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ANTHROPOGENIC HEAVY METALS IN SEDIMENT CORES FROM SALT POND, SAN SALVADOR, THE BAHAMAS

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ABSTRACT

Salt Pond is a shallow, hypersaline lake on the eastern side of the island of San Salvador. Four cores measuring from 21 cm to 77 cm in length were recovered from Salt Pond in January 2008. In the lab, the texture and composition of layers in the cores were described. Sediment was sampled every centimeter and the percentage of organic carbon, water content, and carbonate were measured using the loss on ignition (LOI) method. One radiocarbon date on a plant fragment at a depth of 35.5 cm yielded an age of 1300 ± 40 yr BP. In order to determine the base of the historic period and other chemical signals of human impact on the environment, trace element and heavy metal concentrations were measured at a 2 cm sample interval in one core (BA08SP4) using an Inductively Coupled Plasma Mass Spectrometer. At 18-10 cm and at 5 cm depth in the core, there is a sharp rise in lead, zinc, iron, aluminum, chromium, and manganese levels. The increase concentration of the heavy metals are likely correlative to the historical periods on San Salvador that started when British loyalists fleeing the American colonies established plantations in the British-held Bahamas in the 1780s. An increase of aluminum, iron, and manganese starting at 40 cm depth and continuing to the top of the core may indicate input from soil erosion. These elements are enriched in the lake sediments after 700 A.D. Additional geochronological control, data on historical land use practices, and comparisons to cores from other lakes are needed to better constrain the age, source, and distribution of the metals.

INTRODUCTION

San Salvador Island is located on an isolated carbonate platform on the eastern edge of the Bahamian Archipelago (Figure 1). The island is surrounded by a shallow marine shelf with a coral reef and an eastern wall reaching depths approaching 4700 m. Ocean currents and deep water separate the carbonate environment of the Bahamas from the terrigenous North American and Great-Antilles sediments. Because of its windward position in the archipelago in the northeast trade winds

zone, San Salvador Island is different from other Bahamian islands as it contains many inland lakes with varying water chemistries and depositional histories. The lakes of San Salvador Island, Bahamas potentially contain important high-resolution records of environmental and climatic change.

Chemical proxies for changes in the environment can be preserved in the stratigraphic record. Such signatures are important to archaeologists because they can provide evidence of past anthropogenic activities, both prehistoric and recent (e.g. Wells et al., 2000; Cook et al., 2005).

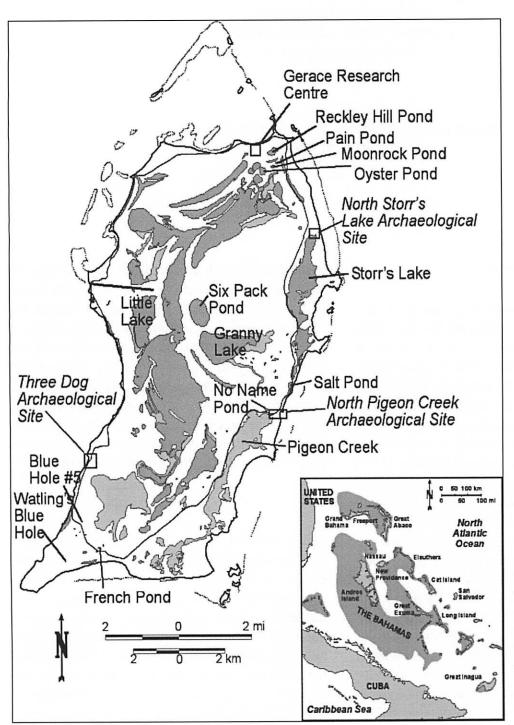


Figure 1. Map of San Salvador Island showing some of the lakes and archaeological sites mentioned in this paper. (GIS map modified from Robinson and Davis, 1999).

Soil and sediment can serve as records of local and regional impact of humans on the environment through time. For example, Donnelly and Woodruff (2007) interpreted the abrupt increase of the elements titanium (Ti) and iron (Fe) in sediment cores from a coastal lagoon to represent the period of massive deforestation and land clearing in Puerto Rico around 1840. Fe and Ti concentrations were also used as a chemical proxy of watershed rainfall and runoff delivered to the Cariaco Basin offshore of Venezuela (Haug et al., 2001). Changes in the elemental concentrations can also be evidence of global environmental and climatic conditions because many trace elements are known to be airborne, traveling long distances until settling out of the atmosphere (e.g. Muhs et al., 2007). Sources of airborne particulates include volcanism, periods of aridity and increased dust, or pollutants from the Industrial Revolution and other historical periods.

On San Salvador, Teeter (1985) hypothesized that increases in aluminum and silica in the upper 22 cm of Fresh Lake located in the northeast side of the island was caused by soil erosion due to "clear-cutting by plantation owners". Teeter et al. (1987) also report elemental analyses of sediment from Salt Pond. In that study the concentration of nine elements was determined from several stratigraphic layers within a 84-cm-long core. The insoluble inorganic residue from acid leaching and furnace heating was analyzed with an electron microprobe. Both aluminum and the amount of insoluble inorganic residue increase from a depth of 28 cm to the top of the core. These data led Teeter et al. (1987) to interpret the "influx of clays from soil erosion following clear cutting of the island by colonists" as the possible cause. Aluminum, however, showed high mole percentages in the lower section of the core in an interval below 55 cm that Teeter et al. (1987) interpret as a wetter climatic period with lower lake salinities based on the ostracod assemblage and sediment type. These authors inferred that higher precipitation rates would increase sediment input eroded

from the watershed to the lake. These inferences are clearly in need of testing.

In this study we use inductively coupled plasma-mass spectrometry (ICP-MS) to detect low-level (parts per billion, ppb) chemical changes in lake sediments from Salt Pond on San Salvador Island. The trace element enrichment in the sediments of the Bahamas is distinguishable from the calcareous sediments of the region and, we propose that increased concentration of trace elements can provide information on environment change and human occupation, agricultural, and industrial practices through time.

STUDY AREA

The topography of San Salvador consists of arcuate limestone ridges formed from lithification of Pleistocene sand dunes and other carbonate rocks (Carew and Mylorie, 1995). Located between the ridges in interdunal swales are many saline to hypersaline lakes. The lakes on the San Salvador Island vary in salinity, controlled by the "degree of development of the (marine) conduit system, the presence of local fresh groundwater lenses, the size of the lake, its elevation relative to sea level, and rainfall" (Teeter, 1995; Park and Trubee, 2008).

Salt Pond is a small coastal lake located on the east side of San Salvador Island (Figure 1). The name is derived from the historical use of the pond as a local source for collecting salt. Halite depositional crusts form after the salina undergoes periodic episodes of evaporation and complete dessication (Teeter et al., 1987; Park et al., 2008, 2009). The water depth in the lake varies from more than 1 m deep in wet years to completely dry (Teeter et al., 1987; Furman et al. 1993; Shamberger, 1998; Shamberger and Foos, 2004). A thin cover of Holocene sediment blankets the bedrock basin floor. Pleistocene bedrock is exposed on the northeast shore that separates Salt Pond from Storr's Lake, as well as a bedrock ridge on the west side of the pond separating it from the Granny Lake basin. Salt Pond is separated from the Atlantic Ocean by a narrow and topographically low coastal dune that is overtopped by hurricanes, mostly recently by Hurricane Frances in 2004 that left a blanket of sand in the lake (Yannarell et al., 2007; McCabe and Niemi, 2008; Niemi et al., 2008). Sand layers found within Salt Pond sediment cores have been interpreted as evidence for past hurricane events (Teeter et al., 1987; Shamberger and Foos, 2004; McCabe and Niemi, 2008; Park et al., 2008, 2009).

CULTURAL HISTORY

Several archaeological sites are located near Salt Pond and within the watershed of the lake. To the south is the large Lucayan archaeological site known as North Pigeon Creek. The Lucayans were the first humans to occupy the Bahamian Archipelago. They utilized caves and built open-air coastal sites. The oldest Lucayan site on San Salvador is the Three Dog archaeological site located on an eroded sand dune on the west side of the island at Sugar Loaf Bay. This site dates to about 700-800 A.D (Berman, 1992, 1994; Berman and Gnivecki, 1995). Rose (1982: 139), one of the excavators of the North Pigeon Creek site, proposed that the Lucayans utilized San Salvador's inland lakes to provide "an effective communications and exchange link with other settlements on the island." Other prominent Lucayan sites on San Salvador include Minnis Ward, Palmetto Grove, Long Bay, and North Storr's Lake that date to between 900 and 1500 A.D. (e.g. Blick, 2007).

Whether based on declining resources, stressed populations, warfare, or other reasons, these seafaring and fishing peoples left Cuba and Hispanola for the Bahamas (e.g. Berman and Gni-



Figure 2. Photograph showing the coring platform and piston corer in Salt Pond, January 2008. View toward the West.

vecki, 1995; Keegan, 1995). The Bahamian islands may have provided a moist environment suitable for root-crop horticulture with their sandy soils, a long growing season, harvestable tree fruits, and adequate rainfall (Berman and Gnivecki, 1995). It is unclear how climate or environmental conditions might have played a role in the migration and colonization of the Bahamas. Paleoclimate and pollen data recovered from lake cores in Haiti, the Dominican Republic, and Andros Island in the Bahamas (e.g. Hodell et al., 1991; Kjellmark, 1996; Higuera-Gundy et al., 1999; Kennedy et al., 2006) show that moist conditions gave way to arid conditions in the Caribbean around 3.2 ka. A brief return to a wetter climate during 1.5 and 0.9 ka (ca. 450-1050 A.D) was then followed by a millennium of arid conditions and notable ecological and land degradation.

The Three Dog and Long Bay sites both yielded material from the Spanish Contact period in the late 15th century (Gnivecki, 1995). It is now widely accepted that Christopher Columbus first made landfall in the Bahamas in 1492 on an island called Guanahani, or San Salvador Island. The native Lucayan population was enslaved by the Spanish, stricken by European diseases, and the Bahamas became rapidly depopulated (Craton and Saunders, 1992; Gnivecki, 1995).

In 1784-1785, more than 6000 British Loyalists fled the southeastern colonies after the American Revolutionary War and resettled in the Bahamas (Wilkie and Farnsworth, 1999). Loyalist-era settlements of Kerr Mount and Fortune Hill are located to the north and west of Salt Pond, and Farquharson's to the south (Figure 1). On San Salvador, the Loyalists brought the plantation culture with them including manor houses built from tabby and hundreds of slaves (e.g. Gerace, 1982; Baxter and Burton, 2006b). Within three decades, the plantations failed and the owners eventually left leaving behind their former slaves and overseers (Craton and Saunders, 1992). In the 19th century, cotton gave way to subsistence farming and raising livestock. Sisal became the dominant

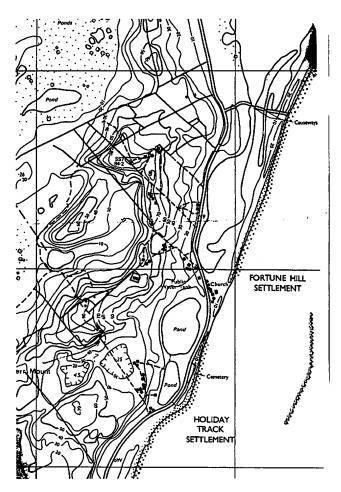


Figure 3. Topographic map showing location of Salt Pond cores (labeled 1-4).

export from San Salvador (Baxter and Burton, 2006b). Large changes occurred after WWII on San Salvador with the establishment of U.S. military bases and later resort hotels.

METHODS

Four cores were collected from Salt Pond in January 2008 using a Livingston-type piston corer (Figure 2 and 3) onboard a modified catamaran boat platform. The core barrel consisted of 2-inch-diameter (5 cm), ABS piping that was pre-split and wrapped in electrical tape to reinforce the pipe. The tops of the core barrels were drilled to fit on to the push core handle and the piston core de-

vice and the bottom of the barrels were sharpened to aid in penetration of the sediment (Sipahioglu, 2008). The cores varied in length from 21 cm to 77 cm. The longest core, BA08SP4, was studied in detail.

The cores were transported to the University of Akron where they were kept in refrigerated storage. The cores were split, photographed, and logged (Figure 4). The core log included identification of the texture, sediment color, and composition of each layer.

The cores were sampled every centimeter and analyzed for carbonate and organic matter concentration using the loss on ignition (LOI) techniques (Dean, 1974; Heiri et al., 2001). One cubic centimeter of sediment was placed into a ceramic crucible and weighed. The crucible was then placed into a drying oven at 105°C, dried for

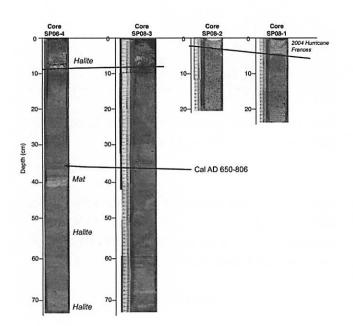


Figure 4. Four cores extracted from Salt Pond in January 2008. The top sand layer represents washover sediment from Hurricane Frances in 2004. Halite and other evaporites are seen in three distinct layers. A prominent microbial mat is found at a depth of 36-40 cm. A radiocarbon date at 35.5 cm depth in Core SP08-4 yielded a 2-sigma radiocarbon age of A.D. 650-806.

24 hours, and weighed again to determine wet and dry bulk density and water content. The crucibles were then placed into a muffle furnace and baked at 550°C for 4 hours to remove any organic matter. After cooling, the samples were re-weighed and then baked again at 1000° C for two hours, removed and cooled, then weighed to determine the carbonate content.

One core (BA08SP4) was sampled every 2 cm for element analyses (Na, Mg, Al, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Pb) using inductively coupled plasma-mass spectrometry (ICP-MS). The 0.050 g samples were dried at 105° C for 12 hours then disaggregated by hand using an agate mortar and pestle. For trace element analyses, only non-metallic, acid-washed equipment was used. The equipment was soaked in nitric acid for 24 hours and then triple-rinsed with 18 M-ohm de-ionized water. Each sample was digested in 2 mL of nitric acid for at least 12 hours in a sealed LDPE bottle, then diluted with 18 M-ohm water to a total mass of approximately 100 g. The samples were then analyzed using a Varian Ultra Mass 600 ICP-MS.

One radiocarbon date was obtained from core BA08SP4. A leaf fragment (most likely mangrove) was collected from BA08SP4 at a depth of 35.5 cm and sent to Beta Analytical Labs for radiocarbon analysis (Beta-244029). The sample yielded an AMS radiocarbon age of 1300 ± 40 yr BP. The two-sigma, calendar age for the sample is cal AD 650 to 806 (based on the OxCal 4.1 online calibration program that utilized the Intcal 09 calibration curves; Bronk Ramsey, 2009; Reimer et al., 2009).

RESULTS

The stratigraphy in the cores was divided into four sedimentary facies including carbonate sand, carbonate mud, algal/organic laminations, and evaporites (Figure 4). The carbonate sand facies is composed of light colored, fine- to coarsegrained bioclastic sand. The carbonate mud fa-

cies ranges from gray to brown-gray in color and contains some fine sand and interbeds of fine- to coarse-grained carbonate sand layers of varying thickness. The algal/organic facies contains laminae that vary in color from dark brown, pink, dark green, to tan and are composed of cyanobacterial and other microbial mats. Halite crystals of varying sizes and evaporite layers were found within carbonate mud and as crusts.

In core BA08SP4, an evaporite layer found at the base of the core (75-77 cm) is overlain by coarse-grained sand and sandy mud to 55 cm depth. This sequence is capped by a second halite layer at 52-55 cm depth. A thick sequence of mud dominates the core stratigraphy between 11 and 52 cm depth. This mud is intercalated with at least six medium- to coarse-grained sand layers each measuring < 1-2 cm in thickness. There are noticeable scour surfaces between some of the beds in this interval that are interpreted as storm deposits. There is also a thick algal mat between 36 and 40 cm depth. Between 4 and 11 cm depth in the core there is an evaporite interval. The upper layer in all the cores is fine- to coarse-grained carbonate sand that varies in thickness from 4 cm in core BA08SP4 to the full core depth of 21 to 24 cm in BA08SP1 and BA08SP2. No overwash sand was found in core BA08SP3 because the upper section appears to be bioturbated—possibly by people walking in the lake. The uppermost sand layer correlates to hurricane washover deposits documented by McCabe and Niemi (2008).

The evaporite horizons can be interpreted as periods when evaporation exceeds precipitation (or other potential water inputs such as groundwater seepage and marine incursion by storms) into the Salt Pond basin. Three evaporite horizons were noted: a basal layer at 75 cm, a middle layer at 50 cm, and the upper layer to 10 cm. These correlate well with measurements of high paleosalinity between 0-10 and 30-75 cm determined from ostracodes assemblages by Teeter et al. (1987). Geochemical analyses of evaporites from a Salt Pond core extracted in 1991 by Furman et al. (1993) also confirmed the presences of evaporite minerals such as gypsum, bassanite, and halite.

The LOI method was performed on all four cores. The results from these analyses show an increase in carbonate in the sand facies where there is little or no organic material and an in-

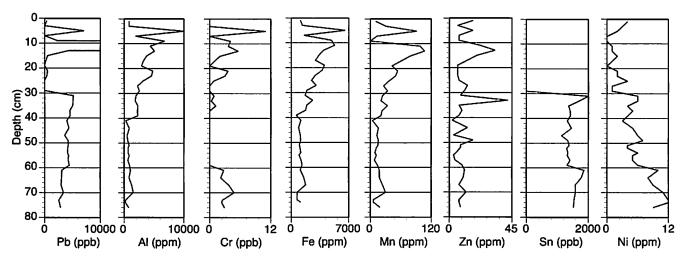


Figure 5. Trace element analyses of sediment from a Salt Pond core. Concentrations of lead (Pb), aluminum (Al), chromium (Cr), iron (Fe), manganese (Mn), zinc (Zn), tin (Sn) and nickel (Ni) are shown in parts per billion (ppb) or parts per million (ppm). The Pb profile is clipped (the peak value is at 350,000 ppb) probably due to the nugget effect.

crease in organic matter in the facies containing microbial mats. The dry bulk density is highest in the sand facies and the water content increases in the laminated organic facies. In some layers, there is a mixture of carbonate sand as well as organic material. The evaporite layers are represented by low amount of organic material, as well as low carbonate material.

ICP-MS analyses on core BA08SP4 show detectable signatures for Pb, Sn, As, Zn, Ni, Fe, Al, Cr, and Mn (Figure 5). Tin had the lowest concentration values in the range of 0 - 20 ppb and iron had the highest concentration values ranging from 0 - 80,000 ppb. Our initial ICP-MS data of lead (Pb) showed a very large spike reaching 350,000 ppb (Figure 5) that may be due to a nugget effect of a single particle. When this outlier was removed from the data, the lead signature correlated much better with the other elemental profiles. Between 18-10 cm and at 5 cm depth in the core, there is a sharp rise in Pb.

Tin (Sn), zinc (Zn), and nickel (Ni) appear to vary over very low concentrations. Sn and Ni increase with depth in the cores. Zn concentrations spike at about 35 cm and 15 cm depth similar to other trace elements. The concentration of Fe, Al, Cr, and Mn appear to follow a similar pattern of chemical enrichment. These elements increase steadily from 40 cm to the surface of the core with noted peaks around 15 cm and 5 cm depth.

DISCUSSION

The trace element profile with depth in the core can be interpreted as a signature of both global and local environmental changes preserved in the lake sediments. There are also anthropogenic influences on the sediments; the increase in concentration of the heavy metals near the top of the core are likely correlative to the historical periods on San Salvador that started when British loyalists fleeing the American colonies established plantations in the British-held Bahamas in the 1780s.

Boutron et al. (1994) reviewed the evi-

dence for lead and other heavy metals in ice cores from Antarctica and Greenland. Heavy metal concentrations in Antarctic ice fluctuate with climate showing natural decreases during interglacial periods and increases in glacial periods. These natural variations are due to an increase in soil and rock dust transported in the atmosphere during glacial periods. Over the last few hundred years, Boutron et al. (1994) report a 200-fold increase in Pb concentration in the Greenland ice sheet. They also found a 7.5-fold decrease in recent years attributed to the rapid decline in the use of lead. Lead and other heavy metal in addition to being documented in ice cores have also been found in other lake sediments globally. For example, analyses of lead isotopes in Swedish lake sediment show a clear increase in pollution-derived lead in the early Roman Empire (ca. 1st century A.D.), during the medieval period, and the Industrial Revolution (Renberg et al., 2001).

Lead and other heavy metals are good indicators of anthropogenic input to the sedimentary record and are especially prevalent since the beginning of the Industrial Revolution. Lead became an additive in gasoline and other products until the 1970s when lead began to be phased out due to findings of its adverse affects on human health. The increase in concentration of Pb with other metals (Fe, Al, Cr, and Mn) begins at 5 cm depth in the core. These metals are likely due to 20th and 21st century industrialization and pollution on the island. On San Salvador, the U.S. military constructed bases on the island in the 1950s. A paved road that circumnavigates the perimeter of the island was also constructed. With the increase in motorized vehicles on the island, Pb from vehicle exhaust is likely to have contaminated the soil and lake sediment. Other modern chemicals brought to the island during the past century are also likely to have contributed to this heavy metal pollution signal.

In Roman and medieval times, lead was mined and also used in the smelting process to extract silver. Thibodeau et al. (2007) documented

Spanish galena (PbS) brought to the New World colony of La Isabela on Hispanola as early as 1498. Lead artifacts were also excavated from the Spanish contact period at the Long Bay and Three Dog sites on San Salvador (Gnivecki, 1995). Other ancient uses of lead include pipes, tanks, roofs, ammunition, cooking vessels, in glass and pottery glaze, cosmetics, as adornments, and other purposes. The top 18 cm of sediment in the Salt Pond core (BA08SP4) is probably historical deposits dating from the early colonialism to present time. However, the lack of direct geochronological control on the age of the sediment does not allow us to definitively draw this conclusion.

There is a spike in Fe, Al, Cr and Mn above 40 cm depth in the Salt Pond core. This is at the depth where we have a calibrated (2 sigma) radiocarbon age on a leaf fragment in the sediment dating to AD 650 to 806. The coincidence of these trace element increases with the age reported for the earliest arrival of the Lucayans at the Three Dog archaeological site of AD 660-865 (Berman, 1992) is noteworthy. Furthermore, Berman and Pearsall (2000) report that aluminum is the only element detected from the inorganic particles adhering to siliceous microlithic tools excavated from the site based on energy dispersed x-ray spectrometry and scanning electron microscopy. Wood, starch, and phytolith analyses of the stone tools clearly demonstrate that the Lucayans planted maize, chili, and other root/tuber crops (Berman and Pearsall, 2000, 2008; Perry et al., 2007). Thus, it is evident that the Lucayans practiced root-crop agriculture on the island. To what degree clearing of the natural vegetation to form cultivable land likely caused erosion of the soil in this early time period is not known. But our data suggest that elements including Fe and Al found in soil begin to increase in concentration in Salt Pond sediment as early as A.D. 700-800.

Soil erosion likely accelerated during the Loyalist period beginning in the 1780s. Building remnants of large plantation such as Polly Hill, Fortune Hill, Farquharson's, Kerr Mount, Sandy Point, and Harbour Estates can still be seen on Sal Salvador (Baxter and Burton, 2006b). Some of these have been surveyed and excavated (e.g. Gerace, 1982; Baxter and Burton, 2005, 2006a). Large tracts of land were cleared for planting cash crops. Some of the field walls from the plantations can still be observed in the dense tropical vegetation. The clear-cutting of the island's vegetation for agricultural purposes at the scale of the Loyalist plantations likely caused soil erosion. Land cleared of vegetation is more prone to lose surface sediment by runoff erosion. These results are similar to those first reported by Teeter (1985) for Fresh Lake and Teeter et al. (1987) for Salt Pond. However, until the strata containing these geochemical signatures are radiometrically dated, the results should be viewed as preliminary.

Possible sources of the trace elements deeper in the core (below 40 cm) most probably derive from the long-range transport of dust containing metals from elsewhere in the world. We should also note that this global and long-range source must also be a component of the input to the upper stratigraphic section. Muhs et al. (2007) proposed three parent sources that are external to the carbonate substrate for the trace elements found in the soils of the Bahamas; volcanic ash, the fine-grained component of distal loess from the lower Mississippi River Valley, or wind transported dust from Africa. Muhs et al. (2007) found that soils on the Bahamas are enriched in light rare earth elements (REEs), similar to African dust. Their Sc-Th-La and Sc-Th-Zr plots do not indicate any volcanic influence in the soils of the Bahamas and can be interpreted as either Mississippi loess or African dust (or both) as parent materials of the soil. The Exuma Cays samples show an unexpected equal amount of African dust and Mississippi Valley loess in their soil. To verify these inputs, we propose to examine the REE input into the lake sediment geochemical profile in a future study.

Our data clearly show that there is not a linear relationship between depth and time in the

sedimentary sequence in Salt Pond. One radiocarbon date at a depth of 35.5 cm indicates deposition of this section over 1200 years ago. A sedimentation rate could be calculated for 35.5 cm over 1200 years yields 3 mm/yr. However, the upper 15 cm of sediment are like historical in age dating to after 1785 A.D. A sedimentation rate of 15 cm over 225 years (from 1785 to 2010) yields a sedimentation rate of 7 mm/yr, more than double the rate since 1200 yrs ago. More in depth discussion of sedimentation rates awaits further radiocarbon analyses of the sedimentary sequence.

Finally, one potential source of error in our interpretation of the geochemical signatures and stratigraphic section at Salt Pond is that historically, the lake basin was mined for its salt. The islander's primary method to harvest salt was to rake the sediment using hand tools to collect the halite. Salt harvesting was obviously done during drought periods when the lake desiccated and when the salt crystals would form as the pond evaporated. It is unclear to what degree the pond was raked or to what extent the sediment was disturbed by this practice.

CONCLUSIONS

Our preliminary interpretation of the trace element record from sediments in Salt Pond suggests that lakes on San Salvador contain a valuable archive for paleoenvironmental reconstruction. Measurements of lead and other heavy metal concentrations in the sediment might successfully be used as a geochronological marker indicating the base of post-Industrial Revolution to 20th century deposits and possibly post-1780 Loyalist-era plantation period. An increase in concentration of aluminum, iron and other elements appears after approximately 700 A.D. These data suggest an increase in land degradation, soil erosion, and sedimentation in Salt Pond that was likely triggered by agricultural practices in the watershed as early as the first peopling of the island. Elemental analyses of sediment appear to be a promising tool for identifying the record of anthropogenic impact in the Bahamas.

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