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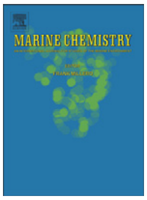

Seasonal dynamics of dissolved Ra isotopes in the semi-arid bays of south Texas

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ABSTRACT

Copano Bay, Nueces Bay, and Baffin Bay, Texas exhibit some of the highest dissolved ^{226}Ra activities observed in coastal waters despite being in a semi-arid region where surface water is scarce. To determine the reason for this, dissolved ^{226}Ra and ^{228}Ra activities were measured in these bays at three periods during the course of their seasonal flushing cycles. CH_4 and dissolved Cl/Br ratios were also measured during the final sampling period to independently assess the possibility of oil-field brine leakage and its potential influence on bay Ra activities. Independent of the high bay Ra activities, evidence for oil-field brine leakage was not found, though we cannot discount this possible influence on the Ra budget. Our results do show that all three bays exhibit pronounced seasonal swings in Ra activity that culminate in high absolute values. Mixing model results indicated that supply from submarine groundwater discharge can balance the Ra budgets of these bays. However, the Ra cycle in these systems is not controlled by a single dominant process, but rather the seasonal relationship of riverine Ra supply, submarine groundwater discharge, input from benthic sediments, and direct evaporation. Thus these bays are best described by a Ra cycle where activities are controlled by several processes in a dynamic, seasonal equilibrium. This illustrates the importance of seasonal controls on estuarine Ra cycling in general, but seasonality may be especially important for semi-arid regions where the hydrologic cycle is influenced by episodic freshwater inputs.

1. Introduction

Sediment pore-waters possess distinct chemical characteristics and can influence surface water chemistry through a variety of exchange mechanisms (Charette and Sholkovitz, 2006; Huettel et al., 1998; Moore et al., 2008). Along coastlines with permeable aquifers, solute exchange can be driven by submarine groundwater discharge (SGD), a combination of fresh terrestrial groundwater and recirculating seawater (Burnett et al., 2003; Charette et al., 2001; Moore, 1999). Even in the absence of terrestrial groundwater discharge, the interaction of currents, waves, and tides with sediment topography can create pressure-induced advection through permeable shelf sands, intertidal sand flats, and beaches (Billerbeck et al., 2006; Huettel et al., 1996; Precht and Huettel, 2004). And even in the low permeability, muddy cohesive sediments found in many intertidal wetlands, estuaries, and bays, the processes of resuspension, bioirrigation, and diffusion can still drive sediment pore-water and surface water exchange (Aller, 1982; Breier et al., 2009; Jahnke et al., 2003). The net rate of sediment pore-water and surface water exchange for many coastal waters is great enough to significantly influence nutrient (e.g., N and P) and trace element (e.g., Fe, Ba, As and Hg) cycling and potentially planktonic processes (Bone et al., 2006, 2007; de Sieyes et al., 2008; Dulaiova et al., 2006; Huettel et al., 1998; Lee and Kim, 2007). However, identifying and quantifying the effects of these chemical exchanges at estuarine- and bay-scales is challenging. To do this, studies have relied on the use of naturally occurring geochemical tracers, most commonly Rn, Ra isotopes, and CH_4 (e.g., Bugna et al., 1996; Gonneea et al., 2008; Peterson et al., 2009). Using this approach, many studies have identified submarine groundwater discharge as one of the dominant mechanisms among those just mentioned. But while numerous estuaries and bays have been studied in this regard, many of these share similar climates, specifically temperate to wet climates, and fewer have examined the seasonal dynamics associated with these tracers or the processes that control them. The work reported here examines the annual Ra cycle of three semi-arid south Texas bays, Copano Bay, Nueces Bay, and Baffin Bay, for which surface water inputs are scarce, evaporation is significant, and unlike previously studied coastal waters, anthropogenic Ra inputs are possible.

Previous studies of Nueces Bay, Texas, found exceptionally high dissolved ^{226}Ra and ^{228}Ra activities, up to 1000 dpm m^{-3} for ^{226}Ra (Breier and Edmonds, 2007). For comparison the ^{226}Ra measured in other coastal waters has typically been <600 dpm m^{-3} (e.g., Breier et al., 2009; Charette et al., 2001; Hancock et al., 2000; Krest et al., 1999; Moore et al., 1995; Rama and Moore, 1996; Veeh et al., 1995). To our knowledge, the only natural waters measured to date with significantly

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greater dissolved ^{226}Ra activities are Tampa Bay and the Dead Sea, for which the observed ^{226}Ra activities of the former are as high as 2810 dpm m^{-3}, attributed to carbonate groundwater discharge, and the latter are >110,000 dpm m^{-3}, attributed to saline brine discharge (Moore, 1997; Stiller and Chung, 1984). For Nueces Bay, a mixing model estimated that an input of 390×10^6 dpm day^{-1} was necessary to balance the ^{226}Ra budget, a Ra flux 100 times the riverine input (Breier and Edmonds, 2007). Synoptic geochemical and electrical sediment resistivity surveys in this area also indicated that the Ra input was relatively localized at the head of the bay (Breier et al., 2005). Collectively, these previous results suggested two possible submarine Ra sources: 1) submarine groundwater discharge and 2) leakage of oil-field brine from the numerous submerged oil/gas wells and pipelines in the area.

^{226}Ra and ^{228}Ra, with half-lives of 1600 yr, 5.75 yr, respectively, are the longest-lived of the four naturally occurring Ra isotopes. All four Ra isotopes are members of the three naturally occurring U-series decay chains and are each the product of Th decay. While Th readily adsorbs to particles, Ra is much more soluble especially in brackish and saline waters where Ra isotopes partition into the dissolved phase leaving the particle-reactive Th parents sediment bound. Thus, Ra isotopes are enriched in brackish groundwater and sediment pore-waters and can be transported into the water-column (Rama and Moore, 1996). In surface waters what little Th is produced by decay of dissolved U is rapidly scavenged by particles and transported to the sediments. Consequently there is relatively little Ra production in surface water and the open ocean has low Ra activities (Krest et al., 1999). This makes Ra isotopes natural tracers of sediment pore-water discharge to the coastal ocean. Oil-field brines are enriched in Ra as well, typically to an even higher degree (Kraemer and Reid, 1984); but compared to groundwaters and surface waters, they also differ in their Cl/Br ratios (Hudak and Wachal, 2001).

In this study we reexamine Nueces Bay Ra cycling by putting it in a broader regional and seasonal context. We compare Nueces Bay with two neighboring bays, Copano Bay and Baffin Bay, and examine interbay differences in Ra activities, CH_4, Cl/Br ratios (an independent indicator of oil-field brine), physiography, and petroleum development. In so doing, we conclude that the Ra cycle of these bays is not controlled by a single dominant process but rather the seasonal relationship of riverine Ra supply, submarine groundwater discharge, input from benthic sediments, and direct evaporation — in a dynamic equilibrium that follows the seasonal flushing of bay water by late-summer and early fall episodic, storm-driven precipitation events.

2. Methods

2.1. Study area

Copano Bay, Nueces Bay, and Baffin Bay are secondary bays in the greater Corpus Christi backbay-barrier island system of south Texas (Fig. 1, Table 1). The bays have a mean semi-diurnal tidal range of 0.15 m (Diener, 1975). The climate is semi-arid: in the Köppen–Geiger classification system this region is at the transition from fully humid-hot summer warm temperate to hot-steppe arid (Kottek et al., 2006). Precipitation decreases significantly from northeast to southwest such that Copano Bay typically receives the most rainfall and Baffin Bay the least. The Nueces River is the largest of the three watersheds but most of the natural discharge is impounded in reservoirs. Relative to bay size, Nueces Bay has the largest wetland area. The Texas coastal plain aquifer system is comprised of several hundred meters of silt, clay, sand, and gravel deposits that are the result of Cenozoic sedimentation from fluvial, deltaic, and marginal marine environments. Groundwater level generally follows the coastal topography except in the vicinity of Baffin Bay where municipal use and lower recharge have caused water levels to drop below sealevel. This is depicted by the regional water table surface elevation shown in Fig. 1, which is based on groundwater measurements from 330 wells measured between 1995 and 2005 (Texas Water Development Board, 2005a).

At the time of this study (2004–2005) there were a total of 624 oil and gas wells in all three bays and Nueces Bay had the highest concentration per area (Fig. 1, Table 1) (Texas Railroad Commission, 2005). A quarter of the wells actively produced oil, gas, and or a mixture of both. Half of all the wells were actively producing oil or gas at one time but were shut down at the time of the study. Of these inactive wells a few were shut off but maintained such that they could potentially be restarted in the future; the rest had been permanently plugged by filling in the bottom of the well with cement. Along with oil and gas, active wells also produce saline water (referred to here as oil-field brine). Oil-field brine is separated from oil/gas and currently disposed of by injection into deep disposal wells (typically into oil formations that are no longer productive). Wells can leak through compromised well casings and plugs or at surface valves and flanges. There were no reported leaks during this study, but subsurface leakage may go undetected. We use wells per bay volume as a metric for interbay comparisons of this risk.

2.2. Sample collection

Surface water samples (50 L) for dissolved Ra analysis were collected from Copano Bay, Nueces Bay, and Baffin Bay at three periods during their seasonal flushing cycles (Table 2, Figs. 1 and 2). The first sampling period (July 2004) followed a period of heavy rain, when river discharges were high and bay salinities were reduced to seasonal lows. During this initial period, Nueces Bay samples ($n=12$) were collected on 10 and 12 July 2004, Copano Bay samples ($n=12$) on 13 July 2004, and Baffin Bay samples ($n=12$) on 15 July 2004. The goal of the second set of samples was to observe each bay at a period when salinities were midway to their final seasonal maxima, based on Breier and Edmonds (2007). This goal was met for the samples collected from Baffin Bay ($n=8$) and Nueces Bay ($n=8$) on 8 December 2004 and 26 January 2005, respectively. The samples collected from Copano Bay ($n=8$) on 1 December 2005 ultimately proved closer to the seasonal salinity maximum than did the final samples. The final set of samples was timed to observe each of the three bays near the end of their seasonal flushing cycles when they approached their highest salinities. During this final period, Copano Bay samples ($n=12$) were collected on 18 May 2005, Nueces Bay samples ($n=12$) on 25 and 27 May 2005, and Baffin Bay samples ($n=8$) on 8 June 2005. Samples were collected by submersible pump and stored in 25 L polyethylene bottles. Water temperature and salinity were determined using a YSI Model 30 Sonde.

Surface water samples (50 L) for dissolved Ra analysis were also collected from the tidal inlet at Aransas Pass at high tide, the primary rivers feeding the three bays, and regional water wells, lakes, ponds, and marshes (Figs. 1 and 2, Table 3). Aransas Pass samples (50 L, $n=32$) were collected biweekly from The University of Texas at Austin Marine Science Institute (UTMSI) pier lab from 16 July 2004 to 29 July 2005. River samples (75 L, $n=4$) were collected from the Mission and Aransas Rivers in the Copano Bay watershed and Los Olmos Creek in the Baffin Bay watershed. Nueces River sampling was included in the bay surveys. Groundwater samples (25–75 L, $n=20$) were collected from wells equipped with downhole pumps, flowing under artesian pressure, or using a portable pump (Table 4). Surface samples ($n=5$) were also collected from brackish ponds, salt marshes, and intertidal areas. Pore-waters were sampled using a 1.8 m MHE Products stainless steel minipiezometer to a depth of 20 cm; in only two cases were sediments permeable enough to collect sufficient water for Ra analysis.

Surface water samples for CH_4 analysis (120 mL) and Cl/Br analysis (50 mL) were collected from Copano Bay, Nueces Bay, and Baffin Bay during the third sampling periods. Air free water samples for CH_4 analysis were collected in polyethylene gas tight syringes and stored