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Journal of Environmental Radioactivity 69 (2003) 159–176

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JOURNAL OF  
ENVIRONMENTAL  
RADIOACTIVITY

# Invariance of isotope ratios of lithogenic radionuclides: more evidence for their use as sediment source tracers

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Received 1 October 2002; received in revised form 1 February 2003; accepted 2 March 2003

## Abstract

Activities of radionuclides in the  $^{238}\text{U}$  ( $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ) and  $^{232}\text{Th}$  ( $^{232}\text{Th}$ ,  $^{228}\text{Th}$ ,  $^{228}\text{Ra}$ ) decay series were determined in sediments from an east Texas watershed and examined with isotope ratios and compared to particulate organic carbon (POC), % fines (< 63  $\mu\text{m}$ ) and total concentrations of Al, Fe and Mn. The objective was to elucidate the presence or absence of relationships affecting the effectiveness of these radionuclides in modeling sediment transport. Strong positive correlations were observed between radionuclides and Mn (Th) and % fines (Ra and Th). Isotope ratios effectively reduce these influences, supporting the contention that isotope ratios offset extrinsic variability in terrestrial sediments. Strong associations of  $^{210}\text{Pb}_{\text{xs}}$  (excess  $^{210}\text{Pb}$ ) and  $^{226}\text{Ra}/^{230}\text{Th}$  with POC agree with data from marine and terrestrial settings, indicating that the role of POC in isotope fractionation, transport and sequestration merits further investigation.

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*Keywords:* Pb-210; Th-232; Th-230; Ra-226

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## 1. Introduction

Knowledge of the sources and dynamics of sediments in river systems is important in many fields of environmental science, including water quality (Langedal, 1997; Swank et al., 2001), the fate and transport of pollutants (Macklin et al., 1997; House et al., 1997; Marcus et al., 2001) and ecological health and diversity (Ryan, 1991; Rice et al., 2001). As a result, many different methods, including use of natural and anthropogenic radionuclides, have been applied in an attempt to quantify both sediment transport processes and rates of sediment deposition in fluvial, lacustrine and marine settings. The focus of this study is to examine the relations between both discrete activities and ratios of natural radionuclides, which are commonly applied to these problems, to extrinsic variables including grain size, POC and major (Al) and transition metal (Fe, Mn) contents in sediments.

A principal requirement in tracer studies is that the marker(s) are conservative over a wide range of environmental conditions, i.e. they are unaffected by extrinsic variability. In terms of fluvial sediment transport and fate studies, the markers need to move with sediment, while retaining the original source signature, and remain associated with the sediment post-deposition to provide reliable chronologic information. The conservative geochemistry of particle-bound thorium, radium and lead is well documented ((Th) Kaufman, 1969; Ivanovich and Harmon 1982, 1992; (Ra) Tanner, 1964; Riese, 1982; Ames et al., 1983; (Pb) Walling and Woodward, 1992; Faure, 1986; Azizian and Nelson, 1998; Kendall and McDonnell, 1998) and has made isotopes of these elements attractive tools to address sediment transport questions.

### 1.1. Previous research

Fallout radionuclides ( $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^7\text{Be}$ ) have been used with success to investigate lacustrine and floodplain sedimentation (e.g. Goldberg, 1963; Krishnaswami et al., 1971; Robbins and Edgington, 1975; Walling and He, 1997) and soil erosion processes (e.g. Wan et al., 1987; Ritchie and McHenry, 1990; Quine and Walling, 1991; Branca and Voltaggio, 1993; Zhang et al., 1998). Lithogenic radionuclides in the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series have also been used to address a range of problems in geology and geomorphology, including provenance determination of coastal sediments (Roberts and Plater, 1999); resolution of sedimentation rates of fluvial sands (Murray et al., 1990) and resolving fluvial sediment sources (Olley and Murray, 1994; Yeager et al., 2002). These radionuclides have been used solely (Olley, 1994; Olley et al., 1997) and together with fallout radionuclides (Olley et al., 1993; He and Owens, 1995) to address fluvial source and transport questions.

In most cases, previous research supports the contention that variability introduced into these radionuclide values (discrete or ratios) by extrinsic variables, such as those considered herein, are minor. The result being that values expressed by radionuclides serve as quantifying tools, representative of physical processes, not geochemical or environmental variability. One example is that differences in particle surface area and site concentration have been shown to influence radionuclide adsorption (Megumi et al., 1982). While an individual radionuclide's activity concentration is a function of

substrate surface area and site concentration, daughter/parent ratios have been shown to often remain constant within analytical uncertainty (Murray et al., 1990; Murray et al., 1991; Olley et al., 1997). This ratio approach has been used when considering natural and fallout radionuclides, including  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ,  $^7\text{Be}$  and  $^{234}\text{Th}$  (Bonniwell et al., 1999; Feng et al., 1999) and lithogenic radionuclides including radium and thorium isotopes (Olley et al., 1993, 1997; Yeager et al., 2002). When considering other variables, the assumption of ultra-conservancy becomes less well supported. One example is particulate organic carbon (POC), which has been shown to strongly and positively correlate with radium isotopes in soils (Nathwani and Phillips, 1979), with  $^{210}\text{Pb}$  in marine settings (Paulsen et al., 1999), and has been described as an important adsorption substrate for thorium (Ivanovich and Harmon, 1992). Another example includes transition metals, such as Fe and Mn, common as both constituents of primary minerals and as coatings of sediments. Radium has been shown to adsorb strongly to Fe (III) oxyhydroxides (Ames et al., 1983) and  $\text{MnO}_2$  impregnated filtration has been used to extract both radium (Baskaran et al., 1993) and thorium isotopes (Buesseler et al., 1992) quantitatively from seawater.

### 1.2. Experimental approach

Alluvial and topsoil derived (interfluvial) sediments are examined to characterize them in terms of radiochemical signatures and to compare these signatures to variables including % fines ( $< 63 \mu\text{m}$ ), POC and metal (Al, Fe and Mn) contents. Metals were determined in bulk and in triplicate leaches to determine if significant compositional or speciation differences existed between the two sample populations. The objective of this research is to statistically examine this suite of variables to ascertain whether the assumption of ultra-conservancy for these radionuclides is valid in natural systems, and if not universally so, to identify which interactions warrant further investigation.

## 2. Study area

The field site is the lower section of the Loco Bayou watershed, below Lake Nacogdoches in Nacogdoches County, Texas (Fig. 1). The entire basin has an area of  $265 \text{ km}^2$ ,  $9 \text{ km}^2$  of which is occupied by Lake Nacogdoches, with the lower section covering  $37 \text{ km}^2$ . Loco Bayou is in the Pineywoods region of the east Texas coastal plain, having a subtropical climate with mean annual precipitation of 1200–1500 mm (NOAA, 2001). Total relief here is  $\approx 60 \text{ m}$ , slopes prevail bordering the dam and valley walls in the north where forests dominate land cover. The southern half of the basin widens into a gently undulated floodplain, much of which has been cleared and utilized for agriculture.

The geology of the lower basin is dominated by the Eocene Weches Formation, marine “green” sand (Fig. 1), while the main channel is underlain by Quaternary alluvium. The Weches Formation is composed predominantly of a sand and berthierine matrix with abundant macrofossils (Hsieh and Yapp, 1999), the heavy mineral

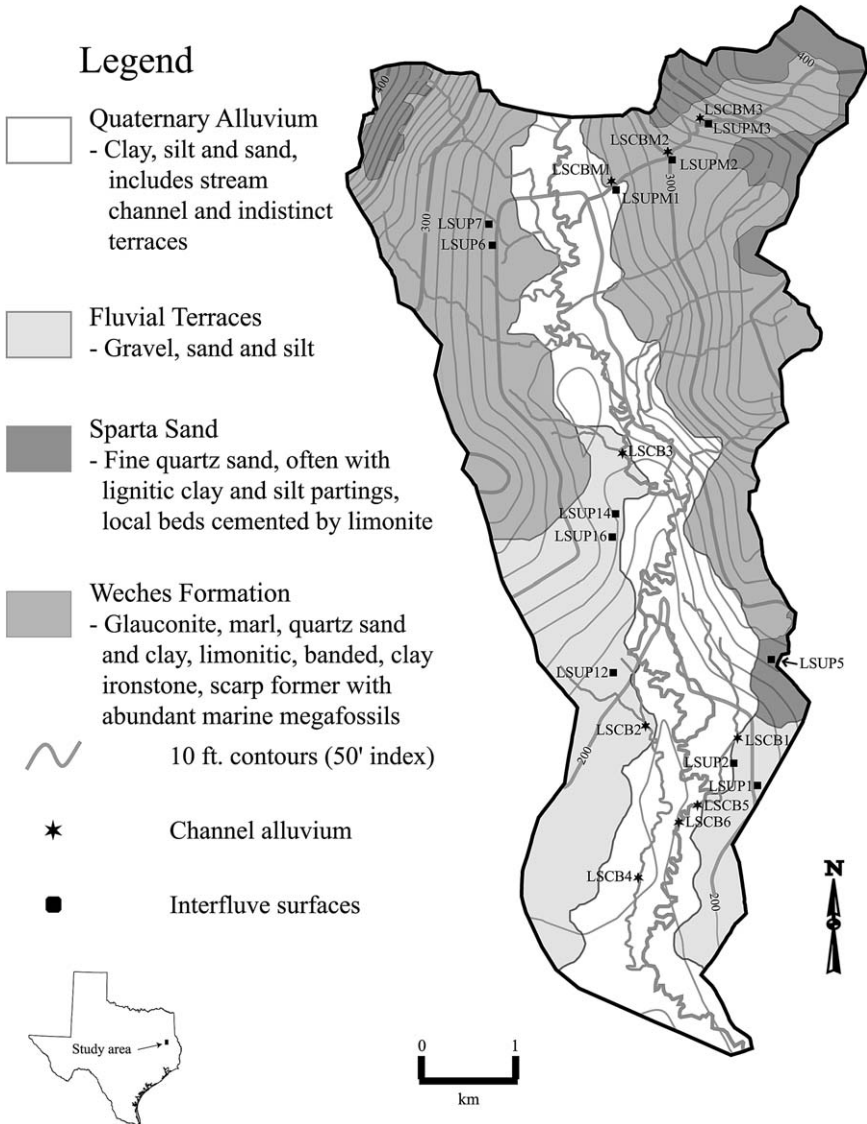


Fig. 1. Lower Loco Bayou watershed geology and sample locations. Bedrock geology digitized from the 1:250,000 scale Palestine sheet (Shelby et al., 1968).

fraction is dominated by zircon, garnet, tourmaline, titanite, apatite, staurolite, green hornblende, epidote, sillimanite, monatite and kyanite (Jobe et al., 1993). Berthierine is a mineral that is rich in Fe (often 30%+ by mass), it is commonly found in unmetamorphosed marine sediments, lateritic and polar soils. Common pedogenic minerals in humid climates such as this include clays, Al oxides and hydroxides and Fe (III) oxides and hydroxides. In the soils of this region the dominant pedogenic

minerals include; goethite ( $\alpha$ -FeOOH), among the most common Fe (III) minerals, along with Fe carbonates ( $\text{Fe}(\text{CO}_3)\text{OH}$ ) and smectite clays (Hsieh and Yapp, 1999). The Loco Bayou soils are categorized into three associations; the upland ridge, redland belt loams of the Nacogdoches-Trawick, sandier, hill slope soils of the Cuthbert-Tenaha and terrace loams of the Attoyac-Bernaldo-Besner associations (Dolezel, 1980).

### 3. Experimental procedures

#### 3.1. Sampling

Samples of channel alluvium and area soils were collected from the near surface (0–2 cm) throughout the study basin (Fig. 1). All samples were combined in the field, consisting of eight to ten sub-samples collected over an approximately 10 m<sup>2</sup> area. In order to assure representative samples from each site, the sampling areas were chosen based on the presence of uniform characteristics. Alluvial sediments were collected from areas that showed evidence of recent deposition (such as accumulations of fine grained sediments with mixed organic detritus on channel margins, etc.) and interfluvial sample areas were chosen where topsoil was in place, secured by vegetation and considered to be relatively stable substrates. All samples were collected between the winter of 1999 and spring of 2001.

#### 3.2. Sample processing and analyses

Bulk samples were dried at 70–80 °C for 24 h, then gently disaggregated with mortar and pestle and passed through 2 and 0.5 mm sieves. The < 63  $\mu\text{m}$  fraction was determined using standard methods, including treatment of the sediment for deflocculation and wet and dry sieving. Sample aliquots were then stored in plastic test tubes and sealed with epoxy for 20 days in order for equilibrium between <sup>226</sup>Ra and its volatile daughter <sup>222</sup>Rn ( $t_{1/2}$  = 3.8 days), an inert gas, to be reached. High-resolution gamma spectrometry was employed to resolve <sup>228</sup>Ra ( $t_{1/2}$  = 5.75 yr., via <sup>228</sup>Ac  $E\gamma$  = 911 keV), and <sup>226</sup>Ra ( $t_{1/2}$  = 1602 yr., via <sup>214</sup>Pb  $E\gamma$  = 352 keV), using Canberra HPGGe well detectors and a multi-channel analyzer, model 747. Standards were prepared and run on each detector in several geometries to determine representative efficiencies for each nuclide. Calibrations (<sup>226</sup>Ra, <sup>228</sup>Ra) were checked against a certified US Department of Commerce, National Bureau of Standards (now NIST) standard, composed of fly ash from coal combustion. Counting and efficiency errors based on standards were less than  $\pm$  2%.

Alpha spectrometry was used to resolve <sup>232</sup>Th ( $t_{1/2}$  =  $1.39 \times 10^{10}$  yr.), <sup>230</sup>Th ( $t_{1/2}$  =  $7.52 \times 10^4$  yr.), <sup>228</sup>Th ( $t_{1/2}$  = 1.91 yr.) and <sup>210</sup>Pb ( $t_{1/2}$  = 22.3 yr.) (<sup>210</sup>Pb<sub>xs</sub> = total <sup>210</sup>Pb – <sup>226</sup>Ra supported <sup>210</sup>Pb) using a Canberra alpha spectrometer, model 7404, mated to a Canberra multi-channel analyzer, model 8224. Thorium samples were spiked with a certified <sup>229</sup>Th tracer solution (NIST, SRM #4328B) and completely digested (HF, HCL and HNO<sub>3</sub>) over heat. The solution was passed through

two sets of anion exchange columns to selectively isolate thorium isotopes, as described by Buesseler et al. (1992). The elution was acidified with  $\text{H}_2\text{SO}_4$  and plated onto stainless steel planchets by sulfate electro-deposition prior to counting, according to methods described by Hallstadius (1984) and Buesseler et al. (1992). Lead samples were spiked with a certified  $^{209}\text{Po}$  tracer solution (Isotope Product Laboratories, #6209-100N) and completely digested ( $\text{HF}$ ,  $\text{HCl}$  and  $\text{HNO}_3$ ) over heat. Ascorbic acid was then added to bind free Fe and a silver disk was added to the solution over heat to provide a substrate for spontaneous deposition of polonium and lead nuclides (Santschi et al., 1980, 1999; Ravichandran et al., 1995a, 1995b). Chemical recoveries for thorium isotopes and  $^{210}\text{Pb}$  averaged  $>70\%$ . The detection limit, generally defined as three times the standard deviation of the background, is low, the highest determined value was approximately 10 Bq/kg for  $^{210}\text{Pb}_{\text{xs}}$ .

Sample preparation for determination of POC entailed subjecting samples to dilute  $\text{HCl}$  (2N) over heat with triplicate rinses to assure destruction of any inorganic carbon present. Samples were stored in sealed vials until analyzed. Sediment samples were run in triplicate on a Perkin Elmer Series 2400 Elemental Analyzer (CHNS/O) using standard methods to determine POC.

For analyses of Al and the transition metals considered (Fe, Mn), both bulk and sequential leaches of sample aliquots (approximately 50 mg) were prepared according to methods described by Landing and Lewis (1991). Leach one (HAc) is reported to dissolve carbonate phases, adsorbed cations and Mn-oxyhydroxides (Chester and Hughes, 1967; Landing and Bruland, 1987), leach two (aqua regia) was developed to dissolve more resistant Fe-oxyhydroxides and metal sulfides, and the third leach employing the three strong acids ( $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ ) to dissolve remaining refractory mineral phases (alumino-silicates).

Both bulk total digestions and all three leachate fractions were evaporated to near dryness, reconstituted in 1%  $\text{HNO}_3$  and stored in sealed vials until analyzed. Samples were run in duplicate on a Perkin Elmer Series 5100pc Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) using standard methods to determine metal concentrations. A NIST certified standard (SRM #1944), sediment from the Hudson River, was used to calibrate the instrument; this standard was chosen due to its similarity to the sediment samples analyzed. Determinations of these metals in the NIST standard were within 5% of the reported value, this and the relatively low deviation of all replicate samples allows us to be confident in an error for all metal determinations at less than 10%.

## 4. Results and discussion

### 4.1. Metals and radionuclides

Total digestions and triplicate leach data for Al, Fe and Mn are shown in Tables 1, 2 and 3, respectively. A paired t test was run to ascertain whether significant differences in physical composition was evident between the two sample populations, considering the variables total Al, Fe, Mn, percent fines and POC. The results are

Table 1

Concentrations (mg/kg) of Al in leach 1 (L<sub>1</sub>), leach 2 (L<sub>2</sub>), leach 3 (L<sub>3</sub>) and total (L<sub>total</sub>). Also shown is the percent distribution of Al into these three fractions, summary statistics for both groups and the combined population, and % fines (< 63 µm) and % POC for each sample.

Sample	L <sub>1</sub>	L <sub>2</sub>	L <sub>3</sub>	L <sub>total</sub>	L <sub>1</sub> %	L <sub>2</sub> %	L <sub>3</sub> %	% fines	% POC
LSUP1	262.6	729.4	13,727.8	14,729.4	1.8	5.0	93.2	48.0	1.0
LSUP2	89.5	422.3	10,678.3	11,193.2	0.8	3.8	95.4	17.0	1.9
LSUP5	202.7	302.4	6553.7	7062.2	2.9	4.3	92.8	38.6	0.5
LSUP6	478.7	1044.9	24,528.4	26,038.6	1.8	4.0	94.2	37.2	1.7
LSUP7	52.5	378.7	9526.6	9954.6	0.5	3.8	95.7	26.2	0.7
LSUP12	110.5	601.2	10,783.3	11,496.1	1.0	5.2	93.8	39.0	1.1
LSUP14	32.6	194.6	7056.4	7282.1	0.4	2.7	96.9	35.3	1.3
LSUP16	139.1	523.2	12,961.1	13,614.6	1.0	3.8	95.2	44.0	4.5
LSUPM1	60.5	1922.4	33,619.9	35,599.2	0.2	5.4	94.4	51.8	1.9
LSUPM2	43.2	916.7	19,552.1	20,516.4	0.2	4.5	95.3	45.7	3.8
LSUPM3	31.4	532.4	10,548.9	11,115.8	0.3	4.8	94.9	26.1	1.3
<i>Low</i>	<i>31.4</i>	<i>194.6</i>	<i>6553.7</i>	<i>7062.2</i>	<i>0.2</i>	<i>2.7</i>	<i>92.8</i>	<i>17.0</i>	<i>0.5</i>
<i>High</i>	<i>478.7</i>	<i>1922.4</i>	<i>33,619.9</i>	<i>35,599.2</i>	<i>2.9</i>	<i>5.4</i>	<i>96.9</i>	<i>51.8</i>	<i>4.5</i>
<i>Mean</i>	<i>136.7</i>	<i>688.0</i>	<i>14,503.3</i>	<i>15,327.5</i>	<i>1.0</i>	<i>4.3</i>	<i>94.7</i>	<i>37.2</i>	<i>1.8</i>
<i>STD</i>	<i>135.5</i>	<i>481.9</i>	<i>8258.0</i>	<i>8759.6</i>	<i>0.9</i>	<i>0.8</i>	<i>1.2</i>	<i>10.5</i>	<i>1.3</i>
LSCB1	260.3	1078.7	22,749.6	24,099.2	1.1	4.5	94.4	48.0	2.2
LSCB2	338.7	1469.4	42,345.4	44,155.8	0.8	3.3	95.9	87.6	2.5
LSCB3	360.8	1046.1	17,480.9	18,877.9	1.9	5.5	92.6	38.0	0.6
LSCB4	242.7	733.9	11,763.6	12,745.0	1.9	5.8	92.3	20.7	0.3
LSCB5	192.0	637.8	20,887.2	21,712.3	0.9	2.9	96.2	46.6	1.3
LSCB6	287.6	975.7	20,080.2	21,339.2	1.3	4.6	94.1	59.5	3.2
LSCBM1	29.6	1522.0	10,461.0	12,010.3	0.2	12.7	87.1	11.7	2.4
LSCBM2	29.2	2603.5	16,186.8	18,821.9	0.2	13.8	86.0	12.3	0.3
LSCBM3	15.2	1932.6	22,625.8	24,593.3	0.1	7.9	92.0	15.7	1.6
<i>Low</i>	<i>15.2</i>	<i>637.8</i>	<i>10,461.0</i>	<i>12,010.3</i>	<i>0.1</i>	<i>2.9</i>	<i>86.0</i>	<i>11.7</i>	<i>0.3</i>
<i>High</i>	<i>360.8</i>	<i>2603.5</i>	<i>42,345.4</i>	<i>45,947.8</i>	<i>1.9</i>	<i>13.8</i>	<i>96.2</i>	<i>87.6</i>	<i>3.2</i>
<i>Mean</i>	<i>195.1</i>	<i>1333.3</i>	<i>20,509.0</i>	<i>22,238.5</i>	<i>0.9</i>	<i>6.8</i>	<i>92.3</i>	<i>37.8</i>	<i>1.6</i>
<i>STD</i>	<i>137.1</i>	<i>627.0</i>	<i>9300.2</i>	<i>9936.9</i>	<i>0.7</i>	<i>4.0</i>	<i>3.6</i>	<i>25.6</i>	<i>1.1</i>
<i>Combined</i>	–	–	–	–	–	–	–	–	–
<i>Mean</i>	<i>163.0</i>	<i>978.4</i>	<i>17,205.9</i>	<i>18,437.5</i>	<i>1.0</i>	<i>5.4</i>	<i>93.6</i>	<i>37.5</i>	<i>1.7</i>
<i>STD</i>	<i>136.0</i>	<i>629.5</i>	<i>9039.2</i>	<i>9716.1</i>	<i>0.8</i>	<i>2.9</i>	<i>2.8</i>	<i>18.3</i>	<i>1.1</i>

shown in Table 4, since the significance (p value) of the comparisons is not less than 0.05 for any tested variable, the two sample populations are statistically similar. Speciation of the metals in the two sample populations are also indistinguishable, as shown in Fig. 2a,b,c. For the combined population, Al was found nearly entirely in the refractory phase (overall mean of ≈ 94%) and Mn was balanced between surface-coating oxides and the refractory phase (≈ 45 and ≈ 32%, respectively). Most of the Fe resolved was in the refractory phase, as opposed to being present as surface-coating oxides (≈ 85 and ≈ 13%, respectively). These results suggest that generally, insufficient time has passed to make available much of the Fe bound in the parent rock and refractory minerals to the soil system. The youth of these soils

Table 2

Concentrations (mg/kg) of Fe in leach 1 ( $L_1$ ), leach 2 ( $L_2$ ), leach 3 ( $L_3$ ) and total ( $L_{total}$ ). Also shown is the percent distribution of Fe into these three fractions and summary statistics for both groups and combined.

Sample	$L_1$	$L_2$	$L_3$	$L_{total}$	$L_1$ %	$L_2$ %	$L_3$ %
LSUP1	51.1	1553.4	33,376.0	34,985.3	0.2	4.4	95.4
LSUP2	81.4	1778.6	26,401.0	28,257.6	0.3	6.3	93.4
LSUP5	116.9	885.1	15,042.0	16,036.2	0.7	5.5	93.8
LSUP6	211.7	1994.9	50,968.0	53,202.5	0.4	3.8	95.8
LSUP7	175.0	2279.0	29,892.5	32,351.2	0.5	7.1	92.4
LSUP12	21.8	1810.6	19,982.5	21,815.0	0.1	8.3	91.6
LSUP14	153.8	1056.8	6343.9	7552.3	2.0	14.0	84.0
LSUP16	47.6	1204.8	16,423.9	17,679.1	0.3	6.8	92.9
LSUPM1	31.4	3559.9	88,621.6	92,225.3	0.0	3.9	96.1
LSUPM2	61.9	4383.1	29,705.5	34,144.2	0.2	12.8	87.0
LSUPM3	259.6	10784.3	9412.3	20,461.6	1.3	52.7	46.0
<i>Low</i>	21.8	885.1	6343.9	7552.3	0.0	3.8	46.0
<i>High</i>	259.6	10784.3	88,621.6	92,225.3	2.0	52.7	96.1
<i>Mean</i>	110.2	2844.6	29,651.8	32,610.0	0.6	11.4	88.0
<i>STD</i>	79.6	2838.3	23,218.8	23,226.4	0.6	14.1	14.4
LSCB1	1220.6	6053.2	28,411.9	35,693.3	3.4	17.0	79.6
LSCB2	852.3	6581.7	45,234.1	52,659.0	1.6	12.5	85.9
LSCB3	524.0	3509.1	21,975.4	26,006.4	2.0	13.5	84.5
LSCB4	698.6	3228.2	17,906.6	21,837.3	3.2	14.8	82.0
LSCB5	913.4	8204.8	20,628.6	29,767.1	3.1	27.6	69.3
LSCB6	915.2	7486.8	26,882.1	35,278.3	2.6	21.2	76.2
LSCBM1	172.8	6165.1	32,937.4	39,257.9	0.4	15.7	83.9
LSCBM2	1291.9	8321.8	42,262.8	51,881.8	2.5	16.0	81.5
LSCBM3	227.0	3390.3	32,425.8	36,028.7	0.6	9.4	90.0
<i>Low</i>	172.8	3228.2	17,906.6	21,837.3	0.4	9.4	69.3
<i>High</i>	1291.9	8321.8	45,234.1	52,659.0	3.4	27.6	90.0
<i>Mean</i>	757.3	5882.3	29,851.6	36,490.0	2.2	16.4	81.4
<i>STD</i>	393.6	2043.4	9404.0	10,476.9	1.1	5.3	6.0
<i>Combined</i>	–	–	–	–	–	–	–
<i>Mean</i>	401.4	4211.6	29,741.7	34,356.0	1.3	13.7	85.1
<i>STD</i>	421.5	2898.6	17,916.2	18,277.6	1.2	11.1	11.7

has been observed by Hsieh and Yapp (1999) and complex weathering patterns exhibited by the Weches Fm. and soils developed on it, attributable to the formation's tendency to be erosion resistant, was examined by Phillips (2001). Total abundances support field observations of an Fe-oxide rich system, mean concentrations (ppm) in these relatively fine grained sediments were Fe (34,355) > Al (18,437) > Mn (341).

Values for discrete lithogenic isotopes and  $^{210}\text{Pb}_{xs}$  are shown in Table 5. Mean and ranges for radionuclide activities are typical for this setting, as no uranium mineralization zones are known in these rocks, and sediment sample types show no marked distinction in activities. There is evidence of disequilibrium between  $^{226}\text{Ra}$ : $^{232}\text{Th}$  and  $^{228}\text{Ra}$ : $^{228}\text{Th}$  in these soils and sediments, with Ra being deficient in both cases. This may be the combined result of disequilibria in the basin's bedrock

Table 3

Concentrations (mg/kg) of Mn in leach 1 ( $L_1$ ), leach 2 ( $L_2$ ), leach 3 ( $L_3$ ) and total ( $L_{total}$ ). Also shown is the percent distribution of Mn into these three fractions and summary statistics for both groups and combined.

Sample	$L_1$	$L_2$	$L_3$	$L_{total}$	$L_1$ %	$L_2$ %	$L_3$ %
LSUP1	122.0	81.2	77.9	281.1	43.4	28.9	27.7
LSUP2	172.3	41.4	18.7	232.2	74.2	17.8	8.0
LSUP5	29.4	8.1	39.0	76.5	38.4	10.6	51.0
LSUP6	4.8	5.0	66.6	76.4	6.3	6.5	87.2
LSUP7	39.2	22.8	96.4	157.5	24.8	14.5	60.7
LSUP12	286.1	81.7	8.7	376.4	76.0	21.7	2.3
LSUP14	123.1	31.9	20.0	174.9	70.4	18.2	11.4
LSUP16	111.7	25.3	75.8	212.8	52.5	11.9	35.6
LSUPM1	225.5	270.9	142.5	638.8	35.3	42.4	22.3
LSUPM2	217.5	41.7	26.3	285.4	76.2	14.6	9.2
LSUPM3	131.7	9.2	26.6	167.6	78.6	5.5	15.9
<i>Low</i>	4.8	5.0	8.7	76.4	6.3	5.5	2.3
<i>High</i>	286.1	270.9	142.5	638.8	78.6	42.4	87.2
<i>Mean</i>	132.9	56.2	54.4	243.6	52.3	17.5	30.1
<i>STD</i>	88.0	75.9	41.2	158.7	24.7	10.6	26.4
LSCB1	145.3	71.7	168.4	385.4	37.7	18.6	43.7
LSCB2	278.8	122.0	135.7	535.9	52.0	22.8	25.2
LSCB3	78.3	74.9	15.2	168.4	46.5	44.5	9.0
LSCB4	49.3	37.6	27.8	114.7	43.0	32.8	24.2
LSCB5	417.5	237.5	595.0	1250.0	33.4	19.0	47.6
LSCB6	730.5	160.8	48.9	940.2	77.7	17.1	5.2
LSCBM1	47.2	4.6	107.6	159.4	29.6	2.9	67.5
LSCBM2	35.1	99.1	304.2	438.4	8.0	22.6	69.4
LSCBM3	10.2	101.4	43.4	155.1	6.6	65.4	28.0
<i>Low</i>	10.2	4.6	15.2	114.7	6.6	2.9	5.2
<i>High</i>	730.5	237.5	595.0	1250.0	77.7	65.4	69.4
<i>Mean</i>	199.1	101.1	160.7	460.8	37.2	27.3	35.5
<i>STD</i>	240.3	68.5	186.3	395.9	21.9	18.2	23.2
<i>Combined</i>	–	–	–	–	–	–	–
<i>Mean</i>	162.7	76.4	102.2	341.4	45.5	21.9	32.5
<i>STD</i>	171.9	74.3	135.9	302.6	24.1	15.0	24.5

and geochemical processes operating on the landscape, as described in Yeager et al. (2002). This condition is not unique and has been documented by other researchers in terrestrial environs (e.g. Olley, 1994; Olley et al., 1997; Kendall and McDonnell, 1998).

#### 4.2. Correlation between discrete activities, activity ratios and extrinsic variables

Since there are no significant compositional differences in the two sample populations, we will consider the combined sample population here. We examine the relative influence of the extrinsic variables on both discrete activities and radionuclide ratios in an effort to determine whether important interactions exist. Discrete activities and isotope ratios were correlated with POC, % fines (< 63  $\mu\text{m}$ )

Table 4  
Results of paired t test, comparing the two sample population's compositional variables.

Compared variable	Paired differences					Test statistic (t)	Significance (two-tailed)
	Mean	Standard deviation	Standard error mean	95% Confidence interval of difference			
Interfluves - alluvium							
Total Al	-6820.54	13,590.94	4530.31	-17,267.47	3626.38	-1.50	0.17
Total Fe	-2700.58	29,863.30	9954.43	-25,655.56	20,254.38	-0.27	0.79
Total Mn	-213.43	432.95	144.31	-546.22	119.36	-1.47	0.17
% Fines	-0.33	33.46	11.15	-26.05	25.38	-0.03	0.97
POC	0.02	1.85	0.62	-1.40	1.44	0.04	0.97

and total Fe, Mn and Al concentrations. We employed multiple regression analysis (Ott, 1993; Kleinbaum et al., 1998), defining the multiple regression coefficient ( $R^2$ ) as;

$$R^2 = \frac{\sum (\gamma_i - \bar{\gamma})^2 - \sum (\gamma_i - \hat{\gamma}_i)^2}{\sum (\gamma_i - \hat{\gamma}_i)^2}$$

where  $\hat{\gamma}_i$  is the estimated value of the dependent variable and  $\bar{\gamma}$  is the mean value. Using this approach, the partial correlation coefficient is defined as a measure of the strength of the linear relationship between two variables, after controlling for effects of the other variables considered. This is an important point, as a straight correlation matrix considering these extrinsic variables resulted in several significant correlations (Al and Fe,  $r = 0.78$ ,  $p < 0.001$ , Al and % fines,  $r = 0.63$ ,  $p = 0.003$  and Mn and % fines,  $r = 0.48$ ,  $p = 0.032$ ). Results are shown in Table 6.

The  $R^2$  values for all discrete isotopes except  $^{210}\text{Pb}_{\text{xs}}$  indicate that a significant fraction of the variance is explained by the model. Also, the significance of the change in F for these  $R^2$  values indicates that the variation explained by the model is not due to chance. Three variables stand out when examining correlations for individual radionuclides, total Mn, POC and % fines. Manganese has strong, significant positive interactions with all Th isotopes considered, but somewhat surprisingly, no significant relations are found between Mn and any Ra isotopes. The second, % fines, interacts positively and significantly with all isotopes save  $^{210}\text{Pb}_{\text{xs}}$  ( $^{228}\text{Ra}$ ,  $p = 0.06$ ). It is surprising that no significant relation between % fines and  $^{210}\text{Pb}_{\text{xs}}$  was observed here. Finally, POC is found to correlate positively and significantly only with  $^{210}\text{Pb}_{\text{xs}}$  (Fig. 3).

Radionuclide ratio relationships indicate that assumptions of enhanced conservancy of ratios, as opposed to discrete activities are well founded. Overall, multiple correlation coefficients ( $R^2$ ) indicate that the chosen set of variables accounts for more of the variance in observed discrete radionuclide activities than those of isotope

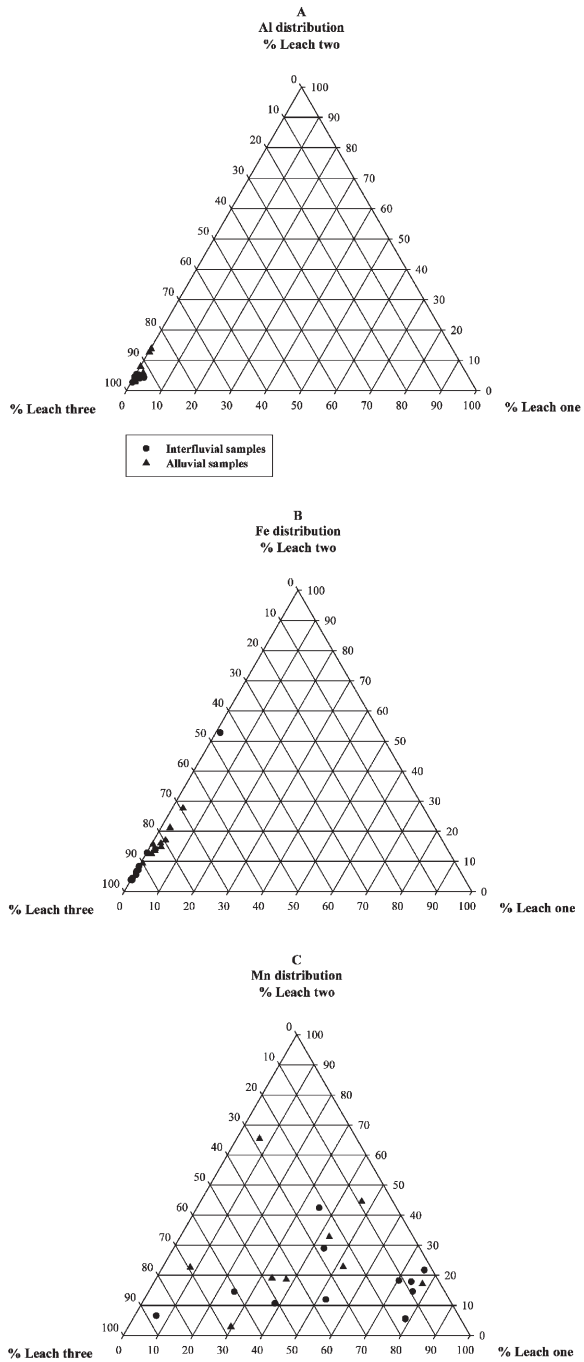


Fig. 2.a,b,c: Ternary diagrams illustrating the speciation of the test metals Al (a), Fe (b) and Mn (c) for all samples.

Table 5  
Activity (Bq/kg) data for all samples, with propagated errors as discussed in Choppin et al. (1995), summary statistics shown for both sample groups and combined population.

Type	Sample	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{232}\text{Th}$	$^{228}\text{Ra}$	$^{228}\text{Th}$	$^{210}\text{Pb}_{\text{xs}}$
Interfluvial	LSUP1	31.5 ± 3.0	36.9 ± 2.1	31.8 ± 3.0	25.8 ± 3.0	32.8 ± 3.1	23.7 ± 4.5
	LSUP2	27.4 ± 2.4	31.6 ± 1.9	27.0 ± 2.3	20.2 ± 2.2	31.6 ± 2.7	29.7 ± 5.3
	LSUP5	30.2 ± 2.2	26.6 ± 2.0	28.6 ± 2.1	15.9 ± 1.9	28.9 ± 2.1	12.4 ± 3.0
	LSUP6	35.2 ± 2.7	27.1 ± 2.0	48.7 ± 3.6	21.4 ± 2.6	47.1 ± 3.5	26.5 ± 4.8
	LSUP7	28.5 ± 2.2	23.5 ± 1.2	37.6 ± 2.8	34.9 ± 3.5	35.9 ± 2.7	0
	LSUP12	39.6 ± 3.1	36.9 ± 2.5	41.5 ± 3.3	30.5 ± 2.8	42.5 ± 3.3	24.6 ± 3.2
	LSUP14	33.3 ± 2.5	41.1 ± 2.8	48.2 ± 3.6	29.9 ± 3.0	45.7 ± 3.4	12.7 ± 4.3
	LSUP16	25.9 ± 2.4	45.1 ± 2.7	35.1 ± 3.1	39.9 ± 3.6	36.6 ± 3.2	64.2 ± 4.1
	LSUPM1	41.0 ± 3.3	28.2 ± 1.6	77.2 ± 5.8	41.1 ± 3.4	82.3 ± 2.9	36.0 ± 2.0
	LSUPM2	24.9 ± 2.0	23.7 ± 1.3	37.6 ± 2.8	25.0 ± 2.3	38.9 ± 2.9	27.4 ± 2.5
	LSUPM3	20.8 ± 1.7	20.6 ± 0.9	22.9 ± 1.8	19.0 ± 1.8	22.9 ± 1.9	22.1 ± 3.1
	Low	20.8	20.6	22.9	15.9	22.9	0
	High	41.0	45.1	77.2	41.1	82.3	64.2
	Mean	30.7	31.0	39.6	27.6	40.5	25.4
	STD	6.2	8.0	14.9	8.5	15.7	16.2
	Alluvium	LSCB1	52.2 ± 4.9	37.9 ± 3.5	57.2 ± 5.3	31.6 ± 2.6	59.9 ± 5.5
LSCB2		51.5 ± 3.5	44.4 ± 3.2	61.6 ± 4.2	52.5 ± 4.5	64.3 ± 4.3	13.0 ± 4.6
LSCB3		44.1 ± 3.7	40.2 ± 1.7	53.5 ± 4.3	40.9 ± 1.5	52.6 ± 4.3	0
LSCB4		34.8 ± 2.9	26.8 ± 1.7	39.3 ± 3.2	21.0 ± 3.3	41.8 ± 3.7	0
LSCB5		52.6 ± 4.2	39.5 ± 0.8	61.4 ± 4.9	34.7 ± 1.6	60.6 ± 4.8	0
LSCB6		66.4 ± 3.2	42.6 ± 1.9	70.5 ± 6.9	39.9 ± 2.0	69.1 ± 6.9	21.1 ± 5.4
LSCBM1		17.4 ± 1.4	16.4 ± 1.0	25.5 ± 2.0	21.3 ± 2.5	26.9 ± 2.1	0
LSCBM2		22.4 ± 1.8	19.7 ± 1.0	31.8 ± 2.4	22.0 ± 2.3	35.2 ± 2.7	0
LSCBM3		18.1 ± 1.4	17.5 ± 1.1	19.9 ± 1.6	25.8 ± 3.4	23.3 ± 1.7	0
Low		18.1	16.4	19.9	21.0	23.3	0
High		66.4	44.4	70.5	52.5	69.1	21.1
Mean		40.0	31.7	46.7	32.2	48.2	3.8
STD		17.6	11.5	18.0	10.9	16.9	7.8
Combined		—	—	—	—	—	—
Mean		34.9	31.3	42.8	29.7	43.9	15.7
STD		13.2	9.4	16.3	9.6	16.3	16.9

Table 6  
 Partial correlation coefficients and multiple correlation coefficients ( $R^2$ ) for variables and discrete radionuclides and ratios. Subscripts denote significances ( $p \leq 0.05$ ).

Isotope/Ratio	Variable Mn	Fe	Al	Organic carbon	% Fines	$R^2$
Overall ( $n = 20$ )						
$^{226}\text{Ra}$	0.29	-0.37	-0.06	0.02	$0.65_{0.006}$	$0.69_{0.003}$
$^{228}\text{Ra}$	0.20	-0.10	0.23	0.09	0.43	$0.61_{0.014}$
$^{230}\text{Th}$	$0.61_{0.012}$	-0.18	0.07	-0.36	$0.58_{0.020}$	$0.73_{0.001}$
$^{232}\text{Th}$	$0.50_{0.048}$	0.31	-0.09	-0.19	$0.55_{0.027}$	$0.71_{0.002}$
$^{228}\text{Th}$	$0.51_{0.044}$	0.36	-0.03	-0.16	$0.53_{0.037}$	$0.73_{0.001}$
$^{210}\text{Pb}_{\text{ss}}$	-0.24	0.40	-0.40	$0.64_{0.007}$	0.28	0.50
$^{226}\text{Ra}/^{230}\text{Th}$	-0.35	-0.18	-0.16	$0.54_{0.030}$	0.03	0.50
$^{226}\text{Ra}/^{232}\text{Th}$	-0.27	-0.33	-0.11	0.24	0.11	0.45
$^{230}\text{Th}/^{232}\text{Th}$	0.10	-0.46	0.10	-0.37	0.13	0.40

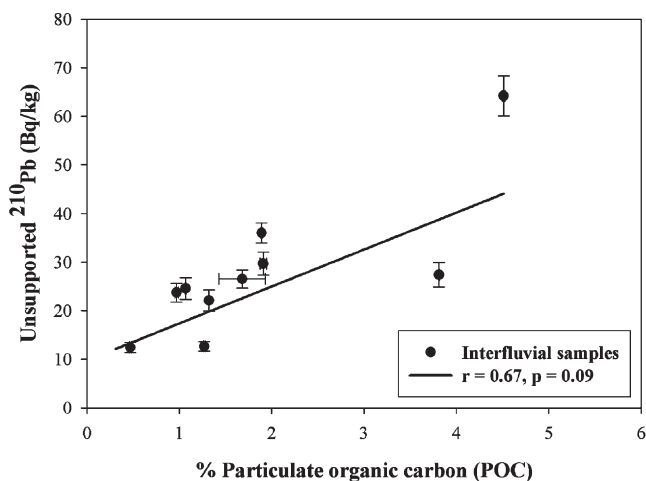


Fig. 3. Linear correlation between  $^{210}\text{Pb}_{\text{xs}}$  and POC for interfluvial samples.

ratios. For the considered ratios,  $R^2$  values drop considerably as compared to the same for discrete radionuclides, indicating that less variance in observed isotope ratios is accounted for by the model. Also, a  $p$  value of less than 0.05 for the change in  $F$  is not found for any of the tested ratios, indicating that variation accounted for by the model may be due to chance and not a causal relationship. The enhanced conservancy of isotope ratios is made even clearer by examination of the partial correlation coefficients and their significances. The influence of Mn and % fines drop precipitously when comparing the results for discrete isotopes versus isotope ratios and none are significant ( $p \leq 0.05$ ). Surprisingly, the only significant partial correlation (+) is found when considering  $^{226}\text{Ra}/^{230}\text{Th}$  data with POC, indicating that the influence of POC may need to be researched further.

The strong affinity of POC for discrete Ra isotopes espoused by [Nathwani and Phillips \(1979\)](#) is not supported by these results. Strong positive partial correlations between discrete radionuclides (except  $^{210}\text{Pb}_{\text{xs}}$ ) and % fines are in agreement with data presented by [Megumi et al. \(1982\)](#), among others. The importance of Mn oxides for adsorbing Th isotopes is apparent here, as proposed by [Buessler et al. \(1992\)](#), but Ra isotopes at ambient levels are not observed to be significantly adsorbed by Mn oxides, as proposed by [Baskaran et al. \(1993\)](#). A significant partial correlation between POC and the isotope ratio  $^{226}\text{Ra}/^{230}\text{Th}$  was observed and is in agreement with data presented by [Lozano et al. \(2002\)](#), suggesting that the role of POC in regulating isotope concentrations requires further attention. This contention is further supported by the significant positive partial correlation observed between POC and  $^{210}\text{Pb}_{\text{xs}}$ , which is in agreement with marine data presented by [Paulsen et al. \(1999\)](#). [Lozano et al. \(2002\)](#) presented strong negative correlations between  $^{226}\text{Ra}/^{230}\text{Th}$  and Mn and Fe concentrations, a finding that is not supported herein. It should be noted that in [Lozano et al. \(2002\)](#), impacted sites located downstream of a uranium mineralized zone, were compared to one “background” or ambient site. It is possible that

while Lozano et al. (2002) did not report correlations for any discrete radionuclide concentrations and only reported two radionuclide ratios ( $^{230}\text{Th}/^{234}\text{U}$  and  $^{226}\text{Ra}/^{230}\text{Th}$ ) versus metals or other variables, significant relations among other variables were not observed. The data herein represent ambient radionuclide activities and their corresponding ratios, as related to other variables, which have been reported previously to interact and influence partitioning, fate and mobility of radionuclides in the environment.

## 5. Summary and recommendations

Ambient lithogenic ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{232}\text{Th}$ ) and fallout ( $^{210}\text{Pb}_{\text{xs}}$ ) radionuclide concentrations were determined for sediment samples collected from upland interfluvial and river channel sources within a small, managed watershed in east Texas. Ancillary variables were determined for these sediments, including total and triplicate leachate fractions of Al, Mn and Fe, % fines (< 63  $\mu\text{m}$ ) and POC. Statistical analyses of compositional variables (total metals, POC and % fines) combined with leachate data (metal speciation) suggest that the two sample populations are very similar, and they are therefore considered as one population. Strong, positive partial correlations were observed between discrete Th isotopes and total Mn and between discrete Ra and Th isotopes and % fines. Overall, application of isotope ratios seems to effectively and significantly reduce these influences, lending support to the contention that isotope ratios are an effective way to mitigate extrinsic variability in terrestrial sediments and hence support their use as source tracers for sediment (e.g. Murray et al., 1990; Murray et al., 1991; Olley et al., 1993, 1997; Yeager et al., 2002). Strong associations of POC with both  $^{226}\text{Ra}/^{230}\text{Th}$  and  $^{210}\text{Pb}_{\text{xs}}$  are in agreement with data presented elsewhere (Lozano et al., 2002 and Paulsen et al., 1999, respectively) indicating that even at ambient levels, the role of POC with respect to isotope fractionation, mobility or sequestration should be further investigated.

These results support the tenet of general conservancy of these radionuclides in the environment at ambient levels and in particular, support the use of isotope ratios to reduce the influence of extrinsic variability. The degree to which extrinsic variables effect radionuclide concentrations and their resultant ratios is a major question of those who seek to employ these radionuclides quantitatively. Further research, specifically to investigate the relations between POC and radionuclides in varied environments and statistical analyses of a larger population of samples, examining these variables and perhaps others (Ca,  $\text{SO}_4$ ,  $\text{PO}_4$ ) and how they interact with natural radionuclides is strongly encouraged.

## Acknowledgements

Funding provided by the Texas Water Development Board, Texas Water Resources Institute, Geological Society of America, The Gulf Coast Association of

Geological Sciences, Texas A&M University and the Texas Institute of Oceanography is gratefully acknowledged. Cooperation of numerous landowners in allowing access to field sites is also appreciated. Thanks are also extended to Mr. Chris Courtney for assisting in both field and laboratory work and Ms. M. Michaele Cerf for laboratory assistance and to the three anonymous reviewers for contributing to the improvement of this manuscript.

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