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Elemental signature of terrigenous sediment runoff as recorded in coastal salt ponds: US Virgin Islands

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ABSTRACT

A high-resolution, multi-proxy approach is utilized on mm- to cm-scale laminated coastal salt pond sediments from St. John, U.S. Virgin Islands, to determine: (1) the sedimentological signature of depositional events/processes, (2) link this sedimentological signature with known depositional events/processes in the historical (past ~100 years) record; and, (3) project back into the recent geologic past (past ~1400 years) to investigate the natural variability of depositional events/processes. High-resolution, short-lived radioisotope geochronology (^{210}Pb, ^{137}Cs, ^{7}Be) combined with high-resolution elemental scanning techniques (scanning XRF and scanning LA-ICP-MS) allows for the direct comparison of well-preserved salt pond deposits to historical records of depositional events (e.g., runoff/rainfall, tropical cyclones, tsunamis) to identify the sedimentary signature of each type of event. There is a robust sedimentary record of terrigenous sediment runoff linked to the frequency of rainfall events that exceed a threshold of ~12 mm/day (minimum to mobilize and transport sediment) for study sites. This is manifested in the sedimentary record as increases in terrigenous indicator elements (%Al, %Fe, %Ti, %Si), which agree well with rainfall records over the past ~50 years. Variability in the sedimentary record over the past ~100 years reflects decadal-scale fluctuations between periods of increased frequency of rainfall events, and decreased frequency of rainfall events. Dm-scale variability in terrigenous indicator elements over the past ~1400 years represents the natural system variability on a decadal–centennial scale, and provides a high-resolution, long-term baseline of natural variability of rainfall/runoff events. A period of increased terrigenous sediment delivery during the 1700s and 1800s likely indicates increased erosion in response to anthropogenic activities associated with the island's plantation era, and perhaps increased frequency of rainfall events.

1. Introduction

Sedimentation from island runoff has been found to be one of the greatest concerns for near-shore marine environments of mountainous tropical islands (Gray et al., 2012; Gardner et al., 2003; Nemeth and Nowlis, 2001; Rawlins et al., 1998; Rogers, 1990). High-relief tropical volcanic islands, such as St. John, U.S. Virgin Islands (USVI), are naturally susceptible to terrigenous (land-derived) sediment weathering, erosion, and rapid down-slope transport to coastal environments during rainfall events. The ultimate fate of these sediments include: (1) deposition within the watershed; (2) coastal buffer zones such as salt ponds, which trap sediments and prevent input into the marine environment; (3) nearshore marine environments (coral reefs, seagrasses, algal flats), many of which are adversely affected by terrigenous sedimentation (Begin et al., 2014; Yates et al., 2014; Brooks et al., 2007; Ralph et al., 2007; Rogers et al., 2007; Thomas and Devine, 2005); and, (4) offshore marine environments. Terrigenous sediment delivery to the coast is magnified in areas where human activities have altered land uses such as removing vegetation, exposing rocks and soils and creating impermeable surfaces (e.g., road and building

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construction) (Brooks et al., 2007; Ramos-Scharrón and MacDonald, 2005; and Brooks et al., 2004). Long term monitoring programs investigating rainfall and associated sediment runoff can be challenging with different approaches having differences in temporal resolution. Rainfall events are often irregular and brief in duration requiring opportunistic field collections or long-term stream gauge stations to measure sediment runoff from the watershed (MacDonald et al., 1997). These methods provide useful information on specific events and data for the past decade. Historical rainfall records are generally short (decades), discontinuous, and geographically limited. Archives such as sediment cores can be directly compared to historical records for the past ~50 years to develop proxies for runoff events, which can provide insight into variability beyond the time-frame of historical databases (Begin et al., 2014; Brooks et al., 2004). This is important as runoff likely varies on multiple time-scales. This approach requires an understanding of the terrigenous sediment dynamics, depositional processes and how these processes are preserved in the sedimentary record for tropical island settings such as the USVI.

1.1. Setting

The USVI are located in the northeastern Caribbean Sea, comprising the eastward extent of the Greater Antilles island arc system. Formed by volcanic activity during the Early and Late Cretaceous, the island of St. John is generally rugged with 80% of the slopes exceeding 30° (Rankin, 2002) (Fig. 1). Flatlands are confined to small, isolated coastal embayments (Graves, 1996). The island can be divided into a series of watersheds, with ephemeral drainage channels, locally know as “ghuts”. Following a rainfall event, sediment-laden water is quickly transported downslope and delivered to the coastal system. Ghuts are only active after a rainfall event and are the primary mechanism to transport water/sediment down-slope, as there are no perennial rivers or streams on St. John. Consequently, the ghut system is either turned on or turned off, which leads to event driven deposition, and may be common for small mountainous islands. The combination of steep topography, moist tropical climate, and unstable volcanic rocks, contribute to the island’s high susceptibility to sediment erosion and runoff (WRI

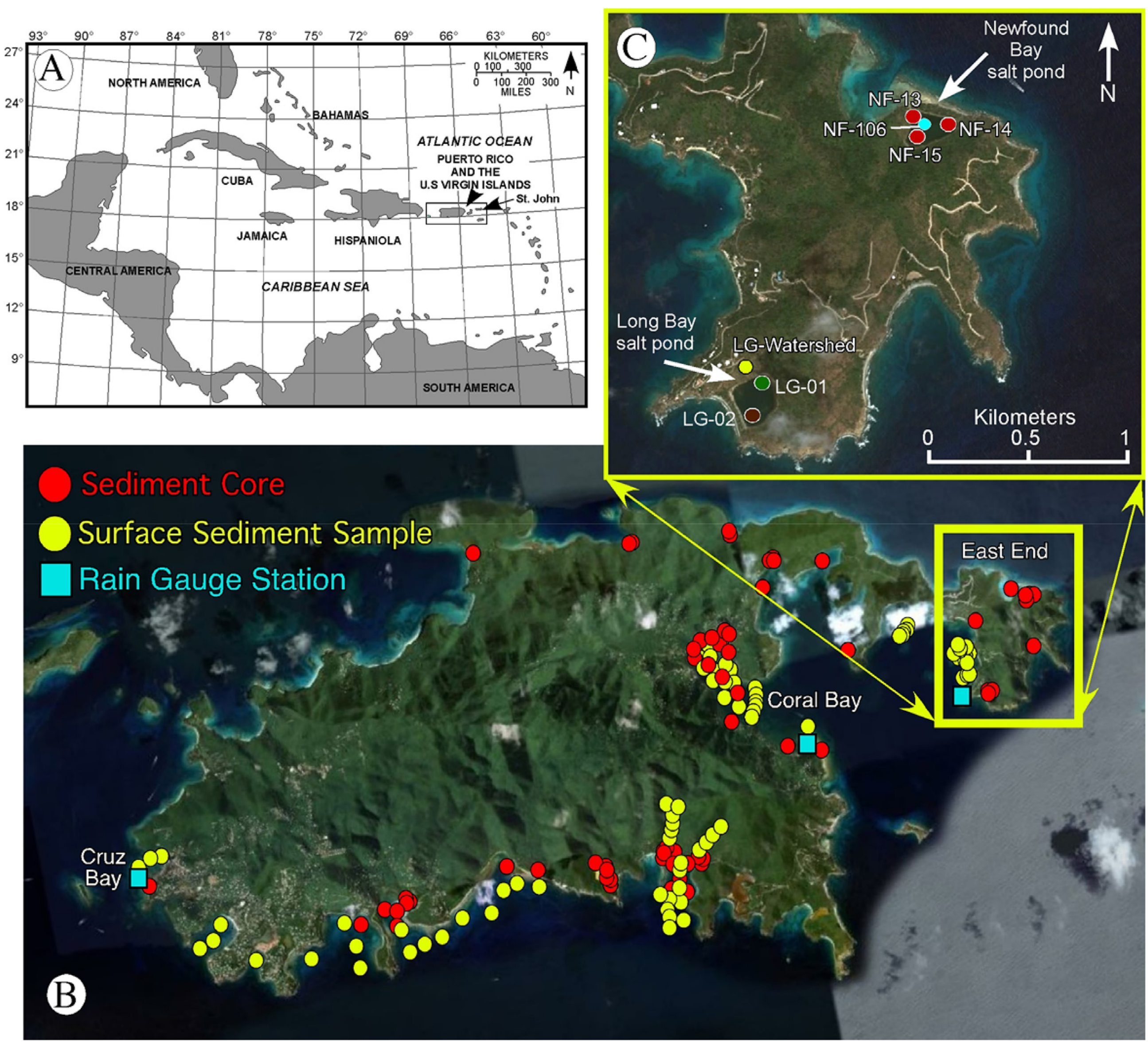

Fig. 1. (A) Location Map of US Virgin Islands in the Caribbean Basin. (B) Satellite image (2003) of St. John, US Virgin Islands showing sediment sampling sites and rain gauge stations throughout the island (modified from Brooks et al., 2004). (C) Satellite Map of East End St. John, showing sampling sites in Newfound and Long Bay salt ponds and watersheds.

and NOAA, 2005).

The USVI climate is considered maritime tropical with most rainfall occurring as short duration events. The seasonal cycle is dominated by variations in rainfall frequency and intensity, as well as wind direction and intensity. Dry conditions occur December–April with easterly tradewinds strongest between December and February. This is followed by an early, weak, wet season in May–June, followed by the mid-summer drought in July–August. The mid-summer drought is theorized to be due to an intensification of the North Atlantic Subtropical High Pressure Cell (NAHP) leading to stronger trade winds and decreased sea surface temperatures (SST), which increases the subsidence of air masses and decreased rainfall in the Caribbean region (Gamble and Curtis, 2008). A more pronounced wet season occurs between September and November (Gamble and Curtis, 2008). Gradients in sea level pressure across tropical latitudes between the Atlantic and Pacific basins exerts a strong influence on rainfall during the late wet season (September–November) and early dry season (December–February). Wet (dry) conditions occur in the Caribbean when the North Atlantic and/or equatorial Atlantic are warm (cool) and the Pacific is cool (warm), and it is under these conditions that the Caribbean has the most pronounced response to El Nino Southern Oscillation (ENSO) (Enfield and Alfaro, 1999). The majority of rainfall is associated with tropical cyclones and cold fronts with rainfall generally increasing with increasing elevation and the east end of St. John being the driest area (Acevedo-Rodriguez et al., 1996).

1.2. Coastal salt ponds

Coastal salt ponds are natural sediment traps for terrigenous runoff and many contain mm- to cm-scale laminated sediment records (Fig. 2). The study sites, Newfound Bay and Long Bay salt ponds, located on the east end of St. John (Fig. 1), are separated from the marine environment by 1–3 m high berms surficially covered by large coral fragments that are cemented together to create a permanent barrier. One theory of salt pond formation involves reefal growth from the headlands across the opening of an embayment, and constriction of the opening. Eventual closure of the opening of the embayment and formation of the berm by rubble deposition, potentially by storms, lead to the isolation of the pond from marine influences and increased terrigenous sediment accumulation (Brooks et al., 2004). Newfound and Long Bay salt pond cores support this hypothesis as they exhibit a basal gravelly-sand unit, containing large amounts of carbonate material including whole shells and coral fragments, which is reflective of higher marine influence and is similar to surficial sediments in the adjacent embayment that is currently open to the sea (Fig. 1). This marine unit is overlain by a sharp transition to laminated salt pond sediments (Fig. 2) (Brooks et al., 2004). The watersheds draining to these ponds are relatively small for St. John, with steep slopes and terrigenous sediment delivery focused at the base of ghuts and adjacent to hillslopes. There are no modern human activities in the Newfound Bay watershed (past ~100 yrs) and there is a single paved road with a few private homes on the northwest side of the Long Bay watershed (Fig. 1). Cores in Long Bay salt pond were collected from the south and east sides of the salt pond where there are no homes or roads in the upslope hills and ghuts.

Sediment sources to ponds include: (1) terrigenous sediment runoff associated with rainfall events, (2) marine overwash associated with tropical cyclones and/or tsunamis, (3) atmospheric dust input (African dust/volcanic ash), and (4) in-situ organic production (Fig. 3). Salt ponds often have little to no animal life (no bioturbation) and can have microbial and/or algal forming mats on the sediment surface. Hence, mm- to cm-scale laminated sediments represent a high-resolution, well-preserved sediment archive of depositional events (terrigenous runoff, marine overwash).

High-resolution elemental scanning techniques measure the variability in sediment composition of mm- to cm-scale laminae. Elemental composition identifies the signature of sediment sources (terrigenous, marine) and provides insight into depositional processes (runoff, overwash) and how they vary over time. High-resolution elemental scans measuring sediment signatures of laminated sediment records combined with short-lived radioisotope age dating allows for the direct comparison of sediment records of depositional events with historical rainfall, tropical cyclone and tsunami data. Once a signature is linked to a depositional event(s) longer-term sediment records (i.e. down core) can be investigated to define natural patterns of event variability (rainfall, tropical cyclones, tsunamis) and provide a baseline to determine deviations from the natural development of the coastal system that may be attributed to human activities.

2. Methods

A multi-proxy approach is utilized on mm- to cm-scale laminated sediment records from St. John, USVI coastal salt ponds to define the sedimentary signature of depositional events (rainfall, tropical cyclones, tsunamis). Short-lived radioisotope (SLR) geochronology (^{210}Pb, ^{137}Cs, ^{7}Be) is combined with high-resolution scanning elemental techniques (XRF and LA-ICP-MS) for direct comparison of sediment records to historical records of depositional events.

Two watershed surficial sediment samples and five sediment cores from two salt ponds (Newfound Bay, and Long Bay salt ponds) were collected on the east end of St. John, with multiple core sites in each pond (Fig. 1). Surface sediment samples (LG-watershed) were collected in the Long Bay watershed for characterization of the terrigenous sediment source. At each salt pond core site location a 3″ diameter aluminum and a 4″ diameter acrylic push core were collected. Aluminum cores were split longitudinally photographed, described, X-rayed, and sampled for ^{14}C age dating, as well as scanning XRF (X-ray Fluorescence) and scanning LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). Four-inch diameter acrylic companion cores were extruded and subsampled at 0.5 cm intervals for SLR geochronology and sediment texture/composition.

2.2. Texture and composition

Bulk density (g/cm^3) measurements were determined at 0.5 cm resolution on extruded core samples. Bulk density was combined with age dating to calculate mass accumulation rates (MAR). Analyses for bulk composition for extruded samples included carbonate content, total organic matter (%TOM) and terrigenous content (all non-carbonate and inorganic). Carbonate content was determined by the acid leaching method according to Milliman (1974). TOM was determined by loss on ignition (LOI) at 550 °C for at least 2.5 h (Dean, 1974). Sediment texture (grain size) was determined by initially wet sieving the sample through a 63 μm screen. The sand-size (>63 μm) fraction was then analyzed by settling tube (Gibbs, 1974) and the fine-size (<63 μm) fraction was determined by pipette (Folk, 1965) to determine %silt/%clay.

2.3. Elemental analysis

Samples from Long Bay salt pond cores LG-01, LG-02, and LG-watershed surface sediment samples (Fig. 1) were analyzed by solution ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for elemental composition. Digestions followed EPA method 305B for

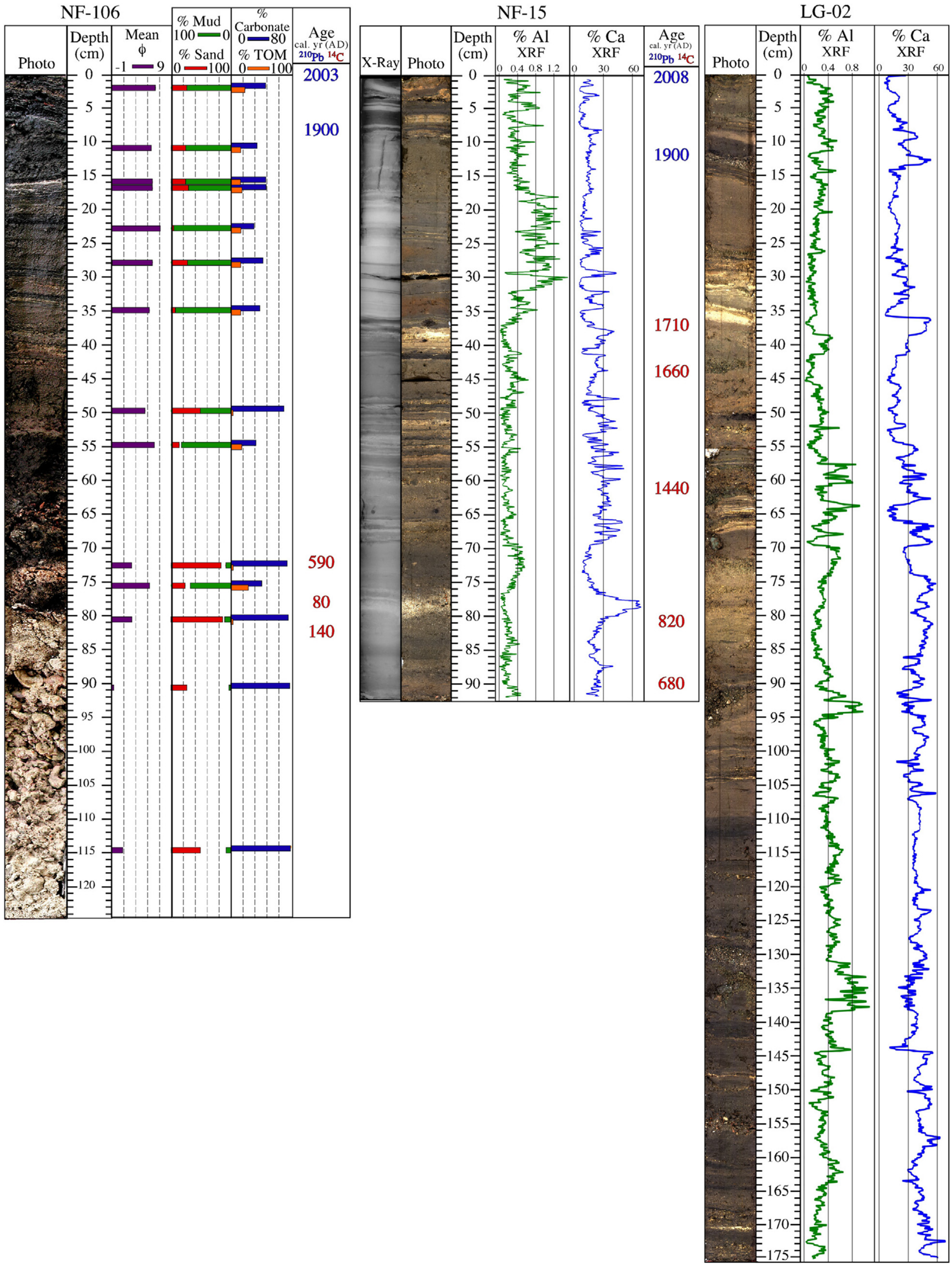

Fig. 2. Cores collected in Newfound and Long Bay salt ponds showing variability in sediment types expressed as mm- to cm-scale laminations in photographs and X-radiographs. Variability in sediment composition as shown by scanning XRF data indicative of sediment source, increased %Al – terrigenous, increased %Ca – marine. Age dating using ^{210}Pb and ^{14}C provide age constraint and timing of sedimentation.

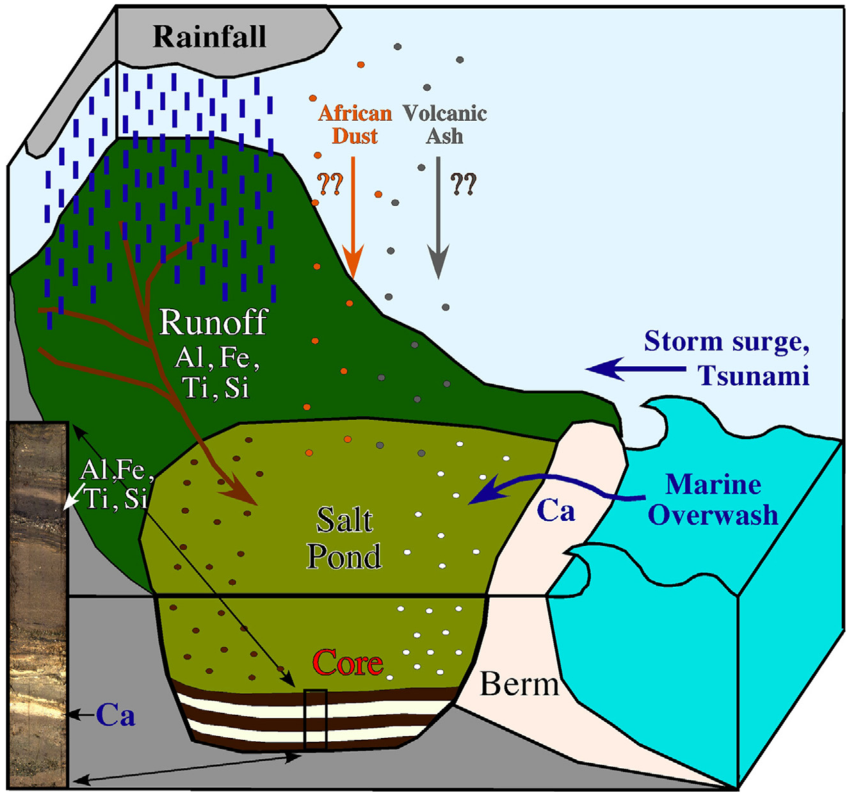

Fig. 3. Conceptual model of sediment sources and their sedimentological signature, as well as depositional processes/events controlling variability in sediments accumulating in salt ponds.

acid digestion of sediments, sludges and soils (EPA, 1996), and included hydrogen peroxide and nitric acid digestions. A blank sample was prepared following the same steps with no sediment. Samples were diluted to 1/20 concentration and internal standards of 10 ppb of Be, Sc, In, and Bi were added. Scandium was measured in the samples prior to addition of the internal standards, therefore, not used as an internal standard for data processing. Samples were semi-quantitatively analyzed on an Agilent ICP-MS in no-gas mode, as well as gas mode (He) for certain elements. A tuning solution of 1 ppb of Y, Li, Tl, Ce, Co and Mg was used to tune the instrument for analysis in gas mode. Data were processed to remove internal standard data and subtraction of values from the analysis of the blank sample from sample data.

Scanning XRF was utilized to determine the elemental composition of the entire core at mm-scale resolution. Analysis was performed at the Royal Netherlands Institute for Sea Research (NIOZ) laboratory in collaboration with the University of Utrecht (The Netherlands) on an Avaatec XRF Core-Scanner with a 1 cm-wide slit by 1 mm window at 1 mm sampling resolution at 10 keV for Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, and Rh. Whole sediment cores were covered with a thin film transparent to X-rays to prevent sediment from sticking to the device and prevent the core from drying out. The chamber was flushed with He to provide more accurate measurements of light elements (Tjallingii et al., 2007). Data were acquired using Avaatech software providing elemental counts per second. Counts per second for each element were recorded and divided by the total counts to determine % of each element.

Scanning LA-ICP-MS analysis was performed at the University of Utrecht for elemental analysis on the micron-scale. The sediment core was sub-sampled in 1 cm-wide by 4 cm-long (down core) sections with ~1 cm overlap between sections. Sections were placed in the ablation chamber mounted on a microscope stage with two standards (Nist 610 and Nist 612). Analysis was performed on a Micromass Platform ICP-MS with a hexapole collision cell (hydrogen) with a Geolas 193 nm excimer laser ablation system. A hydrogen argon gas mixture was used as a carrier gas to the ICP-MS. A 120-micron diameter window (largest possible) was used for the laser to minimize the ablation of individual grains. Laser ablation scanning was achieved by the steady, continuous movement of the microscope stage/ablation chamber along core sections, running the section through the laser beam while the laser was continuously focused. Each section was scanned twice to determine reproducibility and scans were averaged together. Standards were ablated before and after scans to determine instrument precision and efficiency (Jilbert et al., 2010) and were utilized to determine the fractionation/ionization efficiency (ion counts/ppm) during ablation for each element measured with relation to ^{44}Ca. All scan data were corrected for background values of each element due to the carrier gas, the fractionation/ionization efficiency of each element, and for the natural abundance of each element at the mass measured. Counts for each element were divided by the total ion counts to determine % of each element.

2.4. Geochronology

Short-lived radioisotope geochronology was developed at 0.5 cm resolution (extruded cores) for excess ^{210}Pb, ^{137}Cs and ^{7}Be. Samples were run on a GWL Series HPGe (High-Purity Germanium) Coaxial Well Photon Detector for total ^{210}Pb (46.5 keV), ^{214}Pb (295 keV and 351 keV), ^{214}Bi (609 keV), ^{137}Cs (661 keV), and ^{7}Be (447 keV) activities. Data were corrected for counting time, detector efficiency and geometry, as well as for the fraction of the total radioisotope measured yielding activity in dpm/g (disintegrations per minute per gram). Detector efficiency was determined using similar methods to Kitto (1991) using the IAEA RGU-1 standard. A calibration template was produced relating the counts measured to the known activity of the standard for the range of sample weights. The calibration template was validated using the IAEA-447 organic standard, which has a similar density/composition as the sediment analyzed in this study. By using the calibration template for various weights, self-absorption of the sample is included in the detector efficiency calculations.

Cesium-137 is a thermonuclear byproduct and represents the period of greatest atomic bomb testing in the early-mid 1960s (Olsson, 1986). Berillium-7 has a very short half-life (~53 days) and is an indicator of recent sediment deposition (~1 yr) and preservation of the core top. Excess ^{210}Pb ($t_{1/2}$ ~ 22.3 years) is used for dating over the last ~100 years. The activities of ^{214}Pb (295 keV), ^{214}Pb (351 keV), and ^{214}Bi (609 keV) were averaged as a proxy for the ^{226}Ra activity of the sample or background ^{210}Pb. Background ^{210}Pb was subtracted from total ^{210}Pb to determine excess ^{210}Pb (Holmes, 2001). Excess ^{210}Pb data were input into the constant rate of supply (CRS) model to provide dating of each sample analyzed within the last ~100 years (Appleby and Oldfield, 1983; Binford, 1990). This was compared to ^{137}Cs data, an independent dating technique, to determine how well the CRS model was performing. MAR (g/cm^2/yr) were calculated for each data point (i.e. date) produced by the CRS model. The use of MAR corrects for differential sediment compaction down core, thereby enabling a direct comparison of ^{210}Pb accumulation rates throughout the core (i.e., over the last ~100 years).

Carbon-14 age dating was performed on six samples from NF-15 and three samples from NF-106 Newfound Bay salt pond sediment cores by Beta Analytic Inc., to provide temporal constraints on sediment deposition. The bulk organic sediment sample underwent acid (HCl) washes to ensure the absence of carbonate material. Wood material was pretreated with an acid/alkali/acid treatment to eliminate carbonates and remove secondary organic acids (Table 1). Carbonate shell material was pretreated using an acid etch technique to eliminate secondary carbonate material. Carbonate shells were corrected using appropriate local reservoir corrections using MARINE04 and calibrated to calendar years (IntCal04, 2004; Talma and Vogel, 1993).

2.5. Historical data

Daily, monthly, and yearly rainfall records were obtained from NOAA National Climatic Data Center (NCDC, 2009). Data were recorded at a rain gauge site at the east end of St. John, with secondary sites in Coral Bay and Cruz Bay, St. John to create a compiled daily rainfall record between 1957 and 2009 (Fig. 1).

3. Results/discussion

Sediment records in Newfound Bay and Long Bay salt ponds are comprised of mm- to cm-scale laminations that vary in color, density and sediment composition. High-resolution color digital photography and core X-radiographs show strong evidence for stratigraphic integrity of cores (Fig. 2), and laminations represent a variety of sediment types and sources. In general, laminations consist of alternating layers of: (1) dark, fine-grained terrigenous clastic; (2) light, coarse-grained marine biogenic carbonates; and, (3) fibrous, organic-rich muds (Fig. 2). Terrigenous clastic units are interpreted to represent input from the adjacent watershed during rainfall/runoff events and are the focus of this article. Newfound salt pond core NF-15 was collected from the watershed side of the pond and closest to the input of terrigenous sediment and represents a higher resolution record of terrigenous sediment delivery (Fig. 1). This is reflected in the increased accumulation rates in NF-15 as compared to NF-13 and NF-14. Carbonate-rich units are likely deposited by marine overwash events associated with tropical cyclones or tsunamis. Organic-rich layers represent microbial mat growth on the salt pond floor during non-deposition conditions. The salt ponds are floored with these microbial mats, which likely account for the excellent preservation of the underlying stratigraphy. Comparison of dm-scale stratigraphic units in all five cores from Newfound and Long salt ponds suggests some similarity in the sequence of units, but additional age dating of cores is required to determine if depositional units are synchronous due to the variability in accumulation rates between ponds and within ponds.

3.1. Rainfall/runoff sedimentological signature

The elemental composition of mafic/volcanic rocks is dominantly O, Si, Al, Fe, Ca, Na, K, and Mg with smaller amounts of Ti (Spock, 1953). Elemental analysis of sediment samples collected from the hillsides of the Long Bay watershed, LG-watershed, are dominated by Al, Fe, Si, and Ti (Fig. 4), implying these elements may be considered indicators of a terrigenous sediment source. However, the 0.5 cm interval sub-samples from extruded companion cores for LG-01 and LG-02 showed visible Al contamination (likely from the core barrels), and solution ICP-MS Al data seem unreasonably high. Hence, Al data are discarded for extruded samples from LG-01 and LG-02. No signs of Al contamination were present in the cores used for elemental scanning, therefore Al scans are deemed valid. ^{7}Be profiles of two cores from Long Bay salt pond (LG-01 and LG-02) collected at the end of the main wet season (September–November) in November 2009 show significant recent deposition, with measurable ^{7}Be activities in the upper 2 cm (4

Table 1
Radiocarbon ages and associated data (pMC = post modern carbon, RCYBP = radiocarbon years before present with present = 1950, BP = before present).

Core ID	Depth (cm)	AMS/ standard radiometric	Material: pretreatment	Measured age (RCYBP)	^{13}C/^{12}C (ppt)	Conventional age	2 Sigma calibration
NF-106	72	AMS	Shell: acid etch	1480 ± 40 BP	−3.9	1830 ± 40 BP	Cal AD 490 to 660 (Cal BP 1460 to 1290)
NF-106	78	AMS	Organic: acid/alkali/acid	1900 ± 40 BP	−23.9	1920 ± 40 BP	Cal AD 10 to 150 (Cal BP 1940 to 1800)
NF-106	80	AMS	Shell: acid etch	1780 ± 40 BP	1.4	2210 ± 40 BP	Cal AD 60 to 240 (Cal BP 1890 to 1710)
NF-15	26–27	AMS	Organic: acid/alkali/acid	520 ± 30 BP	−22.8	560 ± 30 BP	Cal AD 1310 to 1360 (Cal BP 640 to 590), Cal AD 1390–1430 (Cal BP 560 to 520)
NF-15	36–37	AMS	Wood: acid/alkali/acid	70 ± 30 BP	−26.6	40 ± 30 BP	Cal AD 1710 to 1710 (Cal BP 240 to 240), Cal AD 1880 to 1910 (Cal BP 60 to 40), Cal AD 1950 to beyond 1960 (Cal BP 0 to 0)
NF-15	43–45	AMS	Wood: acid/alkali/acid	270 ± 30 BP	−28.1	220 ± 30 BP	Cal AD 1640 to 1680 (Cal BP 310 to 270), Cal AD 1740 to 1800 (Cal BP 210 to 150), Cal AD 1940 to 1950 (Cal BP 20 to 0)
NF-15	61–62	AMS	Shell: acid etch	590 ± 30 BP	−3.7	940 ± 30 BP	Cal AD 1340 to 1490 (Cal BP 610 to 460)
NF-15	78–81	AMS	Shell: acid etch	1230 ± 30 BP	−3	1590 ± 30 BP	Cal AD 710 to 960 (Cal BP 1240 to 1000)
NF-15	89–91	AMS	Shell: acid etch	1410 ± 30 BP	−4.6	1740 ± 30 BP	Cal AD 610 to 780 (Cal BP 1340 to 1170)

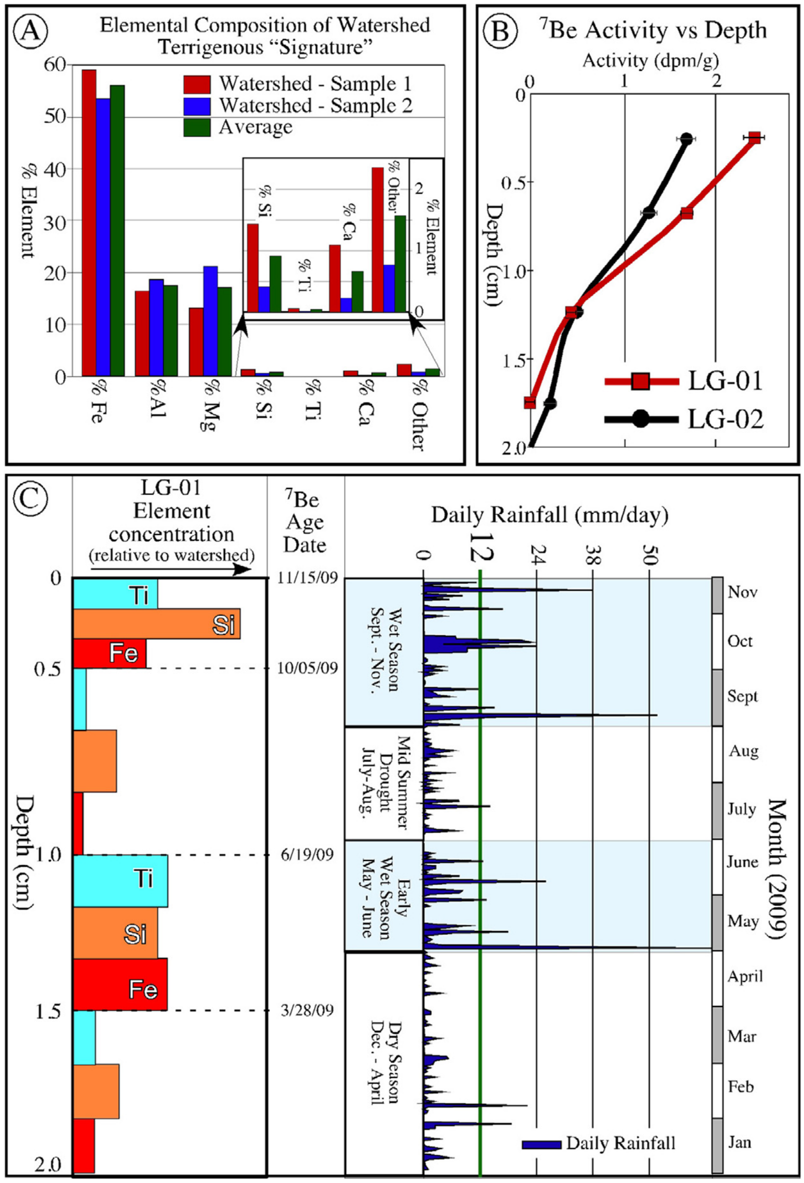

Fig. 4. (A) Elemental composition of watershed sediments showing dominance of Al, Fe, Si, and Ti (terrigenous signature). (B) Profiles of ^{7}Be from LG-01 and LG-02 indicating 2 cm (4 samples) of sediment accumulation over a ~1 year period in 2009. (C) Elemental composition of sediments accumulating in ~1 year period in 2009 compared to daily rainfall records. Green line at 12 mm/day in rainfall record denotes the rainfall threshold (minimum daily rainfall) required to transport terrigenous sediment downslope. Note increased terrigenous signature elements (Fe, Ti, Si) during periods of increased heavy (>12 mm/day threshold) rainfall events occurring in the two wet seasons of the year.

samples) of each core (Fig. 4). The high temporal resolution of the surficial 2 cm of these cores is likely due to the high pore water content and lack of compaction associate with recent deposition. Elemental analysis results for LG-01 show increased levels of terrigenous elements Fe, Si, and Ti during periods of increased frequency of heavy rainfall events (Fig. 4). Thus, a linkage is defined of elevated levels of terrigenous sediment source indicator elements in Long Bay salt pond sediments during periods of higher frequency of rainfall events (i.e., wet season vs. dry season). Accordingly, the elements Al (present in watershed samples), Fe, Si, and Ti will be considered here as the sedimentological signature of runoff from the adjacent island watershed into the coastal salt pond, and down-core variability of these elements will be considered to reflect changes in rainfall/runoff events. The presence of Si may also reflect biogenic silica (diatoms), but since it closely follows the variability of Fe and Ti, we believe it is dominantly attributed to terrigenous sediment. The berm separating the salt pond from the marine environment is primarily carbonate rubble with little to no quartz sands present, and marine sediments in the adjacent marine environments are dominantly carbonate (Brooks et al., 2007). Therefore, it is unlikely that significant amounts of quartz are associated with overwash deposits in this setting.

3.2. 100-year records – linking sedimentological signature, processes, historic events

Elemental composition over the past ~100 years can best be presented by scanning LA-ICP-MS and to a lesser extent scanning XRF results. Scanning LA-ICP-MS and scanning XRF analyses of salt pond cores revealed no Al contamination, and Al provides the most robust signature of terrigenous input (Figs. 5 and 6). Scanning LA-ICP-MS for Al, Fe, and Ti, as well as scanning XRF of Si, show similar patterns of variability indicating episodes of terrigenous sediment input/accumulation (Figs. 5 and 6). Although data are

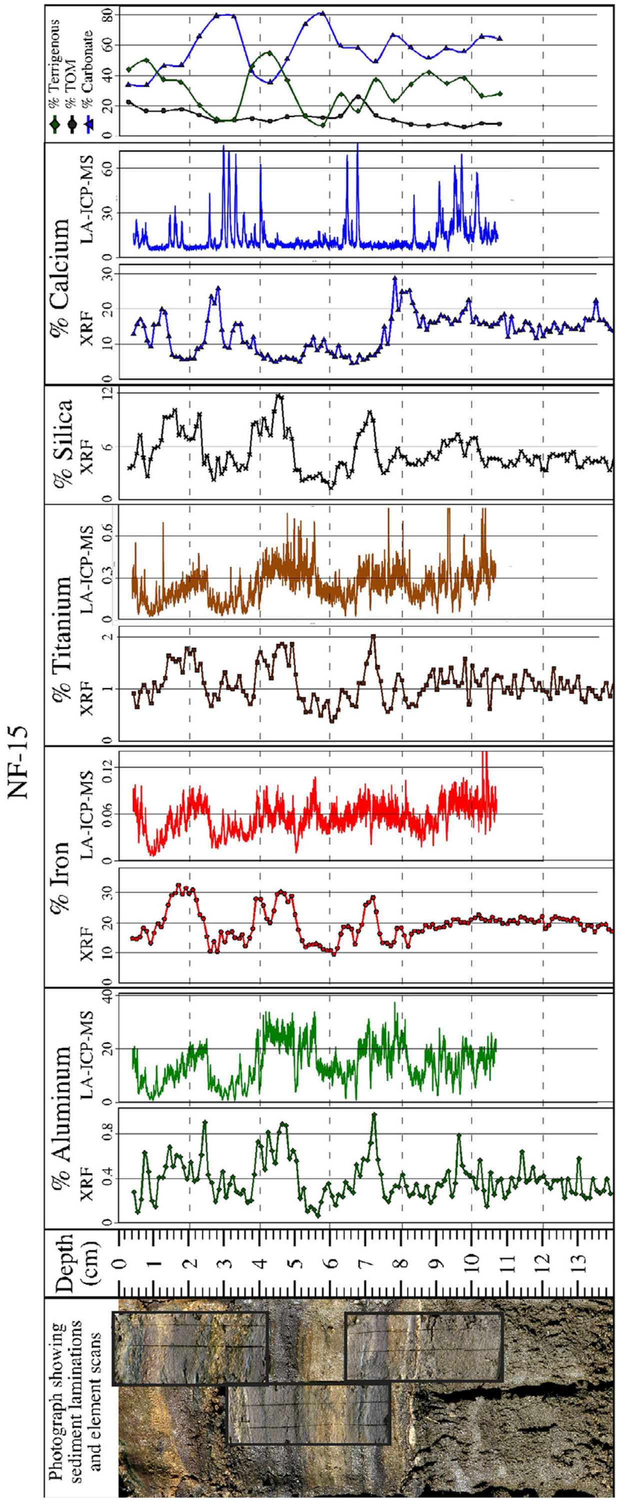

Fig. 5. Upper laminated unit of core NF-15 (Newfound Bay salt pond) with XRF and LA-ICP-MS scans for terrigenous signature elements (%A1, %Fe, %Ti, %Si) and marine signature element (%Ca). Note agreement in variability of terrigenous signature elements.

generally in good agreement, small-scale differences occur, which may be due to variability in watershed sediment composition and/or other inputs (e.g., African dust). Scanning LA-ICP-MS is useful for fine-grained sediments, but issues can arise with coarse-grained sediments as ablation of individual grains may dominate measurements.

This is a complicating factor in the analysis of Ca, as marine sediments are generally coarser, therefore scanning XRF may be a more appropriate technique where coarse grains are encountered (Figs. 5 and 6).

Scanning LA-ICP-MS and XRF analysis for Ca as an indicator of marine sediment source/overwash events is more convoluted than terrigenous sediment indicators. Tropical cyclones approach the island of St. John from a variety of directions and not all storms will create a marine overwash deposit in a single salt pond. Marine overwash deposits can also be caused by tsunamis leading to further complication of interpretation of processes controlling marine overwash events. Due to these complicating factors correlations of historical tropical cyclones as well as tsunamis with Ca elemental records are difficult and linkages between depositional processes and how they are manifested in the sediment record are not well defined. Further work is required to develop approaches for determining variability of tropical cyclone activity using sediment records from multiple sites in order to capture depositional events from cyclones with different trajectories.

Short-lived radioisotope (^{210}Pb, ^{137}Cs, ^{7}Be) analysis of the surficial laminated unit of cores NF-13, NF-14, NF-15 and LG-02 show the variability of sediment accumulation over the past ~100 years (Fig. 7). The presence of measurable ^{7}Be activity in the surface sample(s) reflects recent deposition and retention of the core surface. Lead-210 reaches background (no excess ^{210}Pb) at 7.25 cm in NF-13, 6.25 cm in NF-14, 13.75 cm depth in NF-15 and 10.25 in LG-02, and CRS model results provide age dates for each discrete sediment sample (0.5 cm intervals) with annual scale resolution (Fig. 7). The first occurrence and highest activity of ^{137}Cs occurs at 1957 in NF-13, 1952 in NF-14, 1954 in NF-15 and 1967 in LG-02 supporting the validity of the CRS age model (Fig. 7). Highly variable MAR (up to 10×) over the past ~100 years likely reflect pulsed sedimentation events, but no long term trend in accumulation patterns is evident (Fig. 7). This suggests that Newfound and Long Bay salt pond sedimentation has been dominated by depositional events for at least the past ~100 years.

Comparisons of Scanning LA-ICP-MS values for %Al with annual average rainfall records from 1957 to 2008 are inconclusive, but comparing the same %Al values with daily rainfall records provides insight into the frequency of rainfall events per year that mobilize and transport sediments to the salt ponds. Using linear regression analyses, a range of rainfall threshold values was compared with %Al to determine the best fit. For the Newfound and Long Bay salt pond study sites the minimum daily rainfall threshold ranges between 10 and 15 mm of rainfall/day with the best fit at ~12 mm of rainfall/day. Rainfall events that exceed this threshold are manifested in sediment records as increases in terrigenous signature elements (Al, Fe, Ti, Si) (Fig. 8). The 2009 seasonal record shows this relationship as well (Fig. 4). Thus, we hypothesize that a threshold (minimum in daily rainfall) is required to mobilize, transport, and deposit measurable terrigenous sediment laminae in coastal salt ponds. Other studies on St. John suggest different rainfall amounts to initiate sediment runoff. MacDonald et al. (2001) suggest sediment runoff from unpaved roads occurs when precipitation from a single storm exceeds 6 mm, which is different from our threshold value. There are multiple factors that may influence this difference. The rainfall data utilized in this study are daily rainfall rates vs individual storm amounts reported in MacDonald et al. (2001). MacDonald et al. (2001) specifically targeted unpaved roads, which have been shown to cause the greatest increase in runoff due to land use change (Ramos-Scharrón and MacDonald, 2005). Theoretically, anthropogenic land use change would lead to increased susceptibility to runoff and a decrease in the minimum rainfall threshold for a watershed. Also, the East End study area is the driest, least vegetated and most steeply sloped area of St. John and

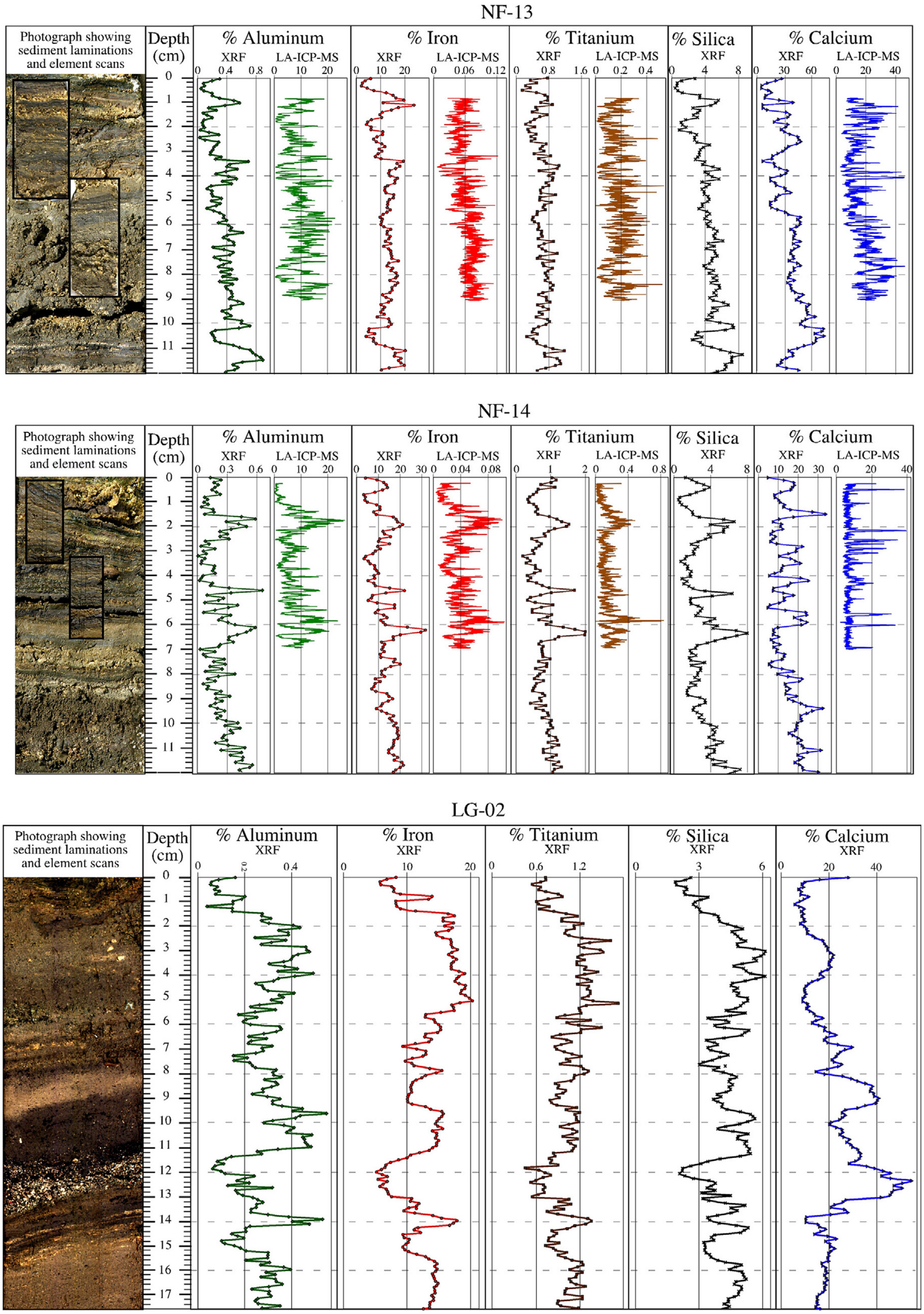

Fig. 6. Upper laminated units of cores NF-13, and NF-14 (Newfound Bay salt pond), and LG-02 (Long Bay salt pond) with XRF and LA-ICP-MS scans for terrigenous signature elements (%Al, %Fe, %Ti, %Si) and marine signature element (%Ca). Note agreement in variability of terrigenous signature elements in all cores.

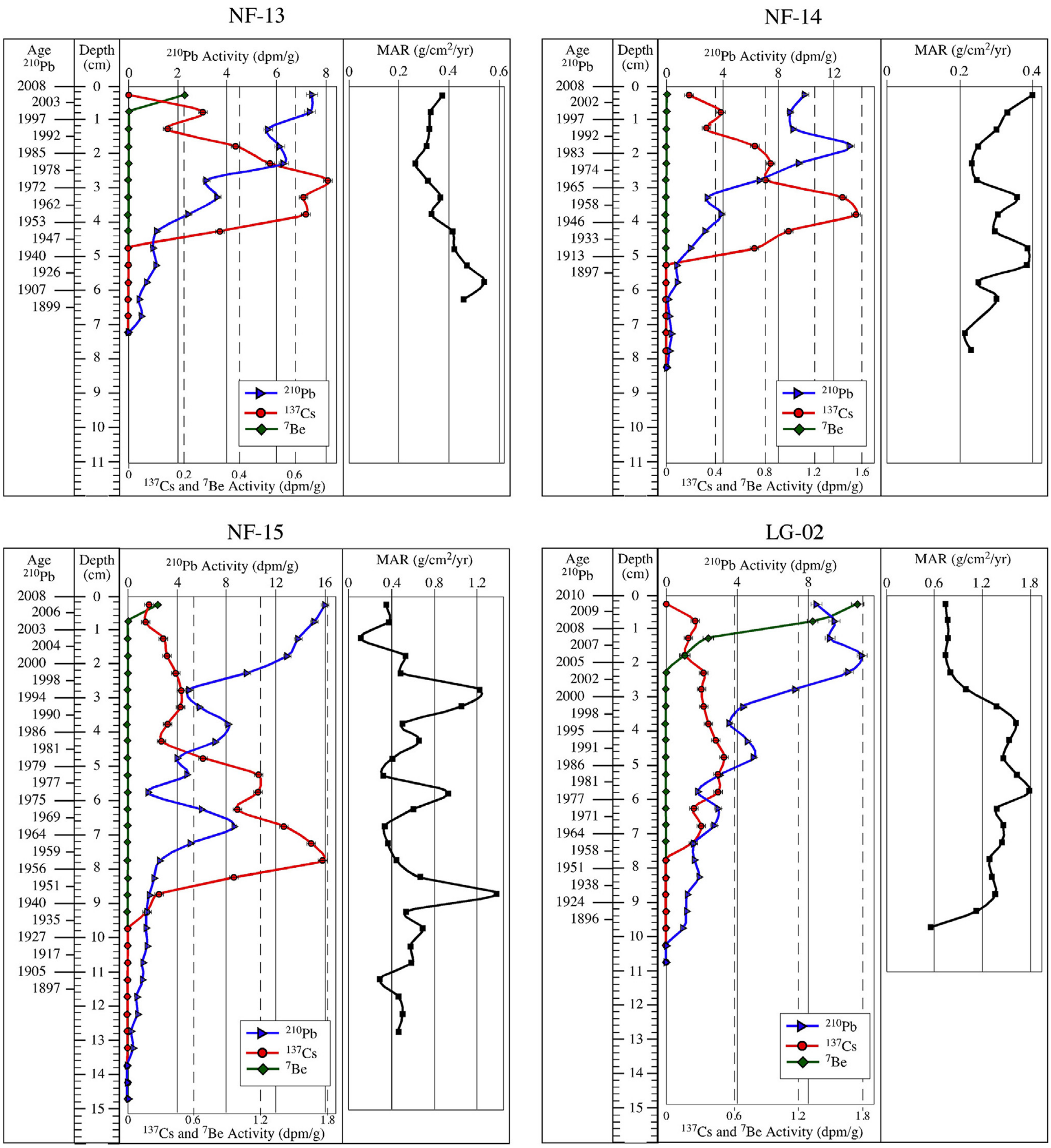

Fig. 7. Short-lived radioisotope profiles, MAR, and ^{210}Pb CRS age dating for NF-13, NF-14, NF-15 and LG-02. Note the first occurrences and/or highest activities of ^{137}Cs are present in the 1950s–1960s in all cores supporting ^{210}Pb CRS model results.

is naturally more susceptible to erosion and downslope transport. Additionally, the concentration of watershed runoff in salt ponds and measurement of fine-grained, mm-scale laminae allows for detection of smaller scale runoff events. All of these factors indicate that the high-resolution approach of this study in the East End salt ponds provide a sensitive proxy for rainfall/runoff. This also suggests that rainfall thresholds for terrigenous sediment delivery to coastal environments likely varies from watershed to watershed due to a variety of factors including watershed size and gradient, vegetation, sediment grain size, and anthropogenic land use change.

Combining elemental core scans with high-resolution SLR geochronology, and projecting down-core prior to 1957 (beginning of rainfall data collection), shows variability of %Al, %Fe, %Ti and %Si. Variability in these elements reflects periods of increased frequency of runoff/rainfall events, alternating with decreased frequency of rainfall/runoff events on a decadal scale over the past ~100 years (Fig. 8). The most complete record of terrigenous rainfall/runoff are likely NF-15 and LG-02 as they were collected in close proximity to sediment input and have higher sediment

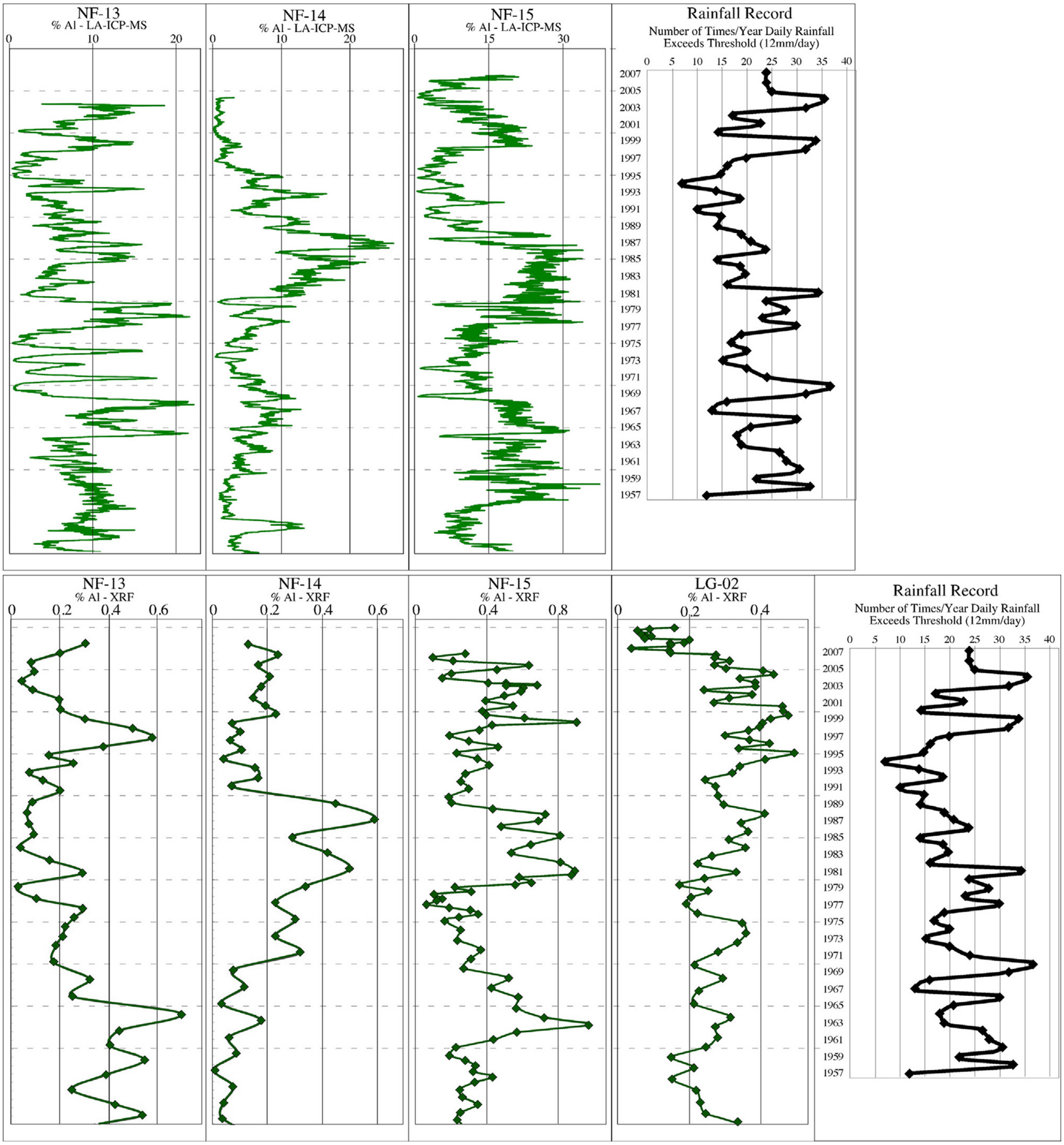

Fig. 8. XRF and LA-ICP-MS scans for %Al for NF-13, NF-14, NF-15 vs. ^{210}Pb CRS age dating to compare to historical rainfall records, which are represented as the number of times/year daily rainfall exceeded the 12 mm/day threshold for sediment erosion and downslope transport. Note increased (decreased) %Al during periods of increased (decreased) frequency of daily rainfall exceeding the 12 mm/day threshold.

accumulation rates providing higher temporal resolution.

3.3. 1400 Year record — natural system variability

Analysis of the entire sedimentary record is limited by decreased sampling and geochronological resolution, and requires making assumptions concerning the age model and rates of deposition. Carbon-14 AMS dates of six samples from NF-15 provides age control on sediment accumulation. The topmost sample (bulk sediment) is interpreted to be unreliable as it yielded an older date than was reasonable. The five remaining ^{14}C dates provide age control with continuous deposition since ~680 AD (Table 1). Merging the ^{14}C and ^{210}Pb data sets (Fig. 9) shows no apparent change in slope between the ^{14}C and ^{210}Pb data interpreted to represent a constant linear sediment accumulation rate ranging from 0.12 cm/yr to 0.17 cm/yr. The change in slope between 60 and 80 cm down-core is interpreted to represent a slower sediment linear accumulation rate to ~0.05 cm/yr as there is no evidence of erosion, a hiatus, or any other disruption in deposition at this depth. Utilizing bulk density measurements for the upper 50 cm of core

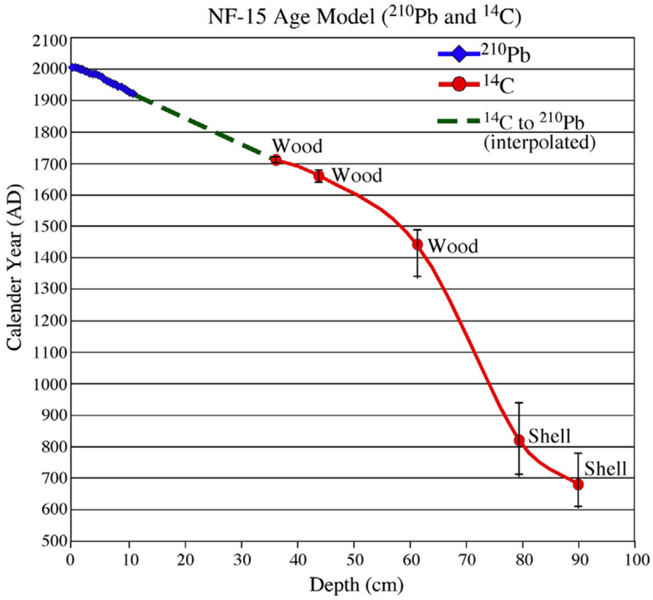

Fig. 9. Age model for the past ~1400 years merging ^{210}Pb CRS age dates and ^{14}C age dates for core NF-15.

NF-15 to calculate MAR over this interval, reflects an average MAR of 0.06 g/cm^2/yr from 0 to 16 cm with an increase in the bulk density between 16 cm and 31 cm associated with a compacted mud/clay unit with a MAR of 0.14 g/cm^2/yr. From 31 to 50 cm the MAR decreases to 0.08 g/cm^2/yr.

Core photographs and X-radiographs show dm-scale variability with units dominated by mm- to cm-scale laminae, alternating with massive, laminae-free units. This dm-scale variability is recorded in XRF elemental scans as well (Figs. 2 and 10). XRF scan data from ~685 to 2008 AD record the variability in terrigenous sediment accumulation, which is interpreted to represent variations in the frequency of heavy (>12 mm/day) rainfall events on the decadal- to centennial-scale (Fig. 10).

A period of increased terrigenous element accumulation between ~1710 and 1860 is represented by the highest %Al recorded for all terrigenous elemental scans and an increase in MAR (Fig. 10). In 1718 Danish occupation and plantation activity began on St. John, with deforestation and cultivation of sugarcane common throughout the island (Armstrong, 2003). Reforestation began following the end of the plantation era in 1850. During the plantation era, subsistence farming occurred in the Newfound Bay watershed leading to increased availability of sediment in the watershed to erosion and downslope transport (Brooks, 2007; Armstrong, 2003). Consequently, this may represent a period of increased frequency of rainfall events, in which terrigenous sediment runoff was magnified by human-induced land use changes in the Newfound Bay salt pond watershed. This is similar to what Lane et al. (2011) found in the Dominican Republic of increased erosion triggered by higher precipitation between 1794 and 1822 A.D. following a period of aridity associated with climatic changes during the Little Ice Age. By establishing the sedimentological signature in coastal salt ponds of terrigenous runoff, these records can be investigated for changes in rainfall/runoff over longer time periods and potentially linked to other climate records in tropical latitudes.

4. Conclusions

A high-resolution analysis of mm- to cm-scale laminated coastal salt pond sediments from St. John, USVI, shows deposits resulting

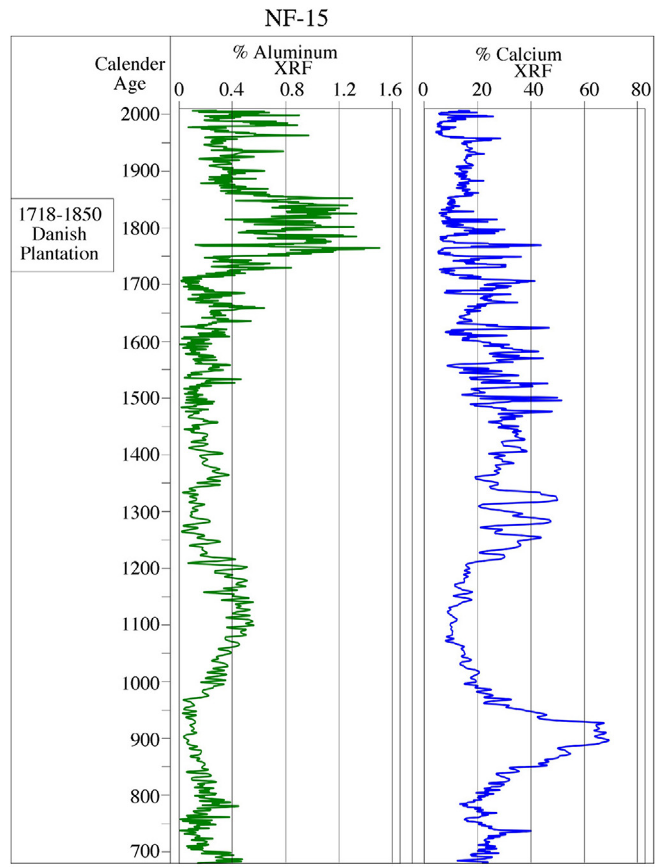

Fig. 10. XRF %Al and %Ca plotted vs. time (age model) showing variability over time as well as potential influence of plantation era activities on %Al.

from rainfall/runoff over a one year period (2009) to have increased Fe, Ti, and Si, which (as well as Al), are the dominant elements in sediments from the upslope watershed. Accordingly, Al, Ti, Fe, and Si are considered terrigenous indicator elements, and represent the sedimentologic signature of rainfall/runoff from the adjacent island watershed in salt pond sediment records. Therefore, increases (decreases) in Al, Ti, Fe, and Si, in sediment core records can be used as a proxy for variability in rainfall/runoff events. Core analysis using scanning XRF and scanning LA-ICP-MS methods (mm to micron-scale resolution) provides the ability to investigate rainfall/runoff patterns preserved in laminated sediment cores that are longer in duration than other proxy records (corals) with the temporal resolution to resolve annual to decadal variability.

Linking high-resolution geochronology (past ~100 years), with the rainfall/runoff sedimentary signature (i.e., increase in Al, Ti, Fe, and Si), and rainfall records from 1957 to 2008, shows good agreement with the frequency of rainfall events exceeding ~12 mm/day. Thus, in the two salt ponds studied, a threshold rainfall rate of ~12 mm/day is required to mobilize/transport sediments through the watershed and into salt ponds. This threshold value differs from what has previously been reported for other watersheds on St. John (MacDonald et al., 2001), which may be a reflection of differences in the techniques used, but also the inherent variability among watersheds including watershed size and gradient, vegetation, sediment grain size, and anthropogenic land use change. Determining a rainfall/runoff threshold for a particular watershed may be important for management implications in that it can be a predictive tool to help guide island development, as some watersheds may be more naturally susceptible to erosion and runoff.

Variability in the sedimentary record over the past ~100 years reflects decadal-scale fluctuations in the frequency of rainfall/runoff events. Defining this decadal-scale natural variability can be utilized to gain a better understanding of how coastal ecosystems respond to these natural fluctuations. Understanding the ecosystem response to natural variability, can be useful in predicting how these ecosystems may respond to anthropogenic activities in the watershed that may enhance runoff, thereby providing another predictive tool useful for management purposes.

Applying this approach to the sedimentary record over the past ~1400 years, dm-scale laminated units with increased terrigenous indicator elements, alternate with dm-scale homogeneous, non-laminated units. Radiocarbon dating indicates this variability to be on a decadal- to centennial-scale, and provides a baseline of the natural system variability over this time frame. A period of unusually high terrigenous indicator elemental levels between 1710 and 1860, correlates with the island's plantation era, and therefore, may be a response to intense anthropogenic impacts during this period, in combination with increased rainfall. Brooks et al. (2007) detected no evidence of changes in sedimentation patterns in nearby Coral Bay due to anthropogenic activities during the plantation era. Factors influencing the lack of evidence in Coral Bay likely include the marine nature of Coral Bay and the decreased preservation potential of sediments due to physical processes (waves, swell) as well as bioturbation. Conversely, the salt ponds in this study have little to no physical currents or mixing and minimal to no bioturbation leading to higher preservation potential of sedimentological units. In addition to the laminated salt pond sediments being better archives, the methods used in this study were much higher resolution, enhancing the detection of high-frequency events. Developing a long-term baseline of natural variability allows for a more accurate determination of the extent to which human activities have altered the natural sedimentation patterns. Results provide a framework that can be applied to other coastal environments around St. John, as well as other mountainous tropical islands, to investigate local records, as well as provide linkages to broader processes such as climate variability in tropical latitudes.

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