. A mixing line for the samples collected over a partial tidal cycle at middle spring *X* and the well samples is shown, while the Perry et al. (2002) relationship for Yucatán groundwater is given for comparison. Seawater and low salinity groundwater end-members are averages of coastal and well samples, respectively, while the brackish groundwater is estimated from the middle spring *X* and well mixing line.

of the brackish high radium groundwater is required to better constrain the nitrate and SRSi concentrations associated with the this groundwater. However, even the lowest nitrate concentration measured in middle spring *X* during the tidal cycle was approximately 6 times greater than the average concentration within the lagoon itself, indicating that both the low salinity groundwater and brackish groundwater end-members are significant sources of nitrate to the lagoon.

3.4. Mixing model

In order to better understand the influence of each of the three end-members throughout the lagoon, the three end-member mixing model described in Section 2.7 was used to calculate the relative contribution of each groundwater source to different areas of the lagoon during the different seasons. Simple three end-member mixing models have been used in various environments including coastal zones and estuaries (Moore, 2003; Moore et al., 2006), streams (Hooper et al., 1990; Genereux et al., 1993) and sediments (Dittmar et al., 2001; Gonneea et al., 2004). In these models natural conservative tracers were used to determine the relative contributions of various end-members to a final mixture. This three end-member mixing model only requires the use of two separate chemical tracers. Since several different chemical tracers appear to be useful in distinguishing the different water sources in Celestún Lagoon the model was tested using each of the following tracers paired with $[Cl^-]$: ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra, $[SO_4^{2-}]$, and $[Sr^{2+}]$. Comparison of the results of each model run provides interesting information about lagoon dynamics, and can be used to focus future research in the lagoon.

The long lived radium isotopes ^{226}Ra and ^{228}Ra (in combination with $[Cl^-]$) appear to be the best choice of tracers for Celestún Lagoon for several reasons. The long lived radium isotopes behave conservatively within the lagoon. This does not seem to be true for the short lived isotopes. Results of the model obtained using the short lived isotopes significantly underestimate the contribution of brackish groundwater throughout the lagoon in comparison to the long lived isotopes, suggesting that the activities of the short lived radium isotopes along the lagoon transects also reflect radioactive decay. This is consistent with the estimated seasonal residence times of 21 to 30 days for water in the upper lagoon, and 5 to 15 days for water in the middle lagoon (Herrera-Silveira et al., 1999). However, a fairly wide range of short lived to long lived radium isotope ratios was measured in the low salinity groundwater from the upper springs and wells in the Celestún area, so it is not currently possible to quantify the effects of radioactive decay versus input of groundwater with different radium isotope ratios. Additional research needs to be done to measure the radium isotope activities in the low salinity water over multiple tidal cycles. Using both $[SO_4^{2-}]$ and $[Sr^{2+}]$ separately paired with $[Cl^-]$ produced problematic results. As discussed earlier, sulfate does not seem to behave conservatively within the lagoon, making it a poor choice for the mixing model. Although $[Sr^{2+}]$ can be used to distinguish between the different water types and behaves conservatively in the lagoon, the differences in $[Sr^{2+}]$:$[Cl^-]$ throughout the lagoon were fairly small, and showed wide variation in the samples potentially representing the low salinity end-member (the upper springs and wells). Small changes in the choice of end-member $[Sr^{2+}]$ for the mixing model resulted in large changes in the calculated contribution of each end-member throughout the lagoon, making this a poor choice for the mixing model.

Due to the issues identified with the other tracers, the long lived radium isotopes, along with $[Cl^-]$, were chosen for the final mixing models. We calculated the mixing model three ways: using ^{226}Ra and ^{228}Ra together, as well as using each isotope with $[Cl^-]$. ^{226}Ra and ^{228}Ra activities are the product of different decay chains, were measured using separate instrumental techniques, and are found in different ratios in each of the three water types. Although there is still considerable uncertainty in the correct values for the low salinity low radium end-member, using the long lived radium isotopes and $[Cl^-]$ made the model less sensitive to changes in end-member choice in comparison to the other tracers. The long-lived radium isotopes are also appropriate for the model because changes in their activities throughout the lagoon are only be due to source inputs and mixing processes, not radioactive decay. End-member values were chosen by averaging samples from all trips which appeared to represent the least-mixed samples of each type. The seawater end-member was calculated using the average values from the July 2002 and October 2001 coastal seawater samples ($[Cl^-]=664.5\pm4$ mM; $^{226}Ra=47.8\pm16$ dpm/100 L; $^{228}Ra=5.56\pm1.27$ dpm/100 L). The freshwater end-member was calculated using the average values of all wells except the drowned well in the lagoon and the Harbor Packing Plant well ($[Cl^-]=16.4\pm3.3$ mM; $^{226}Ra=61.1\pm21.6$ dpm/100 L; $^{228}Ra=4.78\pm3.3$ dpm/100 L). These two wells were excluded from the end-member calculations because the radium activities in the two wells were elevated in comparison to all the other wells, and appeared to already be a mixture of the low salinity and brackish groundwaters (Fig. 4). The results of the partial tidal cycle sampling indicated that both low salinity and brackish high radium groundwater discharge from the middle spring. In order to obtain the best representation of the brackish high radium groundwater, the middle spring sample with the highest overall radium activities (collected during the March 2003 trip) was selected as the sample most representative of this end-member ($[Cl^-]=291$ mM; $^{226}Ra=4134$ dpm/100 L; $^{228}Ra=167$ dpm/100 L). The average results of the three end-member mixing calculations using the pairs ^{226}Ra and ^{228}Ra, ^{226}Ra and $[Cl^-]$, and ^{228}Ra and $[Cl^-]$ are presented in Fig. 7. For all trips, the average differences in the calculated contribution of each end-member at each transect location using these different conservative tracers was 3%, with a highest discrepancy of 18% (calculated contribution of brackish groundwater at Station H March 2003).

Surprisingly, the calculated contribution of freshwater to the lagoon water during March–April 2003 (the dry season) was quite high, and was much greater in the outer (southern) section

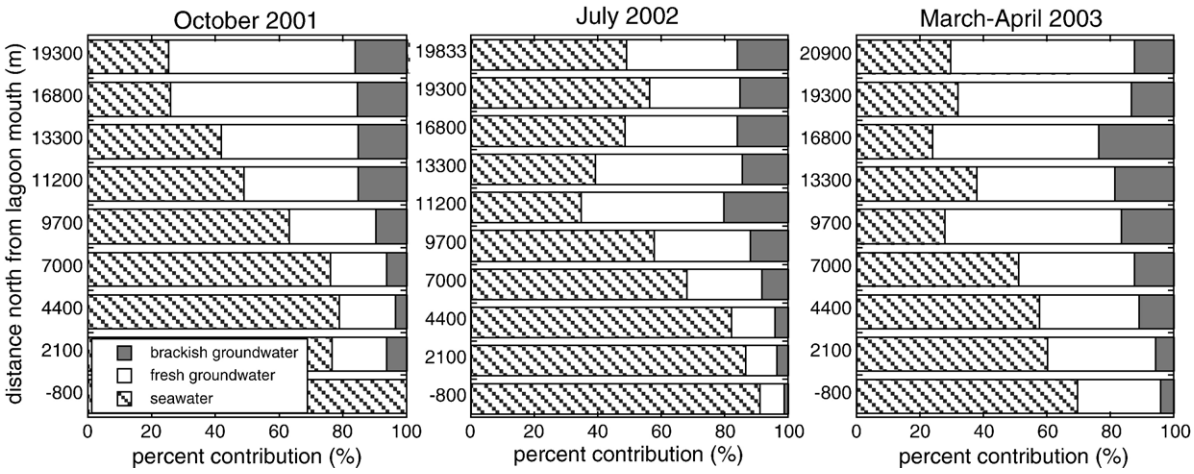

Fig. 7. Relative contributions of each end-member to the lagoon at each of the transect sampling points, calculated using the three end-member mixing model. Results shown are the average calculated contribution obtained from three separate model calculations using the following tracer pairs: ^{226}Ra and ^{228}Ra, ^{226}Ra and [Cl$^-$], ^{228}Ra and [Cl$^-$].

of the lagoon compared to the October and July periods. This was not expected, because overall groundwater discharge is typically much lower in the dry season compared to the rainy season (Herrera-Silveira, 1994b; Herrera-Silveira et al., 1999; Medina-Gomez and Herrera-Silveira, 2002). Overall salinities in the lagoon during this trip were lower than usual for the dry season (Herrera-Silveira et al., 1998), and the combination of lower salinities and somewhat lower radium isotope activities indicates that significant discharge of fresh groundwater was occurring during this time interval. It is quite possible that the high freshwater discharge during this season was related to Hurricane Isidoro, a category 4 hurricane which hit the northwestern Yucatán Peninsula in September 2002.

4. Conclusions

Measurements of radium isotope activities and other chemical tracers indicate that Celestún Lagoon receives input from at least three distinct water sources, two of which are different sources of submarine groundwater discharge within the lagoon (one of which was previously unrecognized), while the third source is seawater. The two groundwater sources appear to be (1) a low salinity, low radium activity groundwater with high nitrate concentrations and (2) a brackish high radium, lower nitrate groundwater. The brackish groundwater is composed primarily of a mixture of the seawater and freshwater end-members, but has certain chemical characteristics that distinguish it from either of the these two components, such as high radium isotope activities and different [Sr^{2+}]:[Cl^-] and [Sr^{2+}]:[SO_4^{2-}] ratios. These differences suggest that mixing and chemical reactions within the aquifer alter the composition of the brackish groundwater prior to discharge.

Seasonal variations in the relative contributions of these three sources to the lagoon water may result in significant changes to the nutrient budgets of the lagoon, which will not be detected if only one of the groundwater sources is monitored. Although both types of groundwater supply nitrate to the lagoon, the low salinity groundwater contains higher concentrations than the brackish high radium groundwater. Both types of groundwater have similar high SRSi concentrations. Anthropogenic nutrient loading of either groundwater source could lead to changes in productivity and possibly eutrophication, while reduction in groundwater discharge from activities such as drinking water pumping or breaching of the coastal aquitard could reduce primary productivity within the lagoon. Eutrophication or reduced primary productivity would likely negatively impact the economically important shrimp, crab, and fish populations of the lagoon and adjacent coastal waters.

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