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Assessing the Ability of Soils and Sediment to Adsorb and Retain Cs-137 in Puerto Rico

by

Warner Ithier-Guzman

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
College of Marine Science
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DEDICATION

Pursuing a doctoral degree was the biggest dream I ever had in my life. As the first member of my family to go to college, this challenge was more than a risk, it was an adventure. This adventure was made possible by the opportunity I received from Dr. Ashanti Johnson. After knowing each other for a few years, she did not hesitate to offer me a position in her laboratory seven years ago. That opportunity I was given has made the difference in my life and in my family. I knew it would not be easy and that I would have to make many sacrifices to reach my goal, but I accepted the challenge and on August 17, 2003 the journey to the Ph.D. began. Today I am grateful that Dr. Johnson introduced me to the fascinating world of geochemistry. This new world has provided me with knowledge and skills needed to achieve my dreams.

Along my journey I found great people that supported my efforts in achieving my goal of obtaining a doctoral degree. These people have made a difference in my life. Some of these supporters were members of my committee and I want to thank them for their continuous support and guidance. I was honored to have Dr. Robert Byrne, Dr. Kathleen Carvalho, Dr. Edward VanVleet and Dr. Brandon Jones, along with Dr. Ashanti Johnson serve on my committee. At several stages along my journey these individuals were extremely intimidating, particularly during my proposal defense, my comprehensive exams and the final process of completing and ultimately defending my dissertation. These same individuals have also provided me with moments of happiness, moments that

I will remember forever. One such moment happened on September 6, 2007 when Dr. Byrne congratulated me on passing my comprehensive exams. He knew that it was a major relief for me to hear him say that I passed, since I had been absolutely terrified of his CO_2-related questions.

During my time at the University of South Florida College of Marine Science, I learned not only about CO_2 systems, organic matter degradation, radiogeochemistry, etc., I also experienced life. Saint Petersburg, Florida became my home and new friends came into to my life. It was some of these friends that provided me unconditional support that helped me survive this process. I called on these friends when I felt as though I had no hope of ever finishing. I can not adequately express the gratitude I have for these friends and my extended "USF family" which include Guillem Mateu, Marta Rodriguez, Karyna Rosario, Michael Martinez and Camille Daniels; my lab mates, Nekesha Williams and Patrick Schwing, as well as several other individuals that started with me and decided to go another route on their life journey. These individuals supported and encouraged me when I suffered, joined me in celebrating my accomplishments and laughed with me during special moments of joy. In short they were there for me when I needed them. For this I am forever grateful. Their friendship is one of the most important things that I will take along wherever the next phase of my journey leads me. I also want to take a moment to thank a person I consider to be more than a friend, he is like a brother, Esteban Martinez. Esteban and his family welcomed me into their home and provided me with great Cuban food every night while I worked on the final stages of my dissertation. There are many other friends that I met through the Florida-Georgia LSAMP Bridge to the Doctorate Program and the MSPHDS Program which made my stay at USF easier and happier. To those members of my "Bridge to the Doctorate family and the MSPHDS Family" I offer my heartfelt thanks.

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Warner Ithier-Guzman

ABSTRACT

As part of the radioactive exercises taking place around the world anthropogenic radionuclides were introduce to Puerto Rico's terrestrial and aquatic environments beginning in 1962. Two major projects took place in the island, the Rain Forest Project and the construction of a Boiling Superheat Nuclear Power Plant (BONUS). While in operation several accidental shutdowns occurred at the BONUS facility. One of these accidental shutdowns released 582 MBq into the nearby environment. Vieques an island located few miles east of the main island has received anthropogenic inputs of heavy metals resulting from military practices conducted by the US Navy. Due to the potential presence of Cs-137 in soils and sediments in Puerto Rico a radiological assessment was performed.

Downcore soil and sediment analysis as well as surface samples analysis was conduct in these three sites indicating the presence of Cs-137. Activity range varies among site from below detection limit to 12 dpm/g at Vieques, 15 dpm/g at Espiritu Santo Estuary and 12 dpm/g at the BONUS Facility. ICP-OES analysis indicates the existence of an oxic environment at the sedimentary system of the island. Cs-137 retention is strongly influenced by particle grain size and at the study sites clay was present in less than 20% for most sites. An X-ray diffraction analysis show that kaolinite and smectite are present at all sampling sites and illite is absent.

To further analysis the ability of soil and sediments to retain adsorption and desorption was conducted using clay reference material and samples from the island. All samples, reference and natural, used in the study were placed in an aqueous solution that contained MES buffer (5.0 micromol, pKa of 6.1), ammonium nitrate (0.010 M) and the five metals (individual concentrations ranged from 0.48 micromol to 1.6 micromol). Solution pH was adjusted by titration with acid or base, depending on the nature of the sample. Results were quantified as distribution coefficients. These results indicate that the absorption and retention of Cs-137 in the sediments in Puerto Rico is driven by the mineralogy of the site.

CHAPTER I: ENVIRONMENTAL MONITORING OF CS-137 IN THE CARIBBEAN AND HYDROGEOLOGY OF PUERTO RICO

INTRODUCTION

Environmental monitoring of Cs-137 after the nuclear era and the Chernobyl accident in 1986 has been performed in many countries around the world. Monitoring of Cs-137 as well as other radionuclides is the result of the introduction of manmade radionuclides into the environment primarily from nuclear powered weapons testing activities and nuclear power plant accidents (UNSCEAR 1982, Aakrog, 1994, Avery, 1996). These activities were conducted by the United States and the former Soviet Union in a variety of environmental settings. Locations for testing included the Hanford Site, WA (US); Savannah River, GA (US); Yucca, AZ (US); Novaya Zemlya (Russia) and Siberia (Johnson- Pyrtle, 1999; Robinson and Noshkin, 1999; Myasoedov, 2000; WHO, 2001; Uyttenhove et al; 2002; Aarkrog, 2003). The testing of nuclear weapons was not restricted to the continents; several islands including the Marshall Islands, Fangatufa and Bikini Atoll and the Caribbean island of Puerto Rico were also utilized for this type of testing (PRNC, 1970, US Navy; 2002, Moon et al. 2003). Monitoring of Cs-137 is useful to understand global fallout processes as well as for use as a chronological and dating tool. Many scientists use Cs-137 and other radionuclides (Pb-210) as chronology tools for sediment dating and as environmental tracers.

Studying the activity of Cs-137 in places where anthropogenic input is known, allows us to calculate external inputs resulting from human activity as well as, the activity resulting from fallout and its retention in depositional systems. Continued assessment will facilitate remediation work and help avoid further radio-contamination at specific sites, thus safeguarding these ecosystems.

Although above ground nuclear testing ended in 1996 after the adoption of the Comprehensive Test Ban Treaty, residual effects may be important as a result of significant levels of radiation fallout in some areas of the globe, especially in the Northern hemisphere (UNSCEAR, 2001). Deforestation, destruction of habitat, water quality degradation, increased erosion and sedimentation, all have the potential to transport radionuclides from their original site, and deposit them in areas where they may not only threaten natural resources, but also pose significant human health risks (Baqar et al. 2003; Hunter and Arbona, 1995).

The current study focuses in the retention of Cs-137 by soils and sediments in the island of Puerto Rico. Performing this assessment in Puerto Rico will provide the only data available on the island for this type of research. Contributions to advance the science of radiogeochemistry on the island are very important, as its population growth and associated development projects (both residential and industrial) are impacting the island's natural resources. Therefore knowing whether past governmental activities had any type of impact on local ecosystem is essential.

Municipalities such as Rio Grande, Rincón and Mayaguez were the main study sites for the Puerto Rico Nuclear Centre (PRNC) in the early 1960's. The municipality of Rio Grande was also used by Odum to conduct his famous project on tropical irradiation at the Caribbean National Forest (PRNC, 1969). Odum's project consisted of the irradiation of forest parcels to examine the effect of radiation on tropical ecosystems. Both projects, PRNC and the irradiation project, were sponsored by the government, and after the introduction of radionuclides into the ecosystem, no further examination was conducted. The use of short lived isotopes as well as long lived isotopes is documented, but no further information on ecosystem status is known.

This environmental monitoring will serve as the baseline information for further activities in Puerto Rico. Many studies have been conducted to study heavy metal concentration, polycyclic aromatic hydrocarbons (PAH), aerosols and Saharan dust, but no one has monitored the Cs-137 global fallout record or the retention of Cs-137 by sediments and soils in the places where they were introduced.

Geology and soil distribution of Puerto Rico

The island of Puerto Rico, just as all islands in the Greater and Lesser Antilles, has a complex geologic history. It has been estimated that Puerto Rico was formed more than 138 million years ago as a volcanic arc system (Larue, 1994). This arc formed due to subduction of the North American Plate below the Caribbean Plate, which began during the Cretaceous and continued throughout the Eocene. Arc volcanism in the Greater Antilles ended after the collision of the Greater Antilles arc with the Bahamas Platform (Larue, 1994).

The tectono-volcanic history of the island of Puerto Rico is found preserved in three main blocks. The Southwest, Central and Northeast litho-tectonic blocks have unique geochemical signals and distinct geologic histories (Larue, 1994). The geographic locations of the studied areas in reference to these blocks are significant because they have a control over pedogenesis and watershed development that will control soil formation and sediment transport.

The southwest block of the island has the oldest rocks found in Puerto Rico. These are found in the Sierra Bermeja Complex and are composed mainly of serpentinites (Larue, 1994). Igneous rocks are also found in this complex having an oceanic island arc affinity, where amphibolites have an oceanic crust signal (Larue, 1994). The rest of this block has a unique array of depositional facies, both volcanoclastic and limestone in origin. Environments range from basin to shallow water carbonate platforms (Larue, 1994). The oldest rocks in the Central block are found in the pre-Robles group composed of basin to shallow water carbonate platform environments similar to the previous block (Larue, 1994). A main volcanic center, Utuado Pluton, contains highly mineralized deposits (i.e., Cu) which, due to mining prospecting, creates areas that are impacted by acid mine drainage. Vieques Island shares the same geologic history with this block, mainly related by volcanic rocks. The last block in Puerto Rico's geology is the Northeastern block.

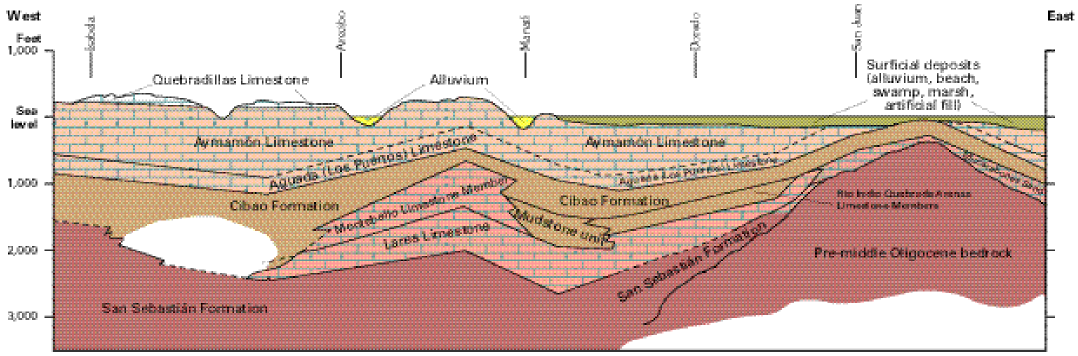


Figure 1. Geological formation of Puerto Rico (Larue, 1994)

The oldest rock comes from deepwater basinal deposit such as Daguao, Fajardo and Tabonuco among other formations. The Northeast block is characterized by abundant limestone formations. Unlike the Central block, no pluton formations are located in this region. The limestone formation extends from west of the Rio Espiritu Santo to Aguadilla, the northwestern tip of the island (Olcott, 1999). The length of this limestone formation is about 145 km and it reaches its maximum width of about 23 km in the area of Arecibo, a town in the north central portion of Puerto Rico (Figure 1) (Olcott, P.G. 1999). The limestone in the island has experienced erosion by dissolution, and the limestone on the north is a good example of karst topography (Olcott, 1999).

The historic volcanic activity resulted in an island that possesses mountain ranges that abruptly rise from the coast and valleys. For instance, the east-west trending Central Mountain Range divides the island into north and south and covers almost half of the island area with an average elevation of 915 meters. The Sierra de Luquillo rainforest commonly known as "El Yunque" is part of the Caribbean National Forest located on the Northeastern block. Sierra de Luquillo's highest peak is El Toro and its elevation is close to 915 meters. The Sierra de Cayey is also a mountain range in the island and its average elevation of 122 meters found in the Central block. There are many geological formations in Puerto Rico, San Sebastian, Lares, Cibao, Aguada, Aymamon and San Juan Formation. The oldest, San Sebastian formations on the island, are composed of limestone.

Table 1. Soil type and soil series at study sites (NRCS, 2003)

Site	Soil Type (Order)	Soil Series	Common Clay Mineralogy
BONUS Area			
Station 1-8	Mollisols	Colinas clay loam, 20 to 60 percent slope, eroded	carbonatic
	Vertisols	Mabi clay, 5 to 12 percent slope, eroded	mixed
Vieques			
Mosquito Bay St. 1-2		Tidal Swamp (ocean sediments)	mixed
	Inceptisols	Vieques Loam 5 to 12 percent slope, eroded	sandy
Kiani Lagoon		Tidal Swamp (ocean sediments)	mixed
	Inceptisols	Vieques Loam 5 to 12 percent slope, eroded	sandy
	Vertisols	Ponceno clay	mixed
Barracuda Lagoon		Tidal flats (mangrove area)	mixed
	Vertisols	Fraternity clay	smectite
North and South Jobalos Lagoon		Tidal Swamp (ocean sediments)	mixed
		Tidal flat	
	Inceptisol	Descalabrado clay loam, 20 to 40 percent slope, eroded	mixed (saprolite, silt)
Operational Post	Inceptisols	Descalabrado clay loam, 20 to 60 percent slope, eroded	mixed (saprolite, silt, hard rock)
		Fraternity clay	smectite
Caribbean National Forest (CNF)			
Cocoa Beach		Tidal Swamp (ocean sediments)	mixed
Espiritu Santo River		Tidal Swamp (ocean sediments)	mixed
El Verde Experimental Station	Ultisols	Yunque cobbly clay, 40 to 80 percent slope, extremely rocky	kaolinite

A wide variety of soils series, specifically 215, are found in the diverse topography of the island. Table 1 summarizes all soil series and the soil types found in the study areas. Since soil formation is driven by many factors, which include topography, climate, parental material, biological factors and time, it is reasonable to have such a diverse soil composition in an island whose origin is volcanic and where micro-climates dominate various ecosystems. For example, the Sierra de Luquillo dominates the topography of the Northeastern block in which more than two hundred inches of rain are received per year. Therefore the most abundant soil types are those formed by high humidity and temperature. El Yunque Cobbly clay 40-80 extremely rocky (this is unclear) dominates the region where samples were taken. The El Yunque series consisted of deep and well-drained soils on slopes. They are the result of weathering from andesitic to basaltic marine deposits. The deposit from which the series is formed comes from the Tabonuco and Hato Puerco Formation (NRCS, 2003). Average temperature in the formation site is 20 ºC and average precipitation is 470 cm of rain per year.

At the Caribbean National Forest (CNF), "El Yunque", the Humatas, Zarzal, Coloso, Cristal, Luquillo and Sonadora soils series dominate the mountain ecosystems, most of them resulting from the weathering of rocks. The other factor that should be considered in the rainforest is the influence of organic matter from leaf litter, which makes the soils acidic.

At the western area of the island, there are more than a hundred soil types. The area of Rincon where the power plant was constructed in the early 1960's is dominated by limestone and epiclastic outcrops. The soils that dominate the study areas are the

Colinas and Mabi clays. The Colinas soil series consists of well-drained soils that are calcareous and moderately permeable. Colinas clays are the result of limestone weathering in a humid to sub-humid climate. The cation exchange capacity of the Colinas soil series has been estimated to be 25-37 meq/100 g for the surface layer of soil, 0-25 cm, and the soil has a pH range of 7.9 to 8.4 (NRCS, 2003). The second dominant soil series at the Boiling Nuclear Superheater (BONUS) reactor site is the Mabi soil series. Mabi soils are deep, poorly drained and have poor permeability. They formed from volcanic material in a climate that ranges between 25-26.1 ºC and 178 to 203 cm of rain per year. Cation exchange capacity of the Mabi soil series has been estimated to be 25-37 meq/100 g for the surface layer of soil, 0-20 cm, and has a pH range of 4.5 to 6.5 (NRCS, 2003).

At the island of Vieques, soil production is the result of the island's bedrock. The bedrocks are mainly from marine deposits of limestone and volcanic lava among other materials (ATSDR, 2002). Five soil series are found in the study areas in Vieques: Vieques, Poncena, Fraternidad, Descalabrado and Tidal flat. The Vieques soil series is best described as moderately deep and well-drained with rapid permeability (NRCS, 2003). The Vieques soil series results from the weathering of granitic rocks and they are commonly in dry ecosystems. Annual precipitation is about 89 cm per year and the average temperature is about 25.5 ºC. Vieques soil series cation exchange capacity is 25-35 meq/100g at the surface layer (0-20 cm) and the pH range is 6.1-7.8.

The Poncena series is a deep soil that is moderately well drained, calcareous and has poor permeability. The series forms from fine-textured sediments derived from volcanic rock and limestone. The temperature remains around 26.1 ºC, and the annual precipitation is 89-127 cm per year. Its cation exchange capacity is 40-55 meq/100g at the surface layer (4 cm) and the pH range is 6.6 to 8.6. Climate for the soil series of Descalabrado and Fraternidad is similar to that discussed earlier where the around temperature is 26.1 ºC and precipitation between 76-89 cm. They were formed from volcanic rock and limestone with respective cation exchange capacities between 30-50 meq/100g and 35-55 meq/100g.

Due to all the precipitation received in the mountainous portions of Puerto Rico we know that the stability of the terrain is also important. Therefore many scientists have used the island as living laboratories to study (landslide) mass movement (Larsen and Torres-Sanchez, 1998, Larsen and Park, 1997, Larsen and Simon, 1993 and Scatena and Larsen, 1991). Landslides are the main source of erosion and sedimentation of the watersheds. This phenomenon has been followed closely in the CNF where Larsen and Torres-Sanchez, (1998), Larsen and Park, (1997) and Larsen and Simon, (1993) have investigated how and where landslides occur. Sediments resulting from landslides reach streams, rivers and reservoirs, and eventually the ocean. Areas such as the CNF are vulnerable to this type of event. Therefore, watersheds in vicinities such as Espiritu Santo Estuary, as well as Rio Blanco and Sonadora among many others, receive a variable amount of sediment on a yearly basis. Hurricanes, tropical storms and human activity such as road construction all contribute to landslides (Scatena and Larsen, 1991). For instance, in 1989 during Hurricane Hugo over 400 landslides were registered at the northeastern mountains of Puerto Rico (Scatena and Larsen, 1991). Such events have not been replicated in recent times.

Hydrogeology of study sites

Since all study sites occur in different geological settings inside the main island and Vieques, it is important to describe some of their hydrological characteristics. The CNF receives over 500 cm of rain per year. At the other end on the western coast in the municipality of Rincon, the average precipitation rate is 102 cm of rain per year. The island of Vieques is divided in two regions. In the western side of the island rainfall precipitation averages 127 cm of rain per year and the eastern portion receives approximately 64 cm of annual rainfall. Rain is the sole source of freshwater on the island and watershed formation is related to regional precipitation. The CNF therefore is one of the main sources for freshwater in the island. More than 13 rivers are born there, producing water for the entire population on the eastern region of Puerto Rico. In the municipality of Rincon near the BONUS nuclear reactor, there are two major rivers, the Rio Grande de Añasco and Rio Loco.

Vieques does not have any major rivers. Several aquifers are the main sources of water. The Esperanza valley is the primary aquifer, while Resolucion, Playa Grande and Camp Garcia are minor ones. These aquifers form within alluvial deposits located in the low flat valley along the coasts. Rainfall is the major source for fresh water recharge of these aquifers, and Esperanza-Resolution Valley aquifers are made of fine grained alluvium from weathering of dioritic rocks. At the main island, aquifers are made of limestone, volcanic rock and alluvium. In the north coast aquifers consist of heterogeneous body of interbedded permeable and poorly permeable material. At the southern region, aquifers are made of alluvium and although the southern region is the driest region of the island, aquifers in this region produce more water than those on the northern coast.

Studies on Cs-137 mobility

Cs-137 is one of the most common anthropogenic radionuclides that have been found in clay-rich, especially illite, sediments (Livingston, 2000, Johnson-Pyrtle et al., 2000, Moon et al., 2003). Cs-137 has a positive charge and it requires a negative charge to form a bond and attach to soil and sediment particles (Arapis and Karandinos, 2004, Olsen, 1981). In the natural environment, binding of Cs-137 to particles preferentially occurs on the negatively charged surfaces of clay minerals. These surfaces are provided by the double layers of illite and smectite and the single layer of kaolinite (Johnson-Pyrtle, 1999). On the island of Puerto Rico, the higher abundance of clay-sized particles may be attributed to the dissolution of carbonates and the weathering of terrestrial minerals (Fox, R. 1982, Moon et al. 2003 and Pett-Ridge, et al. 2009). The lower abundance of some clay particles may reflect high accumulation rates of other sedimentary material including biogenic debris (Moon et al., 2003).

Other factors that affect the distribution of radionuclides in aquatic and terrestrial sediments include particle mixing, cation-competition reactions, salinity and sediment mineralogy (Santschi, 1989; Moon et al., 2003). It has been shown, for example, that the activity of Cs-137 varies as a function of mineralogy, particle size and the salinity in the Siberian Arctic's Laptev Sea-Lena River estuary region (Table 2).

Table 2. Laptev Sea-Lena River estuary region average sediment. Cs-137 activity (Bq kg-1) and grain sized distribution (Adapted from Johnson- Pyrtle and Scott, 2001)

	Salinity	Cs-137 activity (Bq/g)	%Silt + % Clay (< 63 μm)	%Clay (<4 μm)
Marine average values	27.18	6.00	62.63	18.95
Lena River estuary average values	25.65	11.22	83.25	27.06
Study region average values	25.62	7.08	66.99	19.01

Cation exchange reactions that often occur in fine-grained clay-rich sediments can result in radionuclide enrichment or depletion (Fanning et al., 1981). For example uranium is present at higher concentrations in clay minerals than in limestone in Florida Platform (Fanning et al. 1981). The term cation exchange capacity refers to the ability of a particle to retain ions with positive charge (cations) in their negatively charged structure.

Moon (2003) suggests that the stratigraphic record of the upper centimeter of sediments from the Norwest Pacific Ocean is strongly influenced by particle mixing by benthic fauna. This mixing can result in anthropogenic radionuclide enrichment in surface sediments. Cs-137 can also be bioturbated by the activity of plants in the soil. This phenomena by which Cs-137 is absorbed or removed from soil is called the plant-to-soil transfer (Tyler et al. 2001)

Cs-137 mobility in soil and sediment is relatively slow and a factor affecting the slow mobility is the irreversible sorption process in soil particles (Arapis and Karandinos, 2004). In sandy textures, Cs-137 adsorption is low due the high permeability of the minerals (Olsen, 1981). However, in soil and sediment containing high quantities of fine-grained material, the likelihood of adsorption of Cs-137 to particles is much higher (Johnson-Pyrtle, 1999). Slow mobility in porewater is due mainly to the fact that Cs-137 has to compete with seawater cations, especially potassium (Olsen, 1981). This should decrease sorption and therefore increase mobility. Mobility of Cs-137 in freshwater ecosystems such as rivers is related to the interactions of the radionuclide with the suspended particulate matter. It also may depend on pH, the time needed for equilibrium and the nature of the suspended particle in the water among others factors (Ciffroy et al. 2009)

Sources of radiation in the environment

Environmental radiation comes from two sources; background and man-made (NRC, 2006). Background radiation is the result of cosmogenic and terrestrial radiation, while man-made radiation is of anthropogenic origin. Some common terrestrial radionuclides belong to the decay series of U-238, Th-232 and U-235. Due to Uranium's long half-life (4.47 billion years), its decay products (Th-234, U-234, Ra-226 and Rn-220 among others) persist in terrestrial and aquatic environments. They are commonly found in rocks, minerals and groundwater. Some decay products, such as Rn-222 and Ra-226, have become radiation sources to humans as they can be ingested or inhaled after their production (Zikovsky, 2006).

Besides volcanoes, rocks also contribute to the naturally occurring global background. U-238 decay products, K-40, Ra-226, Th-232 and Sr-90 are sources of radiation present in rock. Example locations where these radionuclides contribute to the background levels in soils are Egypt, India and Germany. (Ahmed et al. 2006; Sadasivian et al. 2006; Takeda et al, 2006; Anoruo et al. 2002; Farai et al. 2001; Jibiri, 2001).

Nuclear weapon testing

Many of the studies conducted after the initial nuclear weapons testing have focused on understanding the fate and transport of radionuclides in aquatic ecosystems. When investigating their fate and transport in the environment, researchers have taken into consideration that once deposited in the ecosystem daughter radionuclides can be present as the decay product of the original radioisotope. Researchers have also focused on the effects of radionuclides on local food web dynamics and their associated health implications.

Above ground testing has contributed to the release of radionuclides into the environment via fallout. The characteristics of fallout particles depend on the height of the burst and explosion yield. Once in the atmosphere fallout can occur in two types, dry deposition or wet deposition. Since particles introduced into the atmosphere display various characteristics, their individuality is important during the fallout process. For example, at higher altitudes dust particles may play a role in the condensation of rain drops and this process is responsible for the removal of the smaller particles in the atmosphere. Particles exceeding the 10μm with a density of 2.5 g/cm^{-3} generally fall out within a few hours at sea level. The fate of smaller particles in the troposphere will depend on laws of dispersion. Smaller particles can penetrate the stratosphere. It can take months to years before these particles reach terrestrial and aquatic ecosystems (Beck and Bennett, 2002, Eisenbud and Gessel, 1997). The main parameters controlling the deposition of radioactive particles in the stratosphere and troposphere are the temperature and precipitation. The warmer air in the tropics will allow the particles to reach higher in the atmosphere. Once temperature decreases and precipitation occurs, radioactive particles will be deposited in the ecosystem.

Underground testing has also been broadly conducted. The number of underground nuclear weapons tests in the US alone exceeds 800, a number that surpasses the combined number of above ground tests conducted by Russia, China, France and the United Kingdom (Beck and Bennett, 2002). As a result of nuclear weapons testing more than 40 radionuclides were released to the environment. Some of the most common of these radionuclides are I-131, Cs-137, Sr-90, Te-132 and Pu-239-240 (Simon et al. 2004, Beck and Bennett, 2002).

Environmental risk caused by anthropogenic radionuclides in the Caribbean Region

Twenty years following the introduction of Cs-137 into the atmosphere from the Chernobyl accident, little research has been conducted in the Caribbean region to assess the effects of radionuclides. Cuba, Venezuela, Brazil and Costa Rica are countries where radiogeochemical studies have been conducted. Knowing the response of the ecosystem to Cs-137 is important since it has variable depositional behavior. Zhiyanski et al. (2005) stated that Cs-137 mobility in the tropical rainforest of Bulgaria is affected by litter. This serves as a biochemical agent that enables mobility of Cs-137 and availability for plant uptake. Since the mobility of the radionuclide in the soil depends upon soil conditions, pH, soil series, solid /liquid distribution coefficient and organic matter content among others, plant uptake in the acidic forest soil will affect the mobility of the radionuclide.

Zhiyanski's findings were confirmed by other researchers investigating the Caribbean region. Most of the studies conducted were on the soil to plant transfer in the tropical forest of Venezuela and Costa Rica (LaBrecque and Cordoves, 2004, Bossew and Strebl, 2001). LaBrecque and Cordoves, (2004) found activities levels ranging from 2 Bq/kg to 14.8 Bq/kg in surface soil samples at the Gran Sabana and Sierra Pacarima in Venezuela, and about 15% of the samples had values above 5Bq/kg. These activity levels are similar to those reported by Bossew and Strebl (2001) in the tropical forest of Costa Rica. LaBrecque and Cordoves, (2004) reported that Cs-137 activity was influenced by local rainfall. Rainfall in the region of Gran Sabana and Sierra de Pacarima is very similar to the rainfall received at the Caribbean National Forest, El Yunque, which is about 200-500 cm of rain per year.

LaBrecque and Cordoves (2004) and Bossew and Strebl (2001) proposed a direct relationship between rainfall (precipitation) and the reported Cs-137 activities. Alonso-Hernandez et al. (2006) also reported a similar positive relationship (r^2=0.92) showing an increase in levels of Cs-137 with an increase in wet deposition (rainfall) at Cienfuegos, Cuba. Other studies in the Caribbean region relate elevation and soil chemistry as well as precipitation to higher activities of Cs-137. That is the case of for Venezuelan organic-rich soil and dry deposition by clouds at high altitudes (LaBrecque and Cordova 2004). Alonso-Hernandez (2006) found that grain size also has a direct relationship on the activity of Cs-137 in Cuba.

Health risk associated with radiation

Health risks most often associated with exposure to radioactivity include cancer, developmental effects (e.g. mental retardation), and non-genetic effects (UNSCEAR, 1982). Some types of cancer related to radionuclides exposure are skin cancer, leukemia and lung cancer. Ionizing radiation exposure is a known, and well-quantified, cancer risk factor. Estimation of cancer risk following radiation exposure is very uncertain with respect to regulatory and/or popular concerns. One reason is that risk estimates are usually applied to populations that are different from the populations on which the estimates are based.

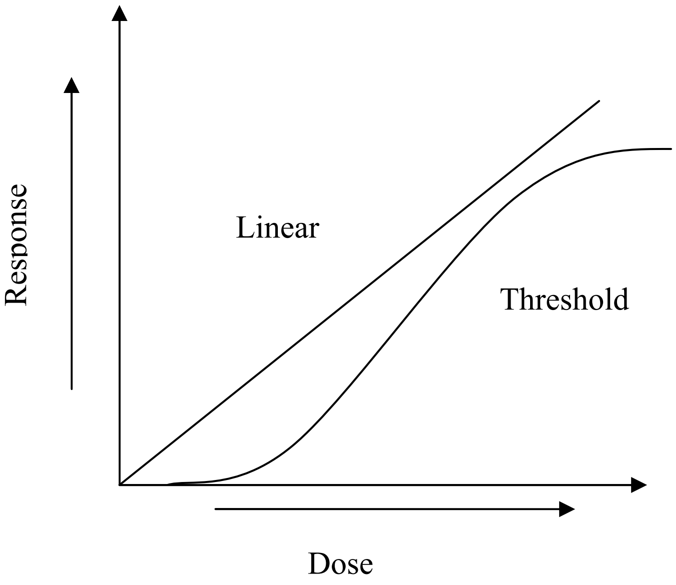


Figure 2. Assumptions for the extrapolation of the cancer risk vs. radiation dose to low-dose levels, given a known risk at a high dose (Alonso-Hernandez 2006).

Alonso Hernandez et al. (2002) measured the dose response of Po-210 and Cs-137 as the result of fish, mollusk and crustacean consumption at Cienfuegos Bay, Cuba. Observations of anthropogenic radionuclides in fish promote an understanding of how of food web dynamics influences the introduction of these man-made nuclides.

Alonso-Hernandez et al. (2002) concluded that the committed effective doses from ingestion of seafood containing Cs-137 are negligible. However, activities (50–125 Bq/kg w.w.) found in fish and mollusks from Cienfuegos, Cuba, actually exceed recommended levels for human consumption reported by the UNSCEAR (2000).

The UNSCEAR as well as the International Atomic Energy Agency (IAEA) and the Nuclear Regulatory Commission (NRC) have created limits based on the hypothetical data of responses from the exposed population after the Chernobyl accident. The no-threshold hypothesis means that increased effects are observed at high doses of radiation, but effects at low doses are not known. Therefore there is no way to determine at which dose the cancer incidence will increase in the population (Figure 2). The As Low As Reasonably Achievable (ALARA) Principal should be followed at all times to avoid exposure to radiation. As documented in the past, doses that exceed (25-50 rems) can become detrimental to human health.

STUDY AREA

Boiling Nuclear Superheated Reactor

During the early 1960's the US Atomic Energy Commission (US AEC) and the Puerto Rico Water Resource Authority (PRWRA) constructed the Boiling Nuclear Superheated (BONUS) reactor facility in order to investigate the technical and economic feasibility of the integral boiling-superheated concept (US DOE, 2003) (Figure 3). The prototype power plant was constructed in a coastal lowland area on the western coast of Rincon, Puerto Rico. The Boiling Nuclear Superheated (BONUS) reactor experienced numerous problems, including 106 unintentional reactor shutdowns, one of which resulted in the release of a radionuclides mixture which concentration was 582.3MBq into the atmosphere (US DOE, 2003).

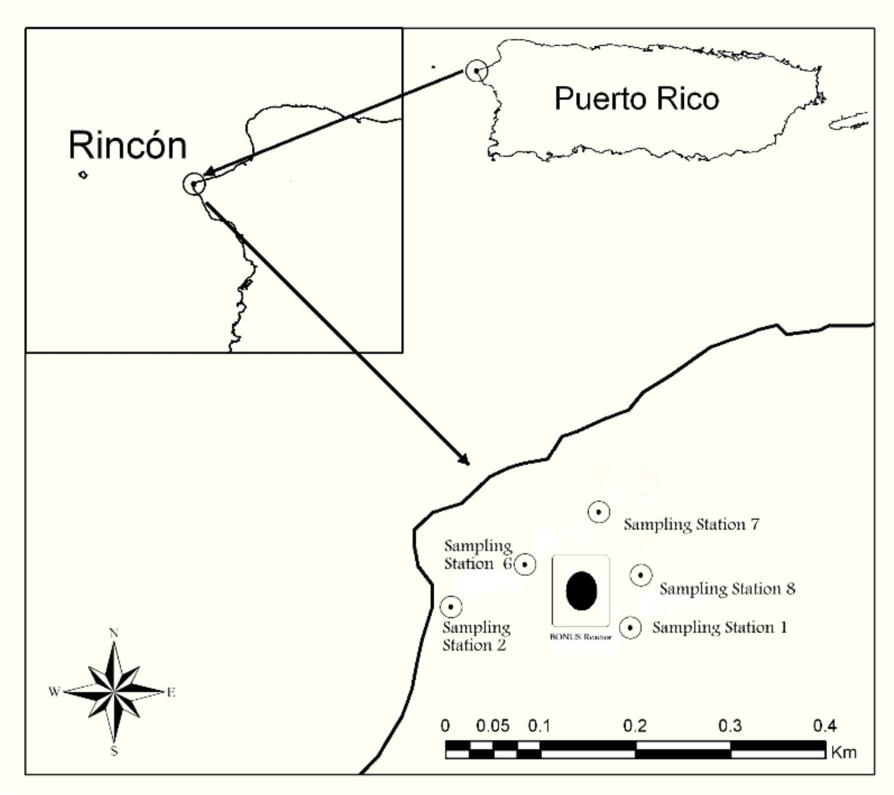


Figure 3. BONUS Reactor sampling area

The BONUS reactor facility was operational for a total of six years (1962-1968) before being decommissioned, a process which was completed in 1970 (US DOE, 2003). In 1993 the basement of the entombed reactor was flooded by rainwater as a result of a failed exhaust fan (US DOE, 2003) which may have resulted in further contamination if radionuclides were present. Recently, the local government proposed to develop a museum at the site of the BONUS facility (US DOE, 2003).

Atlantic Fleet Weapons Training Facility

The island of Vieques is located 11km southeast of the main Caribbean island of Puerto Rico (Figure 4). Vieques is 32 km long and 7.2 km at its widest point. The island is currently inhabited and its population is close to 9,000 people. For more than six decades it was used as the Atlantic Fleet Weapon Training Facility (AFWTF) (US EPA, 2001). During the time that the US Navy used the island for military purposes, the population decreased, about 26% (Ayala Carro, 1999). The population changed from about 10,000 in the 1940's to 7, 800 in the 1970's and recently the number went back to 9,000 people.

From 1999 to 2003 ammunitions containing depleted uranium were released into the atmosphere as the result of military practices, and pollutants made their way into the local aquatic and terrestrial ecosystem (ATSDR, 2002; Lindsay-Poland, 2001; Yarrow, 2000). The US Navy targeting exercises at the AFWTF ceased in 2003 and unexploded ammunitions, shell casings, scrap iron, and other military debris, including depleted uranium ammunitions are still present at the AFWTF (ATSDR, 2002; US EPA, 2001; US Navy, 2002).

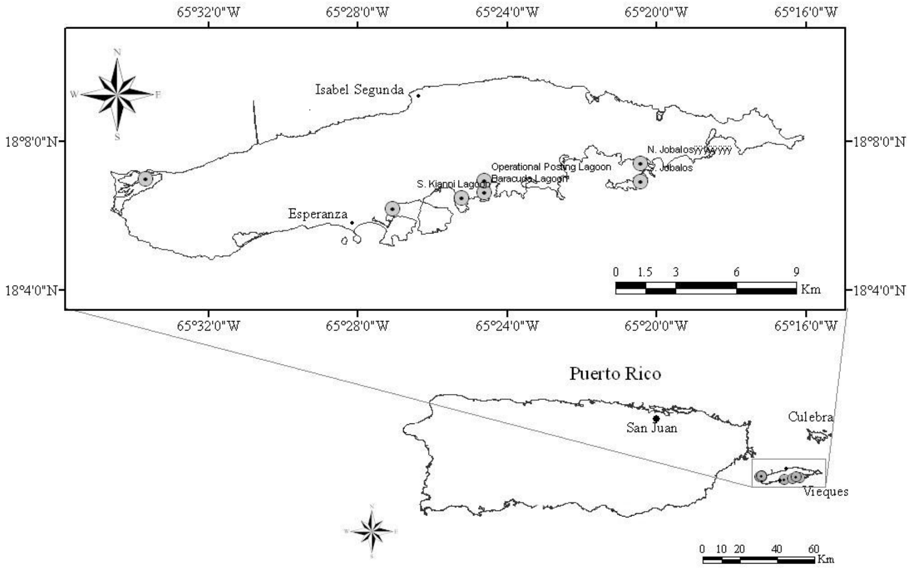


Figure 4. Vieques sampling site

The pollution released into the atmosphere by military practices has traveled more than 7.9 miles reaching the residential area of Vieques, and radionuclides may have traveled that distance as well (ATSDR, 2002). Pollutant concentrations were measured by the Agency for Toxic Substances and Disease Registry based on the information that the ammunitions used in Vieques contained TNT, trace amounts of hydrogen cyanide, aluminum and ammonia among others. It was found pollutant concentrations were below the limits permitted by regulatory agencies.

Other studies conducted on Vieques indicate that copper, lead, nickel, cadmium and manganese are present in high concentrations in plants, crops and vegetables (Diaz and Massol-Deya, 2003). Porter (1999) conducted the sole study of current radiological conditions on the island of Vieques.

Caribbean National Forest

El Verde Experimental Station is the main site of a series of experiments conducted by the Department of Energy (DOE) on the island of Puerto Rico in 1965 (Figure 5) (NRC, 2001; PRNC, 1970). The purpose of these series of experiments by the DOE was to understand the behavior of radionuclides in a tropical ecosystem. These experiments entailed the inoculation and irradiation of trees in El Verde (PRNC, 1970). The radionuclides used for the irradiation and inoculation were Cs-137, Cs-134 and tritium (NRC, 2001; PRNC, 1970). Reptiles, amphibians and insects were also dosed with radionuclides to study toxic effects in the tropical fauna (NRC, 2001; PRNC, 1970).

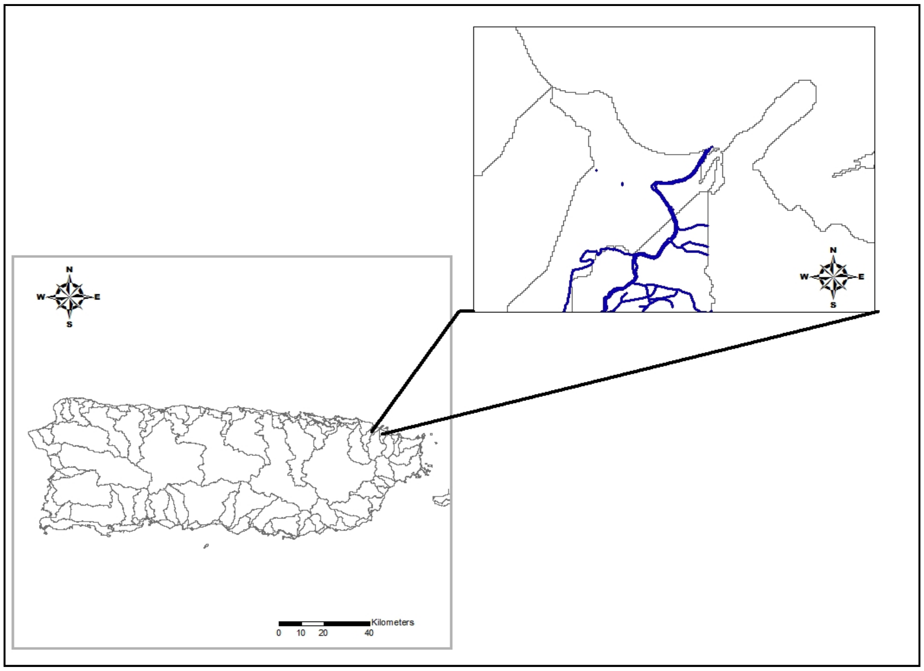


Figure 5. Sampling sites at Espíritu Santo Estuary, Rio Grande, Puerto Rico.

Irradiated Cs-137 was used as a gamma source for radiation experiments on selected vegetation plots (PRNC, 1970). As the results of this experiment, radiation levels in the area increased from 5 mrem/hr to 200 mrem/hr (US NRC, 2001) which is a forty fold increase of the radiation level in the area prior to the experiment. It was also estimated that approximately 50 % of the cesium adsorbed by trees was eliminated. Several trees were inoculated with 777 MBq of tritium at the study site by injecting their trunks with this radionuclide at an angle of 45° and a height of 25 cm above ground to analyze transpiration rates (PRNC, 1970). Reports from the Puerto Rico Nuclear Center (1968) indicated that once released into the environment radionuclides such as Cs-134 and Sr-85 were bound in the litter and to the surface soil of the rainforest. This fact was verified by the rapid increase in Cs-134 and Sr-85 activity in the first 5 cm of the soil where the experiment was conducted (PRNC, 1968).

HYPOTHESES

The introduction of anthropogenic radionuclides in Puerto Rico which occurred as the result of governmental, military and industrial activities has resulted in local distribution of Cs-137 in Puerto Rico. The distribution is expected to vary from site to site. In order to assess the impact of such activities, this proposed work will test the following hypotheses:

1. Cs-137 concentration found in the tropical rainforest watersheds and estuaries will have a down slope gradient and the hill area's higher Cs-137 concentrations will be located near Cocoa Beach.
2. Cs-137 concentration in the island is the result of global fallout and not the result of governmental activities.
3. Mineralogy of the study area will be similar in the three different ecosystems due to geological formation of the island.
4. Mobility of Cs-137 will be determined by the abundance of clays and organic matter in the different ecosystems.
5. There is no difference between the retention of Cs-137 by soil and sediment samples at the study areas
6. Soil and sediments from study areas have the capacity to retain heavy metals and other chemical elements

OBJECTIVES

The overall goal of this study is to describe the behavior and determine the distribution of radionuclides that have been introduced into the environment of Puerto Rico. To meet this goal the following objectives were pursued:

- Quantify gamma activity levels at each study site.
- Examine the fate and transport of anthropogenic radionuclides in the soil and sediments of the three study areas.
- Conduct a grain analysis at each site to quantify the amounts of clay available for anthropogenic radionuclides.
- Assess the chemical composition of sediment and soil samples.

CHAPTER II: RADIOGEOCHEMISTRY OF THREE STUDY SITES IN PUERTO RICO

INTRODUCTION

Samples were collected from three municipalities in the island of Puerto Rico in order to investigate their various radiogeochemical characteristics. The island of Vieques, El Verde Experimental Station, along with the Espiritu Santo Estuary and the adjacent area of the BONUS facility are described below.

Vieques

Vieques is the largest of the adjacent island municipalities of Puerto Rico. Located in the Caribbean Region, the social history of Vieques' is as rich as its environment. Vieques has approximately 115 km^2 of coastline which encompasses various ecosystems. From the dry coast to a central ridge that reaches its highest point at Monte Pirata located in the southwest region. The elevation of Vieques varies approximately 300 m (Renken et al. 2000). Surface freshwater on the island is provided by rainfall which contributes an average of 200 cm of rain per year (Renken et al. 2000). The rain serves as a freshwater source to local rivers and streams that flow intermittently in direct response to rain events (Renken, et al. 2000).

Vieques was formed from igneous and volcanic rock, mostly granodiorite, quartz diorite, and some lavas, which created the bedrock of the island. This bedrock is exposed and weathered on most of the western half of the island and some portions of the eastern half of the island. The island's geologic formations include two alluvial valleys, Esperanza and Resolucion (Renken et al. 2000). The Esperanza alluvial valley is about 0.5 km to 1 km wide and 5 to 6 km long and the alluvial deposits are about 18 m thick (Renken et al. 2000). The alluvial sedimentary deposits generally consist of a self-contained mixture of gravel, sand, silt, and clay (Renken et al. 2000). In 1989, the United States Geological Survey (USGS) reported that groundwater flow in Esperanza valley alluvial deposits was toward the south and toward the sea. The Resolucion alluvial valley is, on average, 9 m thick and overlies the bedrock, which is composed of granodiorite and quartz diorite. This valley also has a semi-confining clay layer at about 6 to 9 m below ground surface. Resolucion, which is located next to Monte Pirata, receives more rainfall recharge than Esperanza (Renken, et al. 2000).

For more than 60 years, the eastern portion of the island of Vieques served as a weapons testing site for the U.S. Department of Defense. During the 1990's, U.S. Navy targeting exercises at the AFWTF involved the use of armor-piercing ammunitions containing depleted uranium (Yarrow, 2000). Impact studies indicate that anthropogenic material released into Puerto Rico's environment resulted in the contamination of natural resources via surface and groundwater transport (Diaz and Massol-Deyá, 2003; U.S. EPA, 2001; Hunter and Arbona, 1995).

Boiling Nuclear Superheated Power Station (BONUS)

The BONUS superheated nuclear power plant prototype facility was constructed to investigate the technical and economic feasibility of the integral boiling-superheated concept. BONUS was the eighth nuclear power plant constructed in the U.S. The main components for the Center for Energy and Environmental Research in Puerto Rico were the BONUS facility and three other sites. This complex consisted of 176 acres managed by the University of Puerto Rico and the Puerto Rico Electric Power Authority. The US Atomic Energy Commission (US AEC) and the Puerto Rico Water Resource Authority (PRWRA) began construction of the BONUS Facility in 1962.

The BONUS facility was constructed within the coastal lowland area on the western coast, near Rincón. BONUS was constructed less than a mile from the merging Caribbean Sea and Atlantic Ocean. The beach next to the facility is considered to be one of the islands' best surfing beaches and is frequented by many surfers. No nearby river or stream is adjacent to the BONUS facility. As such, surface water-mediated soil and sediment transport depends on local rain events, which are generally only a few centimeters per year.

During its operation (a total of six years 1962-1968), the BONUS reactor experienced 106 unintentional reactor shutdowns. As of yet, there are no conclusive studies to assess the total environmental impact of this facility. Records indicate that during one unintentional shutdown, the BONUS reactor released 582.3MBq into the atmosphere and a radiation dose between 180-110 mrem was received by two employees at the BONUS facility (US DOE, 2005). A variety of radionuclides were used in the daily operation of the prototype power plant.

Major efforts were made to remove all radioactive material associated with the BONUS facility during the decommissioning process. During this process, the reactor and radioactive material were entombed within a concrete monolith (Table 3). Recent reports indicate that radioactive material remained in the BONUS facility after the decommission process was completed (Table 4). After decommissioning the plant, approximately 4.81×10^8 Bq of radioactivity was contained in the pipes, as well as other external components to the power plant (US DOE, 2005). Approximately $1.96\ 10^{15}$ Bq was left inside the entombment system with the expectation that the total activity would decrease as time passed as a result of characteristic decay processes of individual radionuclides (US DOE, 2005).

Table 3. Past activities (measured in 1968) and recent activity estimates (determined in 2001) of principal radionuclides entombed with the BONUS reactor for 1968 and 2001 (Adapted from US DOE, 2005).

Radionuclide	Half-Life	Activity (Bq)	
		1968	**2010**
Cobalt-57	271 days	8.247×10^{13}	0
Cobalt-60	5.27 years	5.764×10^{14}	2.300×10^{12}
Nickel-63	96 years	3.108×10^{13}	2.323×10^{13}
Manganese-54	312 days	3.785×10^{13}	0
Iron-55	2.7 years	1.242×10^{15}	2.903×10^{10}
TOTAL	**-**	**1.971×10^{15}**	

Table 4. Past activities (measured in 1968) and recent activity estimates (determined in 2001) of principal radionuclides external to the entombed BONUS reactor for 1968 and 2001 (Adapted from US DOE, 2005).

Radionuclide	Half-Life	Activity (Bq)	
		1968	**2010**
Manganese-54	312 days	4.070×10^6	-
Cobalt-60	5.27 years	3.7×10^8	1.477×10^6
Zinc-65	244 days	5.92×10^7	-
Silver-110m	250 days	3.11×10^5	-
Antimony-125	2.77 years	1.41×10^6	-
Cesium-137	30 years	5.5×10^8	2.088×10^7
TOTAL	**-**	**4.81×10^7**	

During the period of operation Cs-137 was the primary radionuclide present at the BONUS facility. Ni-63 was also found at the facility when the reactor was being utilized. Ni-63 has been identified as the radionuclide of greatest concern, primarily because of its 96 years half-life. Ni-63 is the main contributor to radiation in the entombed system (that was buried in the facility) at the BONUS facility. However, Cs-137, was the greatest contributor to the total activity of the entombed system's external pipes and other various structural components at the BONUS facility.

During hurricane George in 1998, the enclosed dome was flooded and the basement doors leaked its contents (US DOE, 2005). Debris from the plant was then carried down slope through storm water runoff (US DOE, 2005).

It is important to understand the geochemical characteristics of soils surrounding the BONUS facility because of the existing potential for leakage at the BONUS facility, as well as the previous introduction of material from this prototype power plant to the local environment.

Given the history of the BONUS facility and the potential release of radionuclides into the local environment, geochemical properties of soils surrounding the BONUS Facility should be determined. Previous researchers have identified the erosion of radionuclides as a secondary source of sediment contamination (Claval et al. 2004 and Charmasson, 2003). Radiogeochemical properties of the nearby Dome Beach depositional system were examined in order to investigate the potential for local Cs-137 deposition and removal, as well as to identify the potential for BONUS-derived material to be incorporated into the local food web.

El Verde Experimental Station and Espiritu Santo Estuary

The Caribbean National Forest (CNF) is the only tropical rain forest in the United States National Forest System. This unique ecosystem has been protected since 1876 when it was declared the first natural reservoir of the Caribbean region. In 1903, the US

National Forest System began managing this forest of 5,115 acres. Today the CNF is composed of more than 28,000 acres and its boundaries are shared by thirteen municipalities on the east coast of the island of Puerto Rico.

The CNF environment is characterized by its year round tropical climate and the large amount of rainfall. It has been calculated that precipitation at the CNF exceeds 508 cm of rain per year. Trade winds bring all the clouds to the highest point of the rainforest where the highest elevation is 1,076.9 m causing condensation and further precipitation which will increase riverine input to local ecosystem.

Stream flows in the rainforest are highly variable (ten-fold increases in discharge have been recorded within an hour), and fluctuate with rainfall (Larsen and Torres-Sanchez, 1998). Within this tropical rain forest, streams are often located in steep, bedrock- and boulder-lined channels within narrow valleys. Headwater channels, frequently lined with trees, have shallow pools (<0.75 - 1.0 m deep) and exhibit relatively constant temperatures ranging throughout the year between 18 ° and 24 °C (Larsen and Simon 1993). Second and third-order tributaries present in CNF are typically shallow (< 1 m deep) and have relatively open canopies (Larsen and Torres-Sanchez, 1998). The pH of the rivers in the rainforest ranges between 7 and 7.7 with an average pH of 7.2.

Because of its specialized ecosystem the CNF has often served as a living laboratory for numerous scientific investigations. CNF also serves as a model for many other reserves worldwide. One of the biggest experiments that occurred at the CNF was performed during the nuclear testing era. The El Verde Research Station, which encompasses 156 acres of the CNF, served as a site for local terrestrial ecology radiation experiments that were managed by the US Atomic Energy Commission (AEC) from 1964 to 1976. These experiments were undertaken 424 m above sea level as part of the Rain Forest Project (RFP) of the Puerto Rico Nuclear Center, (Odum and Drewery, 1970). Researchers involved with the RFP conducted a wide array of experiments designed to investigate the rainforest's response to radiation. These experiments examined a variety of processes, including mineral cycling and water movement. The primary experiment conducted at the El Verde site involved the irradiation of a forest parcel with 3.7×10^{14} Bq Cs-137 source.

The US Department of Agriculture compared the results of this study with those obtained from similar experiments within the Panamanian forest (Odum and Drewery, 1970). Forest metabolism and water exchange studies were also conducted. Major objectives of this initial and subsequent smaller-scale gamma irradiation experiments conducted at the study site were to: 1) determine the radiation effects on a rainforest ecosystem (technically classified as a subtropical wet forest), 2) examine the cycling of fallout elements, and 3) gain additional understanding of vertical and horizontal forest structure and ecological processes including nutrient cycling, energy flow, and forest regeneration.

The Rainforest Project

Researchers conducted metabolism and defoliation experiments using various radionuclides in order to observe measurable changes in the forest vegetation (Table 5). The radiation source of 10^{14} Bq of Cs-137 (close source) was installed in December, 1964. The period of irradiation was January 19, 1965 to April 26, 1965 (Desmarais and Helmuth, 1970). Desmarais and Helmuth stated that "damage around the radiation source was quite obvious by the end of the radiation period and persisted throughout the following year". They also reported that the damage was confined within an area of 12 m radius of the radiation source.

Table 5. Summary of radionuclides used at the Rainforest Project.

Isotope	Date Applied	Original Activity (Bq)	Half-life
^{3}H	Jan. 6 1967	74 x 10^{7}	12 years
^{3}H	May 1968	18.5 x10^{8}	12 years
^{32}P	May 1969	3.7 x 10^{7}	14.5 days
^{32}P	May 1972	17.02 x 10^{8}	14.5 days
^{137}Cs	Sept. 18, 1968	17.02 x 10^{6}	30 years
^{86}Rb	Sept. 18, 1968	65.453 x 10^{7}	45 days
^{85}Sr	Sept. 18, 1968	7.03 x 10^{6}	64 days
^{54}Mn	Sept. 18, 1968	12.58 x 10^{6}	313 days
^{85}Sr	Aug. 10, 1967	3.7 x 10^{7}	64 days
^{134}Cs	Aug. 10, 1967	29.6 x 10^{6}	2.062 years
^{65}Zn	Aug. 3 , 1967	11.1 x 10^{7}	244 days
^{85}Sr	Jan. 6, 1966	3.7 x 10^{7}	64 days
^{134}Cs	Jan. 6, 1966	3.7 x 10^{7}	2.062 years
^{54}Mn	Jan. 6, 1966	3.7 x 10^{7}	313 days

The local destruction of forest structure resulted in new patterns of succession (Odum and Drewery, 1970). The vegetation structure of a tropical rainforest is measured by the number and quantity of species found, and form and position of plants within the forest. Of great importance for the RFP was the development of the ability to understand the succession pattern. In November 1965, the radiation source area was re-sampled and it was determined that the area that was impacted by the radiation had grown from the original 12 m radius to a radius of 24 m. Defoliation had taken place in the damaged area and the optical density had declined (less leaves will absorb less light) (Odum & Drewry, 1970). The irradiation of the ecosystem with Cs-137 resulted in a notable increase in the number of crownless plants within a24 m radius and almost a complete loss of leaves from the local vegetation (Odum & Drewry, 1970).

Table 6. Radionuclide movements on vegetation after their injection (Activity in Bq/g dry weight) (From: PRNC, 1985)

Sample	Cs-137 on *Matayba sp*		Rb-86 on *Dacroydes sp.*		Sr-85 on *Dacroydes sp.*	
	20 days	132 days	20 days	132 days	20 days	75 days
Leaves	2.405	15.059	84.027	562.141	0.22	0.444
Twigs	0	18.796	0	2409.292		0.873
Wood, 1 ft above injection hole	206.053	17.168	739.667	536.352		2.346
Wood, at level of injection hole	1.702	26.042	967.254	507.677		0
Wood, base of tree	219.373	13.801	3255.63	1568.911	0.0	0.081
Bark, base of tree	6304.134	229.585	23178.65	Below detection limit		125.245

Water movement in soils was further examined using 74 x10^7 Bq of tritium in the form of titrated water. The tritium was applied to a soil parcel of 0.94 m^2. Results of this experiment indicated that although most of the tritium passed through the upper 18 cm of the soil as a pulse, a fraction remained in the clay-rich soil. Another component of the water movement experiment involved injecting tritiated water into trees, via holes bored into tree trunks near the ground (Kline and Jordan, 1970). Leaves from the injected trees were collected and analyzed for tritium.

Cs-137, Sr-85, Rb-86 and Mn-54 injection experiments on trees were conducted (Table 6) in order to investigate the effects of radioactive fallout in tropical ecosystems (PRNC, 1970). These 'fallout' radiation experiments, conducted from 1966 through

1970, included studies on insect and amphibian ecologies, food web dynamics and effects of rainfall on the fate of radionuclides (dissolved and particulate) (PRNC, 1970).

The diverse aquatic and terrestrial ecosystems of the island of Puerto Rico and its municipalities have been studied by many researches over the past decades. Cs-137 was locally introduced at two of the three study sites that were examined during this investigation. One of the major goals of this investigation is to determine the fate of the Cs-137 that was utilized during the previously described experimental activities. Another goal of this study is to document the retention and post-depositional behavior of global fallout Cs-137 in Puerto Rico's various ecosystems.

METHODS

Soil and sediment samples were collected from the BONUS facility, CNF, Espiritu Santo River Estuary and Vieques using a polycarbonate core liner. At eight cores were collected at the BONUS facility. These cores were collected, in pairs, from each side of the fenced facility. Samples from the CNF were collected from the Radiation Center (used by Odum during the Rainforest Project) and inside the protected area where tree injection experiments took place. At Espiritu Santo River Estuary, samples were collected from mangrove areas, as well as from a low energy beach and along the mouth of the river. Surface sediment and soil samples, ranging 1-5 cm in depth, were collected from six sites (Operational Posting Lagoon, Kiani Marsh Lagoon, North and South Jobalos Lagoon, Baracuda Lagoon and Green Bay Lagoon) within restricted areas of the Vieques National Fish and Wildlife Refuge (VNFWR). These restricted areas at the VNFWR are not open for public use as they represent a potential threat to public health and safety, due to the potential existence of unexploded ordinance.

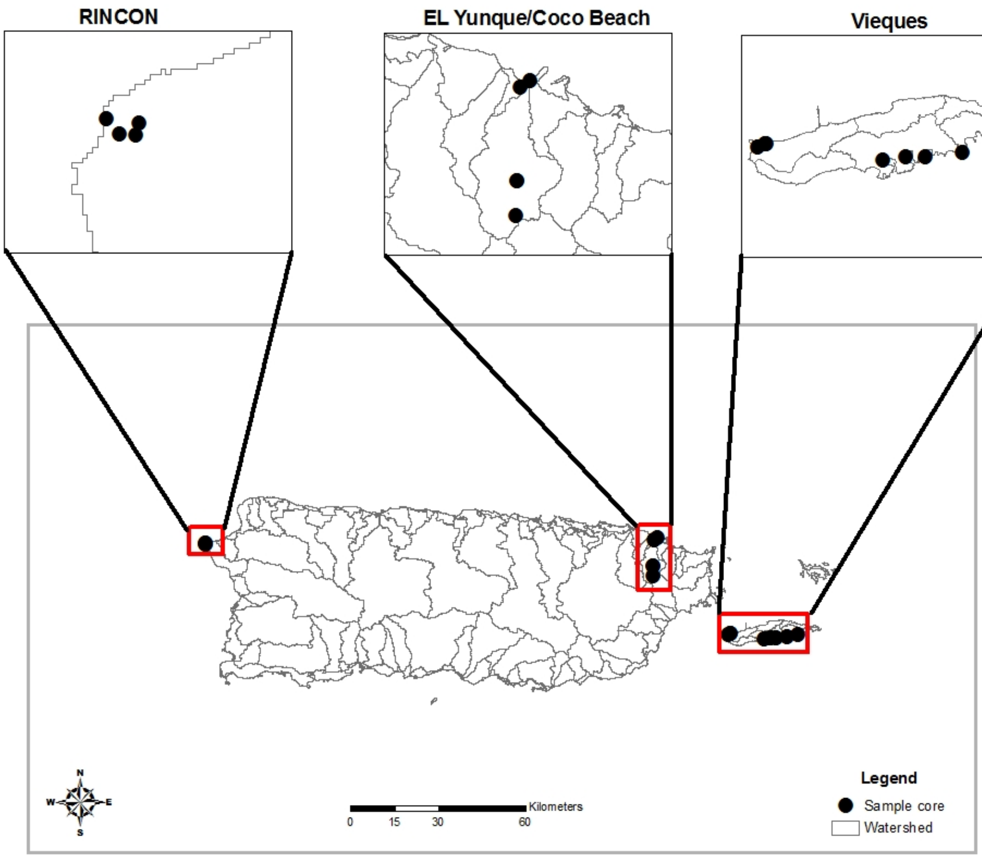


Figure 6. Sampling sites in Puerto Rico

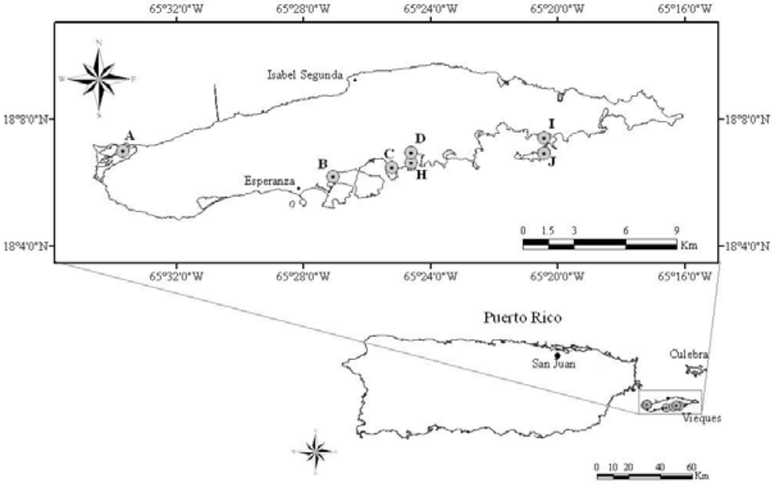


Figure 7. Surface and downcore Sampling Sites in Vieques, PR.

Two types of samples were taken during this project, surface samples and core samples. Surface samples (1-5 cm deep) were taken using a shovel. Core samples were taken using the polycarbonate core liner (3 m long, 5 cm radius). Once collected, cores were sectioned using an extruder. The extruder was built to allow for 0.5 cm and 1 cm sampling intervals. Core samples within the uppermost 10 cm were sectioned at 0.5 cm thickness. Samples from 10 cm in depth and beyond were sectioned utilizing 1 cm thickness intervals. Samples were cut using polycarbonate spatulas, which were rinsed with water between each sample to avoid cross contamination.

The sectioned samples were stored in commercial brand zip-lock bags. The stored samples were transported to the USF College of Marine Science Aquatic Radiogeochemistry Laboratory in portable coolers and upon arrival placed in -4 °C commercial freezer. In preparation for laboratory analysis, samples were allowed to thaw and then aliquots of each section were weighed, dried, and reweighed to determine the sediment porosity. The samples were dried using a freeze drier at -20 °C for approximately 72 hours.

Table 7. Sampling location, description of habitat conditions. Mangrove Forest indicated by MF. Lagoon indicated by L. Marsh indicated by M

Sample Site	*Location*	*Type of Sample*	*Type of Environment*	*Water Depth (cm)*
Mosq.Bay	Vieques	Sediment	MF	30 cm
Kiani Lagoon	Vieques	Sediment	MF	15 cm
Green Bay	Vieques	Sediment	M	10 cm
South Kiani Lagoon	Vieques	Sediment	M	10 cm
Baracuda Lagoon	Vieques	Soil	L	N/A
Operation Posting Lagoon	Vieques	Soil	L	N/A
S. Jobalos	Vieques	Sediment	MF, L	10 cm
N. Jobalos	Vieques	Sediment	MF, L	10 cm

Gamma analysis for Cs-137

Sediment and soil samples were prepared for radionuclide analyses following techniques described in Johnson-Pyrtle and Scott (2001). The samples, packaged in plastic test tubes, were assayed for gamma emitters using two Canberra® high purity germanium well gamma detectors, connected to a Canberra Genie multi-channel analyzer which records the gamma spectra in 4096 channels. The two detectors were calibrated using U.S. National Institute of Standards and Technology 4357 Ocean Sediment multi-line and Canberra Industries MGS-5 sediment standards.

The resulting spectra were analyzed for the Cs-137 specific energy peak at 661 keV, and the activity of each sample was then determined. Detector performance was verified using a multiline liquid standard, a Peruvian soil standard, Columbia River sediment standard and Ocean sediment standard prepared by NIST.

Cs-137 inventories for each core were calculated as follows:

$$I = k \quad \rho_i \, t_i \, C_i,$$

Where I = Cs-137 inventory ($\mathrm{Bq/m^2}$) for each sediment core,

C_i = Cs-137 (Bq/g) measured in each increment,

ρ_i = average particle density ($\mathrm{g/cm^3}$),

t_i = the thickness of each increment (cm),

k = 10,000, a constant for converting ($\mathrm{Bq/cm^2}$) to ($\mathrm{Bq/m^2}$)

Gamma analysis of Pb-210 and Ra-226

Sealed in plastic vials, Ra-226 and Pb-214 were allowed to come into secular equilibrium by waiting for a period of no less than 30 days prior to gamma analysis. This period corresponds to approximately 8 half-lives of Rn-222, the immediate daughter of Ra-226. Pb-214 is a daughter product of Ra-222 and a precursor to Pb-210. Therefore, the activity of Ra-226 can be determined by determining the activity of Pb-214,.

By subtracting the Pb-214 (Ra-226) activity from the Pb-210 activity, the amount of unsupported excess Pb-210 was determined. Samples were analyzed for gamma emitters for at least 24 hours using the low background, germanium well detector. Sample activities at 46 keV (Pb-210) and 351 keV (Pb-214) were determined. Energy and efficiency performance were calculated and factored in prior to determining the actual activities (see appendix G).

Grain size analysis

Particle size distributions were determined for all sediment and soil samples using the traditional sieving method and a Micromeritics Saturn DigiSizer® 5200 (a high resolution laser particle size analyzer) (Jackson, 1958; Micromeritics Instruments Corporation, 2003). Prior to grain size analysis, one gram of each freeze-dried sample was sieved using a 63 µm mesh size screen, and a 5 % solution of Sodium Tripolyphosphate (Calgon). This process created a slurry which facilitated the wet sieve of the sample**.** Particles larger than 63 µm were collected from the sieve, air dried and weighed. Finer-grain size material that passed through the 63 µm sieve was weighed and grain size fractions were determined utilizing the Saturn DigiSizer. Particle size classes were defined as follows: clay size $\leq 4\ \mu m$; $4\ \mu m <$ silt $\leq 63\ \mu m$; sand and larger $> 63\ \mu m$. The Saturn DigiSizer analysis provided a raw percentage of each particle class. This percentage was then subtracted from the data obtained from sieving and weighting of the sample to obtain a final class percentage.

Loss on ignition analysis

Organic matter content was determined using standard Loss on Ignition (LOI) analysis procedures (Heiri et al., 2001, Dean, 1974). Soil and sediments samples were ground and subsequently homogenized by either stirring by hand or shaking in a closed container. Immediately afterwards, the powdered samples were placed in pre-weighed crucibles and dried in an oven at 105 ºC for 24 hours. The dried samples were allowed to cool to room temperature in desiccators and afterwards were weighed in order to determine the initial dry weight (DW 105) of each sample. Once the initial dry weight was obtained, the samples were heated in a furnace to 500-550 ºC for 4 hours. Samples were then cooled to room temperature again in desiccators and re-weighed in order to obtain the dry weight of sample (DW_{550}) in grams. LOI was calculated as follows:

$$LOI_{550} = ((DW_{105} - DW_{550}) / DW_{105}) * 100$$

Where: LOI_{550}=Loss on Ignition (as percent at 550 ºC)

DW_{105}= dry weight of sample after 24 hours at 105 ºC

DW_{550}= dry weight of sample after 4 hours at 550 ºC

The weight loss determined from this procedure is proportional to the amount of organic carbon contained in the sample (Heiri et al., 2001) (see Appendix C for details).

Inductively coupled plasma-optical emission spectrometer (ICP-OES)

Inductively coupled plasma-optical emission spectrometer analysis allowed for the determination of Fe and Mn profiles and the likelihood of oxic, suboxic or anoxic conditions at the study sites. The procedure utilized during this investigation was adapted from EPA Method 3050b (see Appendix D for details). The procedure is not a full digestion. It is a strong acid digestion that dissolves almost all elements that could become environmentally available.

The ICP-OES method utilizes 1-2 grams of the homogenized sample. The initial acid addition consists of 10 mL 1:1 HNO_3 (1 part DI water to 1 part conc. HNO_3). After the acid addition was introduced to the sample and stirred utilizing a glass rod, the mixture was covered with a watch glass. The sample was subsequently heated on a hotplate at $95^oC \pm 5^o$ for 10 to 15 minutes, and afterwards allowed to cool. After reaching room temperature, 5 mL concentrated HNO_3 was added to the solution. The sample was stirred again, the watch glass replaced and the sample reheated to $95^oC \pm 5^o$ for 30 minutes. If brown fumes (an indication of oxidation of the sample by HNO_3) were generated during this process, the previous step was repeated and another 5 mL of concentrated HNO_3 added. Afterwards the sample was returned to the hotplate and the supernatant was allowed to evaporate to approximately 5 mL by heating at 95^oC, without boiling, for two hours. Complete evaporation or drying of the sample was avoided.

The sample was allowed to cool to room temperature. Afterward, 2 mL of water and 3 mL of 30 % H_2O_2 were added. The beaker was covered with a watch glass and warmed to 60^oC. Aliquots of 1mL of 30 % H_2O_2 were added until bubbling subsided . Less than 10 mL of 30 % H_2O_2 were added. The sample was then covered with a watch glass and heated (max of 95°C) until the volume was reduced to approximately 5 mL. Next, 10 mL concentrated HCl was added to the sample, covered and stirred and heated for 15 minutes and then allowed to cool to room temperature.

After attaining room temperature, the sample mixture was diluted to 100 mL with deionized water and subsequently centrifuged at 2,000-3,000 rpm for 10 minutes to remove digested particulates. Once centrifuged, another 10 mL of concentrated HCl was added to the sample, which was then heated and stirred for 15 minutes. This mixture was then filtered through a pre-weighed and pre-labeled Whatman No. 41 filter paper. An aliquot of the filtrate, collected in a 100 mL volumetric flask, was analyzed via the ICP-OES instrument.

Mineralogical analysis by X-ray diffraction

The mineralogical composition of soil and sediment samples from the various ecosystems in Puerto Rico was determined using an X-ray diffraction technique (see appendix E). The mineralogical composition of the samples was examined utilizing a Bruker XRD D4 Endeavor. The operating conditions for the instrument are 20.5 °C and 65 % humidity. The step-size and count time used for analyzing the clay size fraction (<2 µm) were 0.02° 2Theta and 30 seconds.

Sample preparation prior to analysis was performed following and adaptation from Jackson (1958). Samples were treated with an acidic acetate solution for 24 hours to remove organic matter that may have been present. Afterwards the sample was centrifuged for 15 minutes at 1300 rpm, and subsequently placed in a water bath at 50 °C for 3-4 hours. After being allowed to cool to room temperature, the sample was centrifuged again at 1300 rpm for 15 minutes and treated with hydrogen peroxide and a NaOAc buffer solution at pH 5 to remove calcium carbonate. This procedure was performed in a water bath for 30 minutes with intermittent stirring. After 30 minutes, the sample was centrifuged and rinsed with 1 N NaOAc. Afterwards a smear of the sample was placed on glass slides and allowed to air dry in preparation for XRD analysis.

Each clay mineral has a specific feature that can be used for identification via XRD analysis. Peak analysis was initially performed after each sample was air dried and once again 24 hours after the application of ethylene glycol. Peak identification of expandable clays was validated by peak shifting which resulted from the ethylene glycol treatment. Illite is a non-expanding group, which is characterized by intense 10-angstrom 001 and a 3.3-angstrom 003 peaks that remain unaltered by ethylene glycol (Poppe et al. 2001). Kaolinite is characterized by a peak at 7 angstroms which will not shift as a result of the glycol treatment (Poppe et al. 2001). Smectite yields XRD patterns that are characterized by basal reflections that vary with humidity. When saturated with ethylene glycol, the 001 reflection of most smectites will swell to about 17 angstroms (Poppe et al. 2001).

RESULTS

Gamma spectroscopy

Downcore Cs-137 activities at Kiani Lagoon and Mosquito Bay range from 0 (or below detection limit) to 2 dpm/g and from 0 to 12 dpm/g, respectively (Figures 9 and 10). Cs-137 activities, in general, are higher at Mosquito Bay, where a maximum activity of 12 dpm/g is located at 1 cm depth. This is likely a result of higher concentrations of clay-size material at the Mosquito Bay site which led to increased adsorption and retention of radionuclides compared to the Kiani Lagoon site. Cs-137 peaks for Mosquito Bay are located at 1 cm, 20 cm and 25 cm depth. Kiani Lagoon exhibits lower Cs-137 activity with a maximum at 1 cm.

It should also be noted that excess Pb-210 data for Mosquito Bay shows a trend of peaks that coincide with Cs-137 peaks throughout the core (Figure 10). In terms of activity for excess Pb-210, the activity does not seems to be as high as Cs-137 at Mosquito Bay but it does show peaks that reach 4 dpm/g at that site. Kiani Lagoon excess Pb-210 activity reaches a maximum value of 9 dpm/g. The higher activity is located at the surface of the core. The activity in general decreases with depth. There were three sub surface peaks found in this core at 18 cm, 24 cm and 34 cm depth (Figure 9).

Inventory calculations for Kiani and Mosquito Bay demonstrate that Kiani Lagoon has a higher Cs-137 inventory (0.1 dpm/cm^2) when compared with Mosquito Bay

(0.04 dpm/cm^2). If it is assumed that the initial distribution of the Cs-137 fallout input was uniform, the deviations in the measured distribution of Cs-137 from the local fallout inventory should represent the net impact of soil redistribution during the period following Cs-137 deposition.

Lowest Cs-137 activities were determined for surface sediment and soil samples collected from Green Bay (below detection limit) and Baracuda Lagoon (below detection limit), respectively (Figure 11). Cs-137 activities in surface samples collected at these two locations are generally below detection limits. The highest surface Cs-137 activity, 0.1 dpm/g, was determined in a soil sample collected from the Operational Posting Lagoon (Fig.11). Cs-137 activities for surface samples collected from mangrove forest environments ranged from 0.036 dpm/g at S. Jobalos to 0.0198 dpm/g at Kiani Lagoon (Table 8, Fig.11).

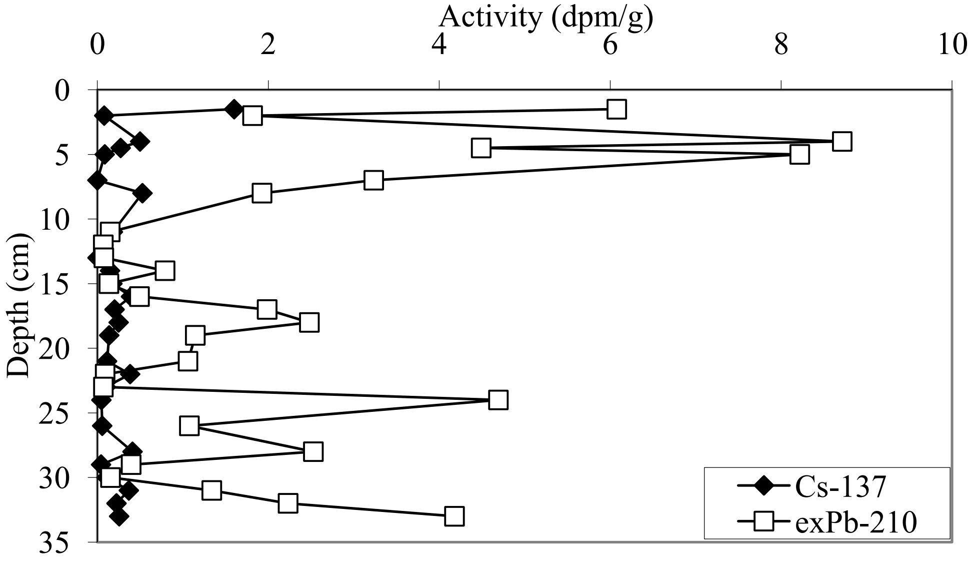


Figure 8. Downcore Cs-137 and exPb-210 Kiani Lagoon, Vieques, PR.

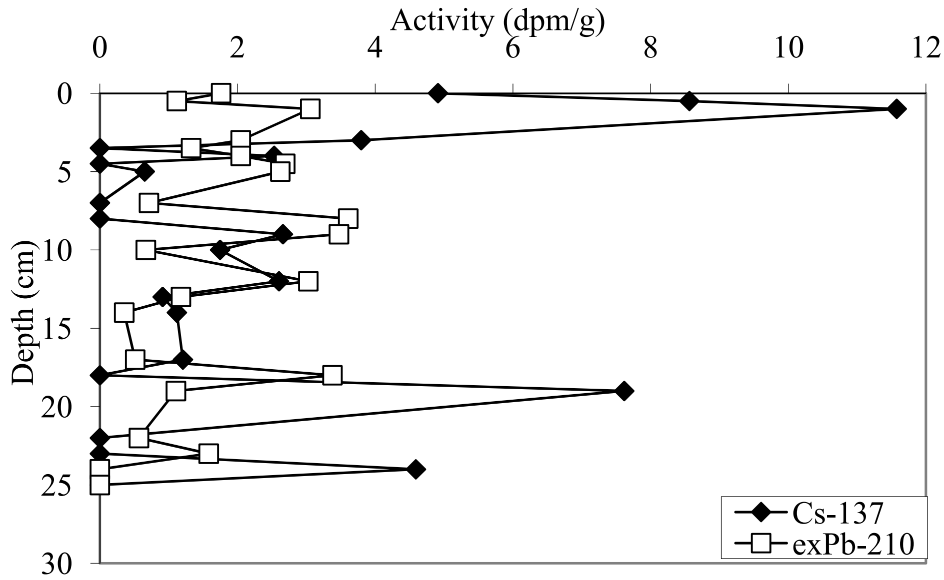


Figure 9. Downcore Cs-137 and exPb-210 Mosquito Bay, Vieques, PR.

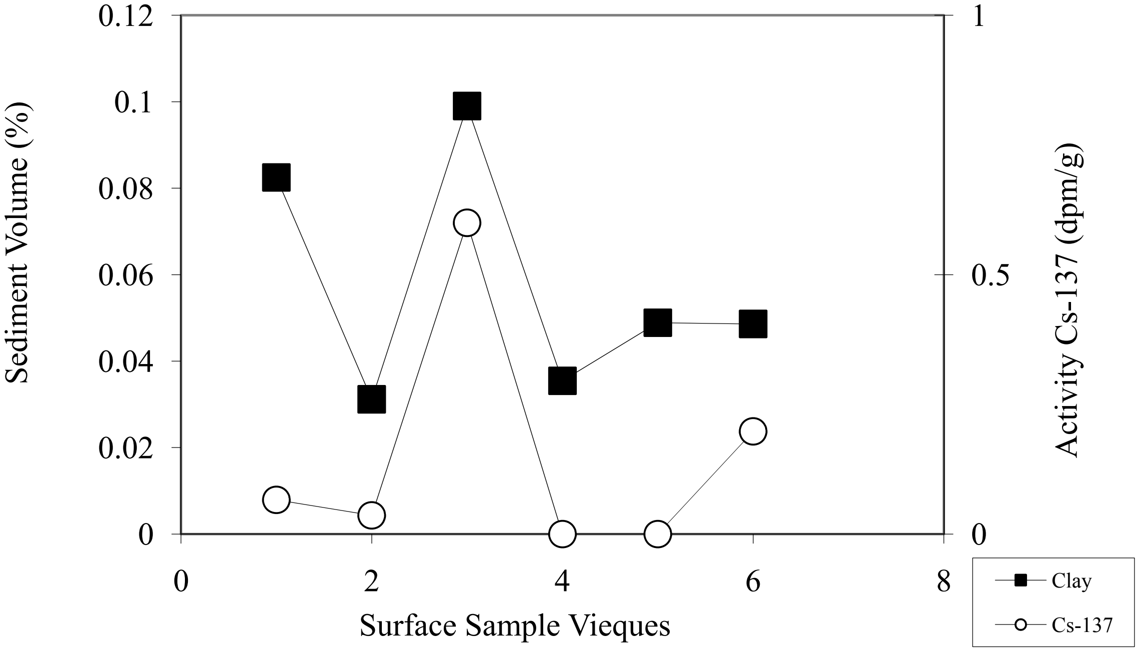


Figure 10. Surface samples gamma analysis and clay content

Downcore profiles for Cs-137 at the BONUS facility area for Station 1 and Station 2 show activities that range from 4 dpm/g to 12 dpm/g and from below detection limits to 1 dpm/g respectively (Figure 12 and 13). Station 1 profile shows two peaks, the first one at 6-8 cm depth (7 dpm/g) and the second peak at 10 cm depth (12 dpm/g) (Figure 12). The exPb-210 profiles show an activity that decreases as a function of depth. One peak stands out at 10 cm depth, which also coincides with the highest activity peak of Cs-137.

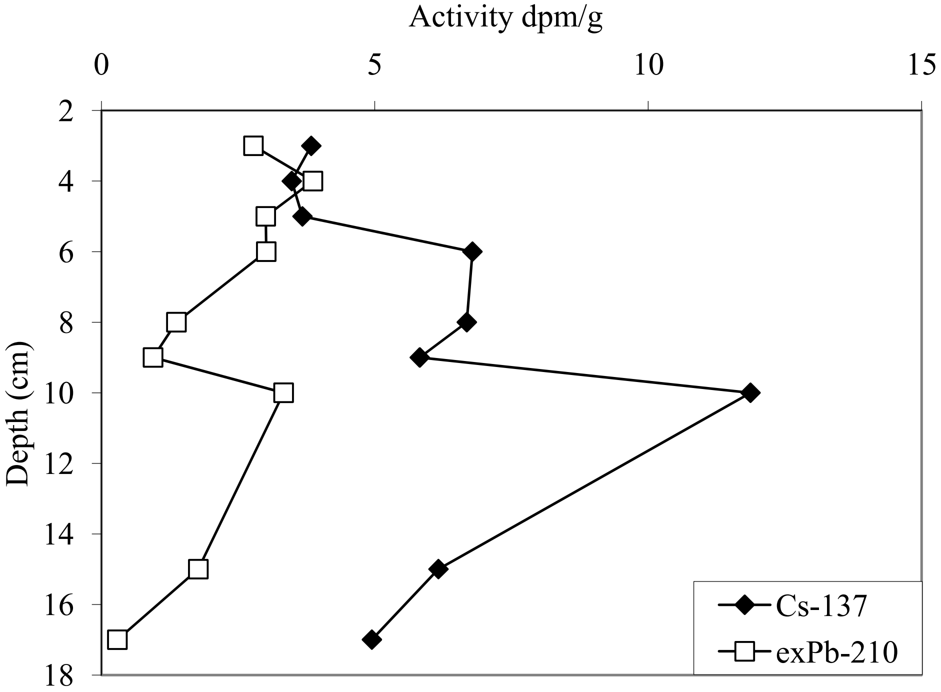


Figure11. Downcore Cs-137and exPb-210 at BONUS St. 1, Rincón, PR

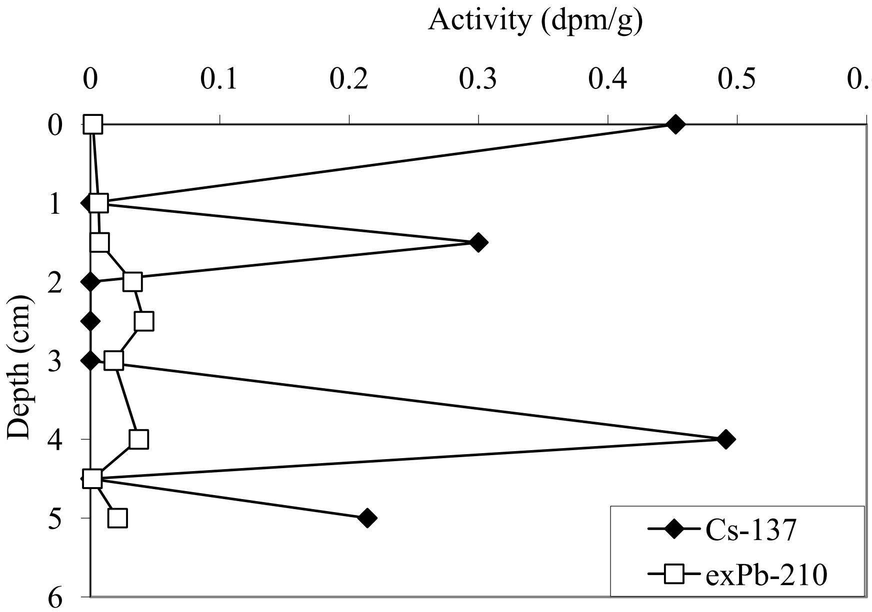


Figure 12. Downcore Cs-137and exPb-210 at BONUS St.2, Rincón, PR

Cores samples from Station 2 of the BONUS facility exhibit Cs-137 activities that are less than those determined at Station 1. In this core, most sample increments displayed activities that have zero activity of Cs-137 and four increments showed activities that ranged from 0.2 dpm/g to 0.4 dpm/g. Cs-137 activities determined at all of the other stations at the BONUS area were higher than those observed at Station 2 (Figure 13). At Station 1, the highest activity is 12 dpm/g (10 cm depth). In contrast, at Station 2 Cs-137 activity does not exceed 0.5 dpm/g.

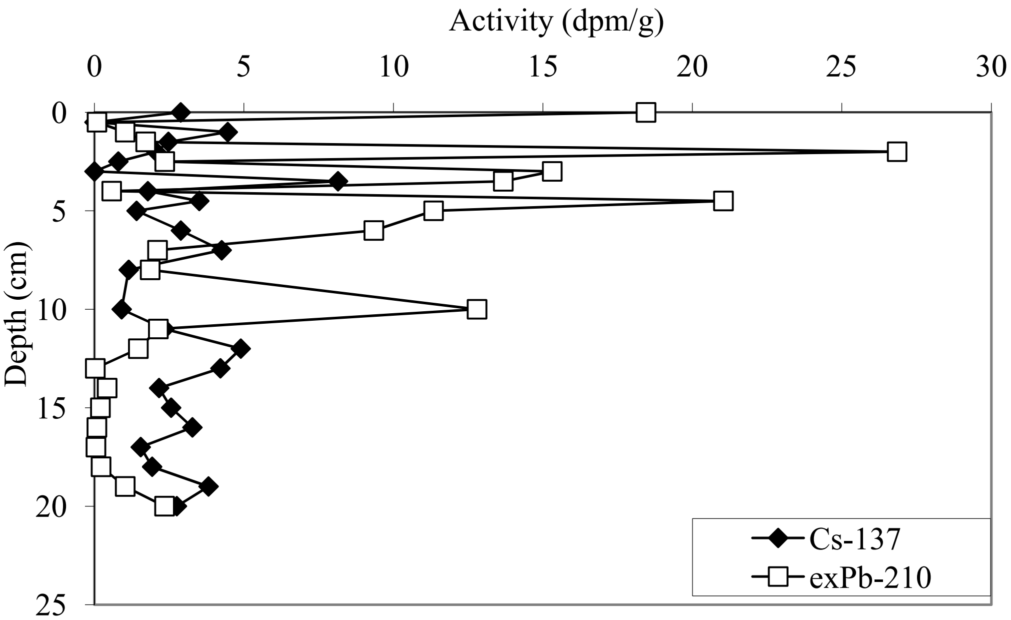


Figure 13. Downcore Cs-137and exPb-210 at BONUS St. 3, Rincón, PR

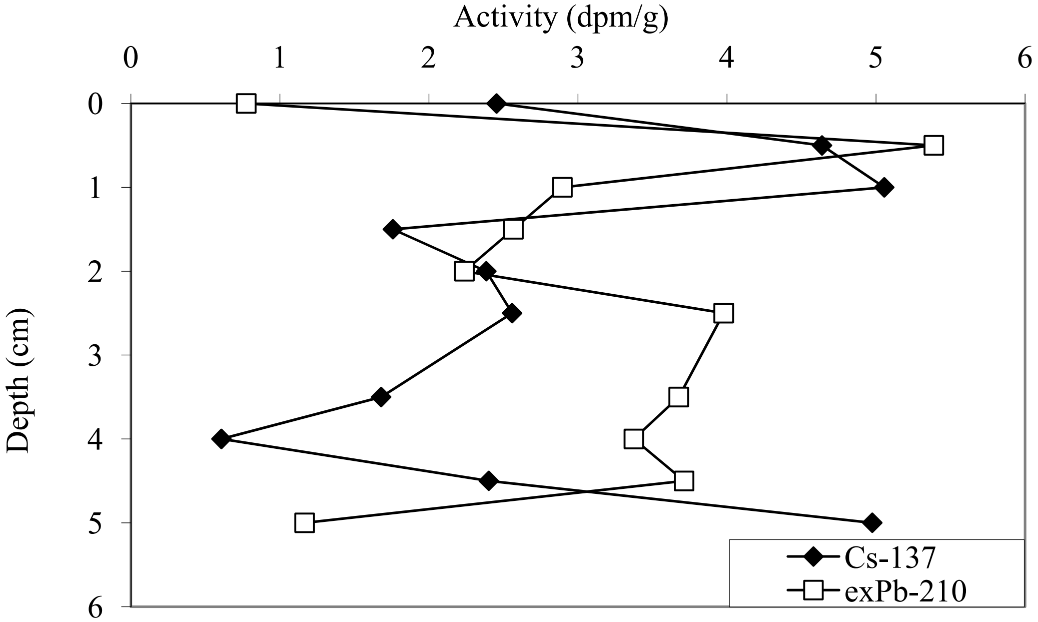


Figure 14. Downcore Cs-137and exPb-210 at BONUS St. 4, Rincón, PR

Maximum activities for cores at stations 3 and 4 are in 9 dpm/g at 4 cm depth and 5 dpm/g at 1 cm depth (figures 14 and 15). One peak of Cs-137 (5 dpm/g) was found at 4 cm of the core at station 3, activity throughout the rest of the core fluctuated between 0.5

dpm/g to 5 dpm/g . ExPb-210 at station 3 exhibited higher activity peaks (a maximum of 27 dpm/g) in the upper few centimeters of the core. Only two increments displayed Cs-137 and exPb-210 activities that were below detection limits. Station 4 was the shallowest station at the BONUS site. However, Cs-137 activity levels at the site exhibited two peaks for Cs-137, the first one at 1 cm (5 dpm/g) and another at 5 cm depth (5 dpm/g) (Figure 15). The exPb-210 showed two peaks, one of 5.5 dpm/g at 0.5 cm and another at 2 cm of 4 dpm/g. Cs-137 inventories calculated for all stations at the BONUS facility ranged from 1.2 dpm/cm^2 to 11 dpm/cm^2. Inventories for stations 1-4 were as follows, 11, 1.2, 6.7 and 5.4 dpm/cm^2, respectively.

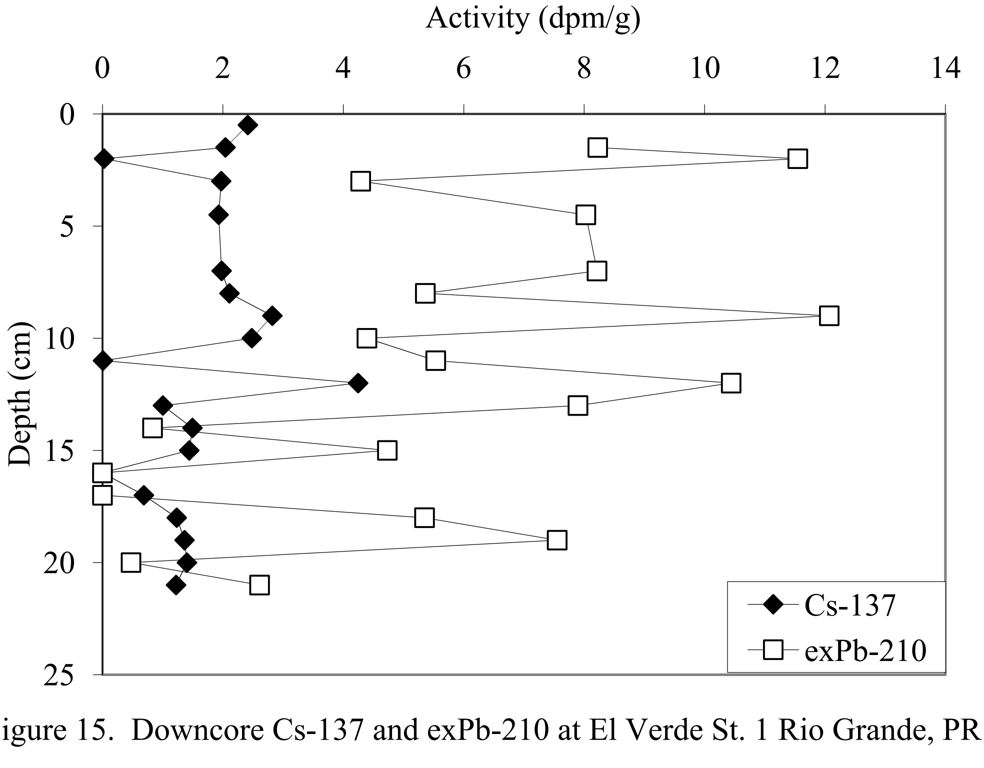


Figure 15. Downcore Cs-137 and exPb-210 at El Verde St. 1 Rio Grande, PR.

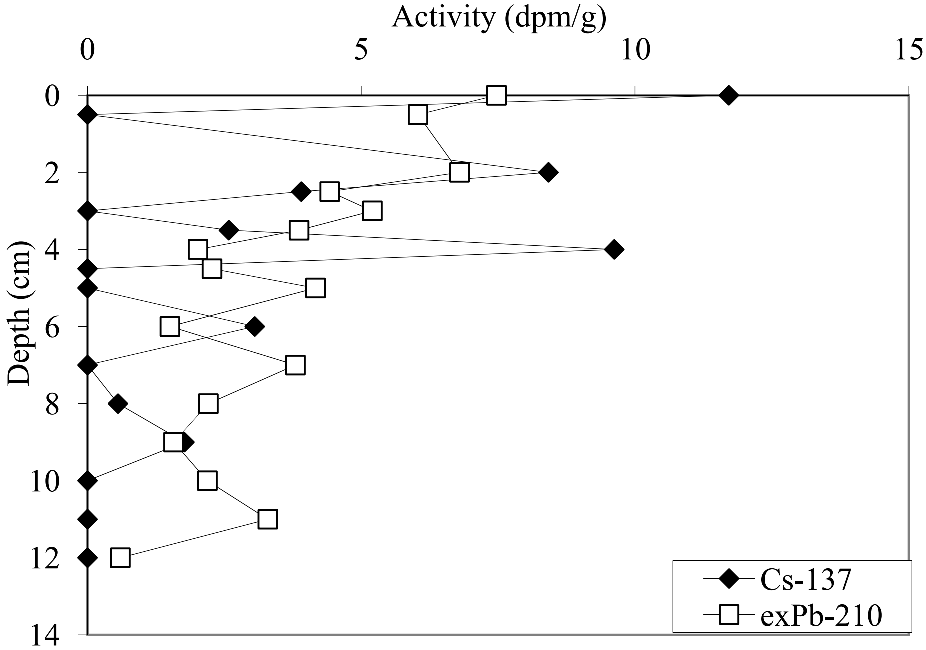


Figure 16. Downcore Cs-137and exPb-210 at El Verde St. 2 Rio Grande, PR.

Downcore gamma spectroscopy analysis was performed on cores collected from the CNF's El Verde Experimental Station and Espiritu Santo Estuary (Figures 16-19). Results differed from site to site. Samples obtained from the El Verde Experimental Station were collected from various elevations, ranging from 250 to 500 m above sea level. Mean annual rainfall for this region is 3456 mm, and monthly temperatures range from 21-25 ºC. The Espiritu Santo Estuary samples were collected from the estuary; station 1 at an open beach area and station 2 in a low impact environment. Figure 17 shows Cs-137 activity was higher in the upper 5 cm of the core at the El Verde Experimental Station 2. At station 2 the higher activities were 3 dpm/g (9 cm below the surface) and 4 dpm (11 cm below the surface). At station 2, higher activity was located at the top of the core, 12 dpm/g (at the surface), 8 dpm/g (2 cm below the surface) and 10 dpm/g (4 cm below the surface). There were three and eight downcore segments in which Cs-137 activities were below detection limits at station 1 and station 2, respectively.

ExPb-210 activity was generally higher than Cs-137 activity in both cores. But at El Verde station 2 exPb-210 activities decreased with depth. The trend was not visible at El Verde station 1, where excess Pb-210 activity ranged from 4 dpm/g to 12 dpm/g. There were 2 increments where exPb-210 activity was below detection limit. At El Verde station 2, samples ranged from 8 dpm/g (at the surface) to 1 dpm/g (at the bottom of the core).

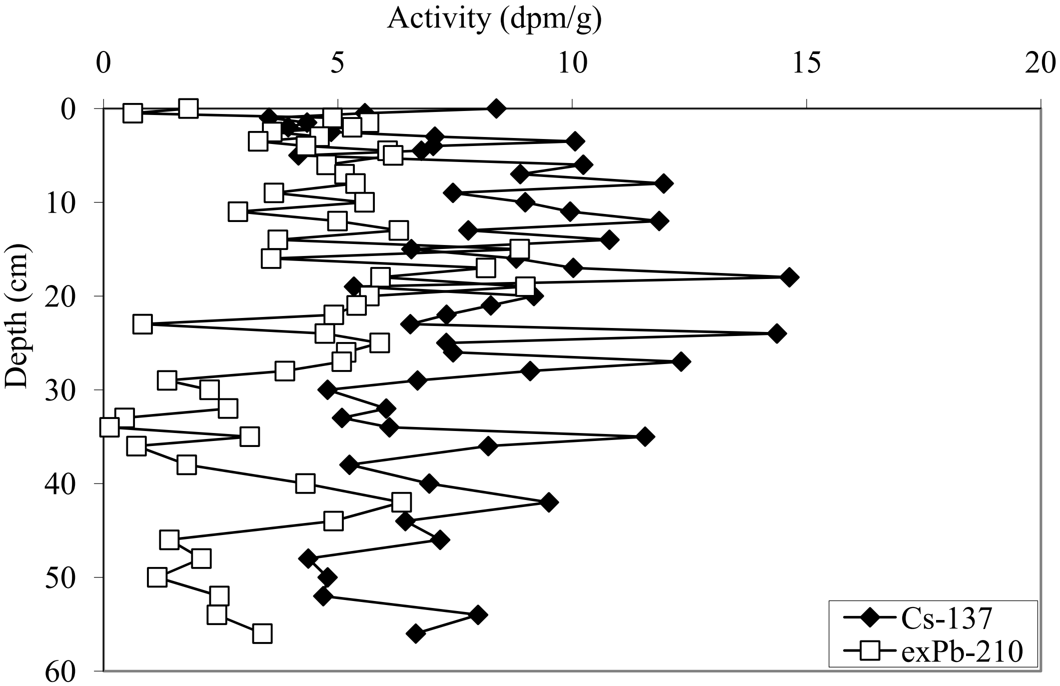


Figure 17. Downcore Cs-137 and exPb-210 at Esp. Santo Estuary St.1 Rio Grande, P.R.

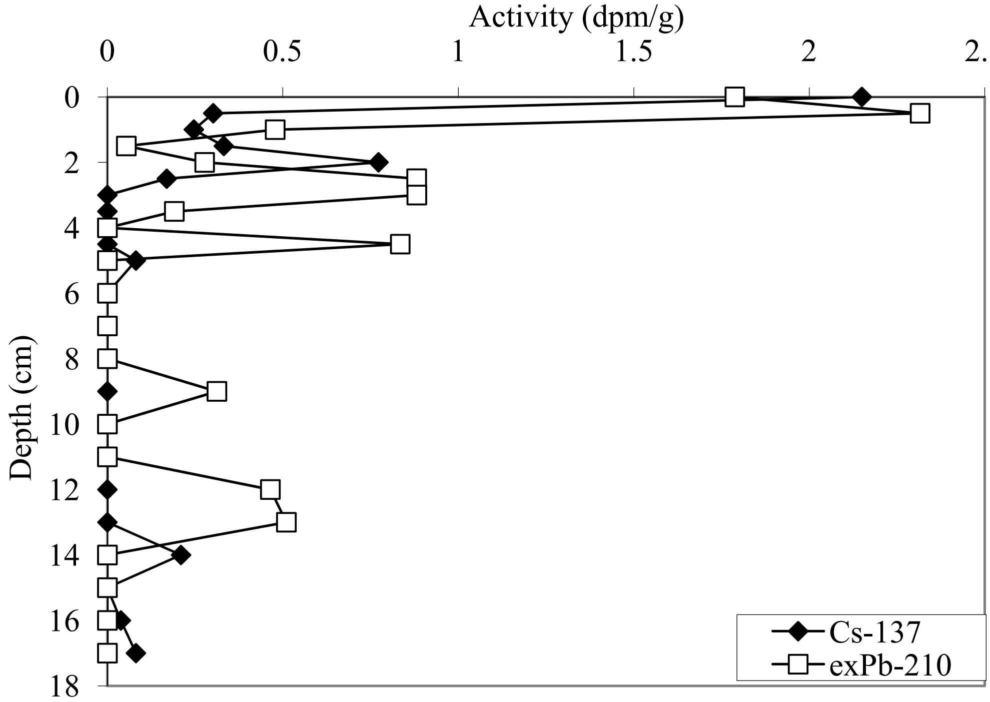


Figure 18. Downcore Cs-137 and exPb-210 at Espiritu Santo Estuary St.2 Rio Grande, P.R

The pattern observed at El Verde stations 1 and 2 was not observed at the Espiritu Santo Estuary (ESE). Station 2 was located on an open beach. The core collected at ESE station 2 possessed many increments in which Cs-137was below detection limits. In fact, Cs-137 activity was below detection limits for 12 out of 23 sample increments. ESE station 1 is located within a red mangrove protected area, near the mouth of the river. The Cs-137 activity for this core was above detection limits for all sample increments. The average Cs-137 activity level at ESE was 8 dpm/g for station 1 and 0.02 dpm/g for station 2.

The highest activity for Station 2 was 2 dpm/g (at the surface of the core). The highest activity for station 1 was 15 dpm/g (19 cm below the surface). Cs-137 activity is present at ESE station 2, a robust peak is shown at the upper centimeters of the core and the remaining of the core only shows how the activity decreases as a function of depth. Several Cs-137 peaks were observed at station 1. It should be noted that the core obtained for station 1 was longer than that which was obtained for station 2.

Data from these four rainforest stations revealed an elevation gradient. This gradient could be an important factor when analyzing the total activity of the cores. For instance, surface samples collected from the radiation center and the injection area showed the highest activity of 22 dpm/g. There are some surface samples that also showed Cs-137 activities that were below detection limits. On average, the highest activities were found at the highest elevations of the rainforest study sites. One interesting fact is that although the activities increased with higher elevation, the higher inventory was located at the Espiritu Santo Estuary station 1, with an inventory of 22.92 dpm/cm^2 (figure 18). At higher elevations of El Verde, station 1 had an inventory of 10 dpm/cm^2 and station 23 dpm/cm^2 (figure 19). Values for ESE station 1 versus the inventory value for ESE station 2 represent a substantially larger concentration of Cs-137 activity (figure 19). Inventories for the stations located at the higher elevation did not show such a difference in the inventory. Station 1 of El Verde is 3 times higher than the Cs-137 activity at station 2 which is located at roughly the same elevation (figure 19).

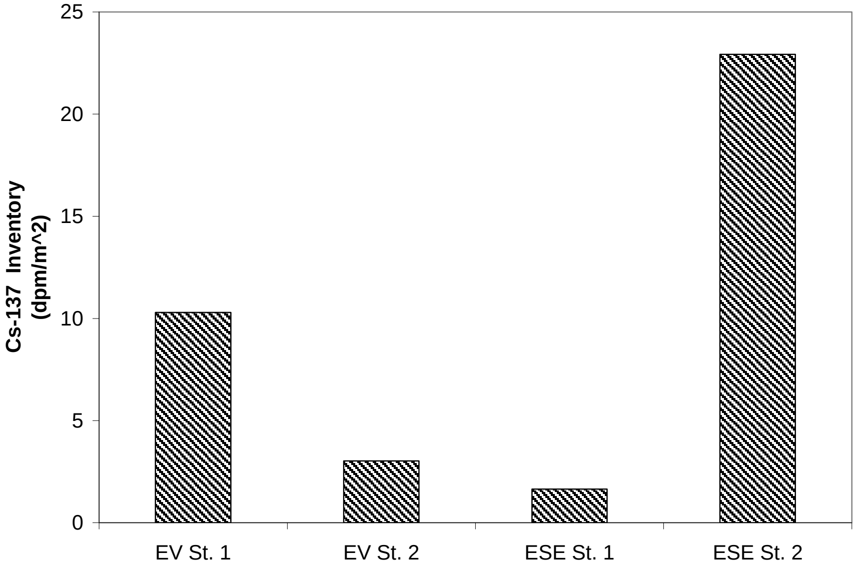


Figure 19. Cs-137 Inventories for Stations at the El Verde and Espiritu Santo Estuary.

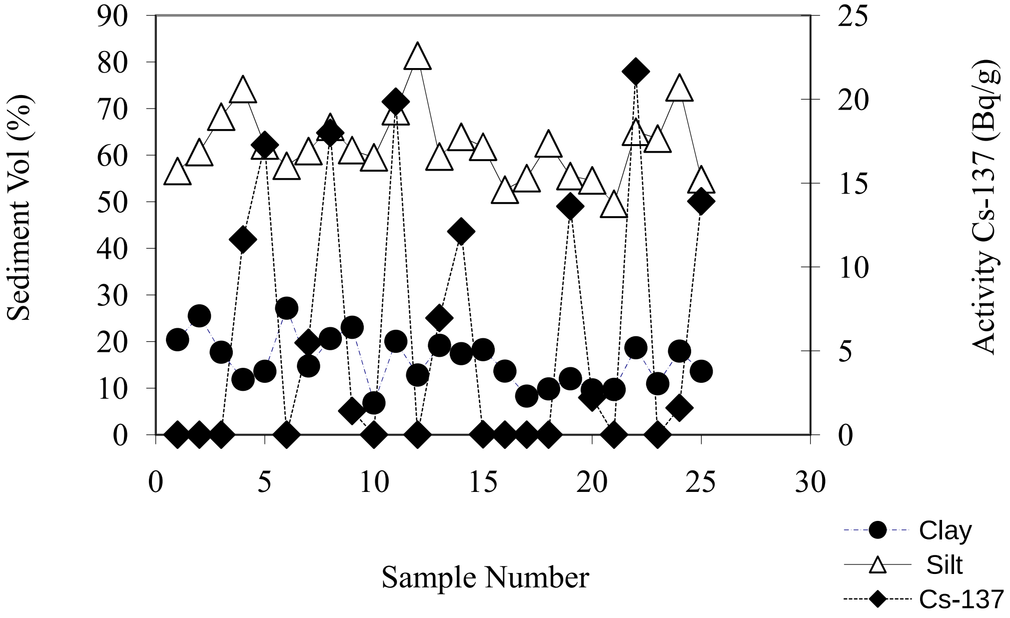


Figure 20. Correlation between Cs-137 activity on surface samples from the radiation center at El Verde Experimental Station and finer particle size distribution

Grain size analysis

Vieques surface samples were collected from a variety of ecosystems located within restricted areas of the Vieques National Wildlife Refuge (VNWR). Fine grain clay-rich sediments possess a greater ability to absorb and retain radionuclides than sediments dominated by larger particles. Grain size analysis indicates that the average concentration of clay size particles varied at each location and the average concentrations at Kiani Lagoon (9 % clay) was slightly higher than at Mosquito Bay (6 % clay) (Figures 22-23). Maximum silt size concentrations were determined in the upper 5 cm of Kiani Lagoon Station 1 (65 %). A core collected from Mosquito Bay contained maximum silt size particles distribution of 35-40 % (station 1) in the upper 5 cm of sediments (Figure 23). Average sand size concentrations were higher at the Mosquito Bay (73 %) than at Kiani Lagoon (63 %).

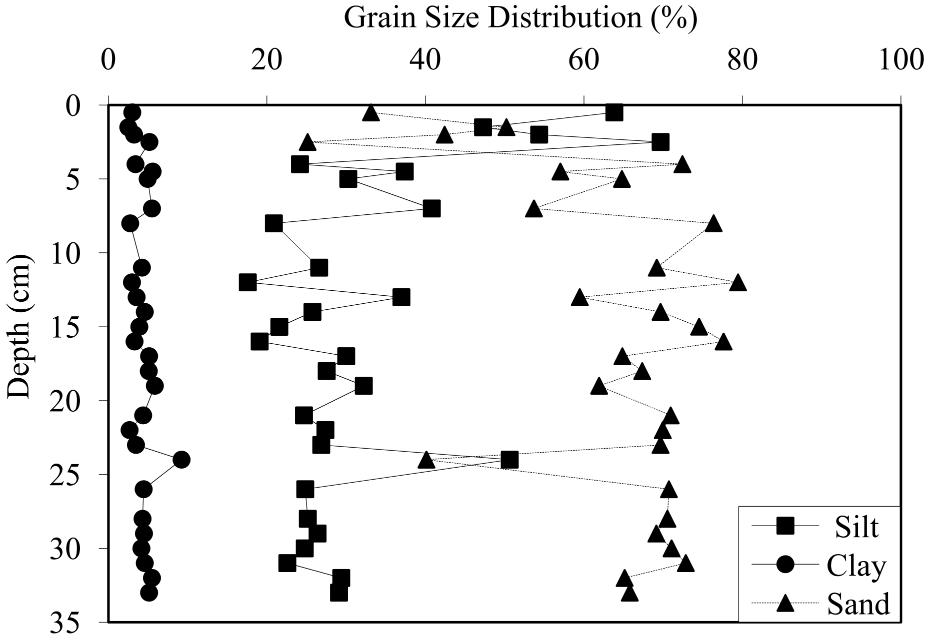


Figure 21. Grain size distribution at Kiani Lagoon Station 1, Vieques, PR

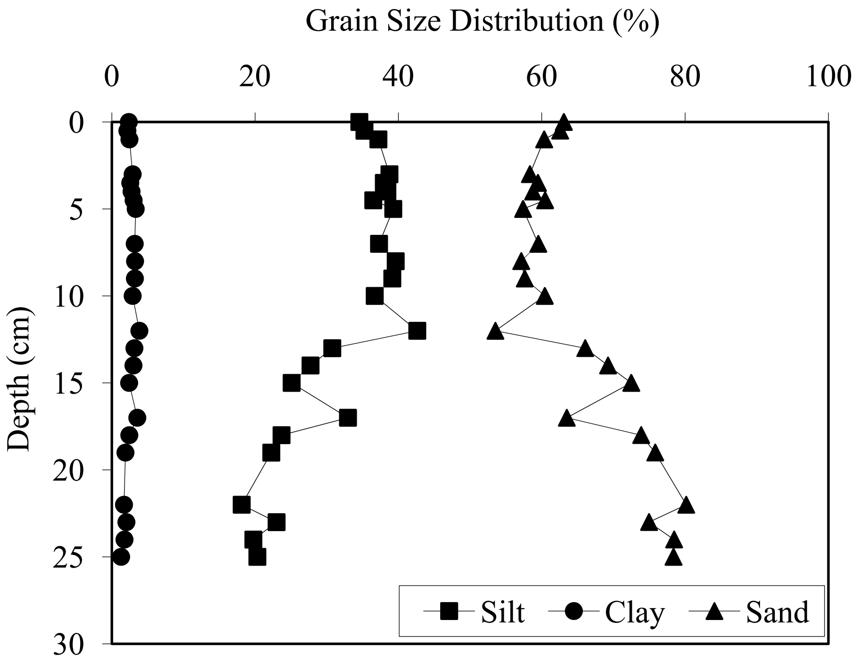


Figure 22. Grain size distribution at Mosquito Bay Lagoon Station 1, Vieques, PR

BONUS Area, Rincon, grain size characteristics were fairly consistent for all of the BONUS stations. The clay distribution is the smallest component, followed by silt and then sand, which was the most prevalent particle size at the BONUS sample locations. Clay distributions ranged from less than 10 % at Station 1, to almost 30 % at Station 4 (Figures 24-27). Silt distributions range from 20 % to 50 % for the sampled areas. Silt size distributions were higher than the sand component at Station 4.

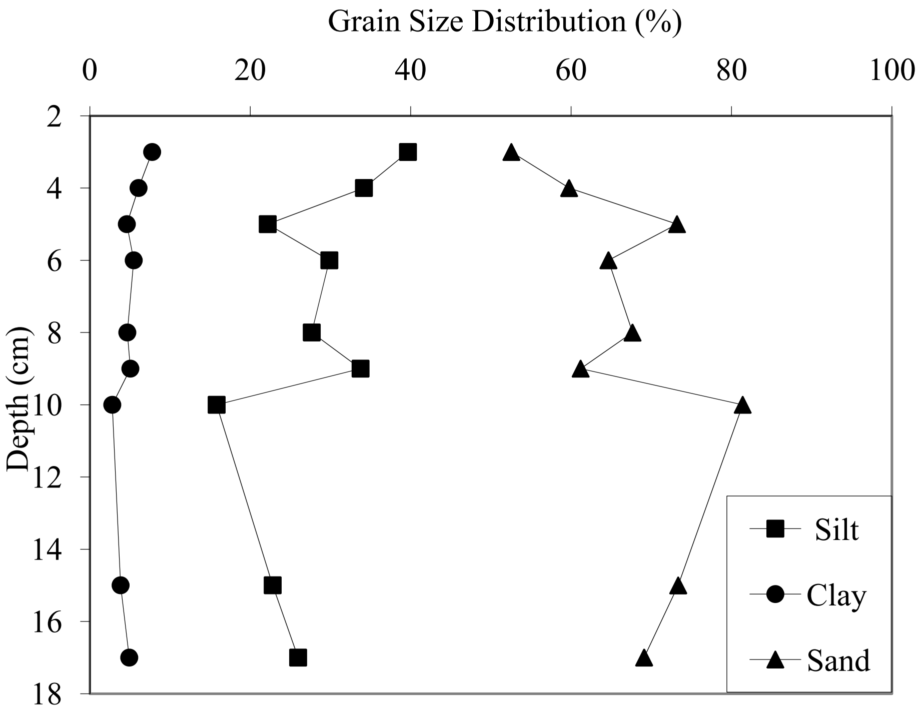


Figure 23.Grain size distribution at BONUS Area, Station 1, Rincón, PR

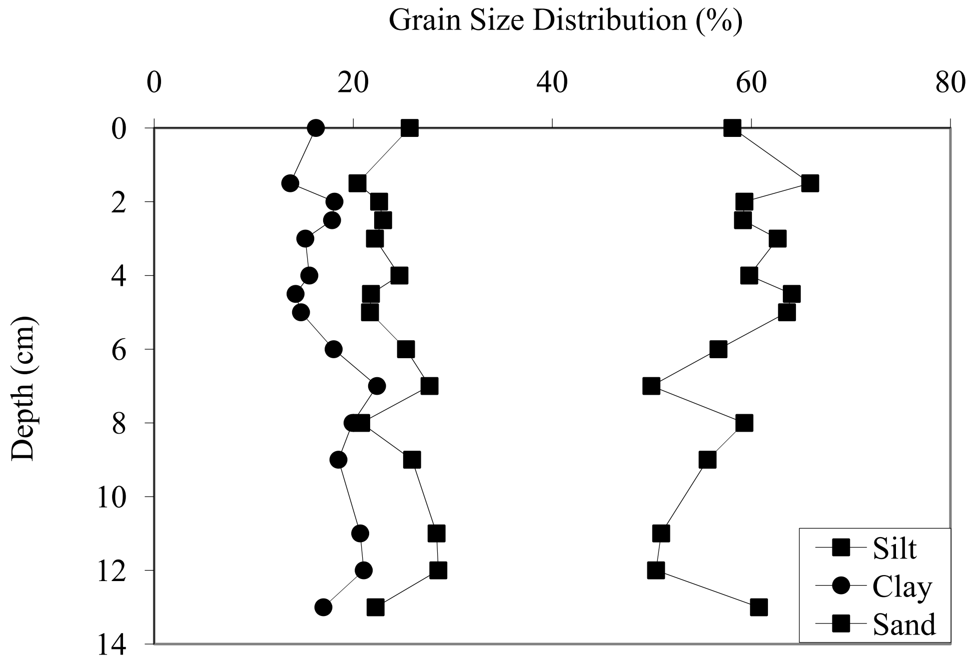


Figure 24. Grain size distribution at BONUS Area, Station 2, Rincón, PR

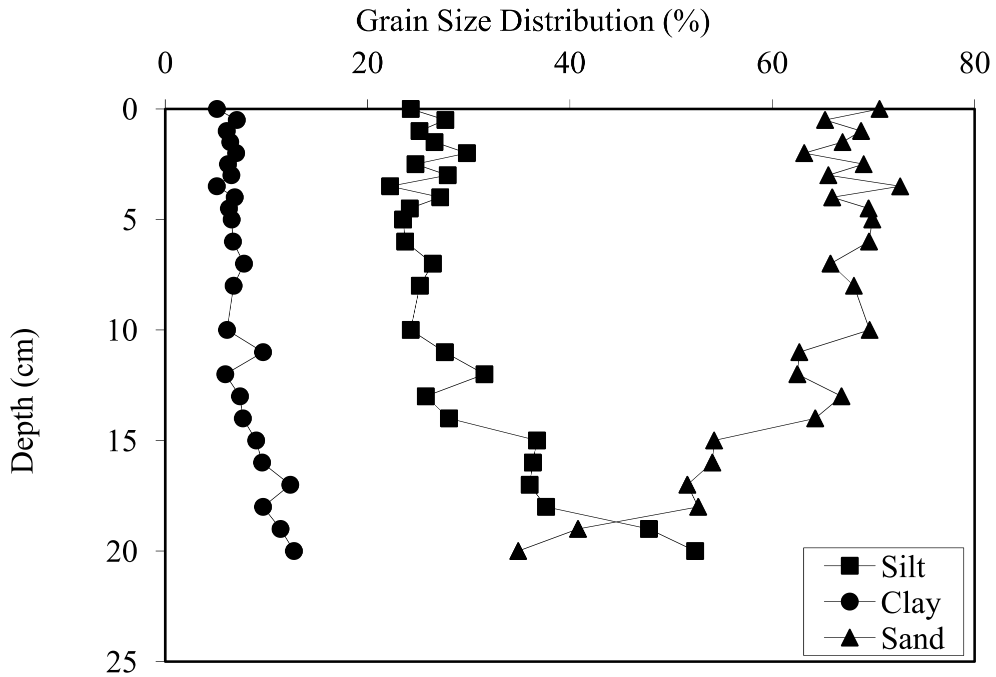


Figure 25. Grain size distribution at BONUS Area, Station 3, Rincón, PR

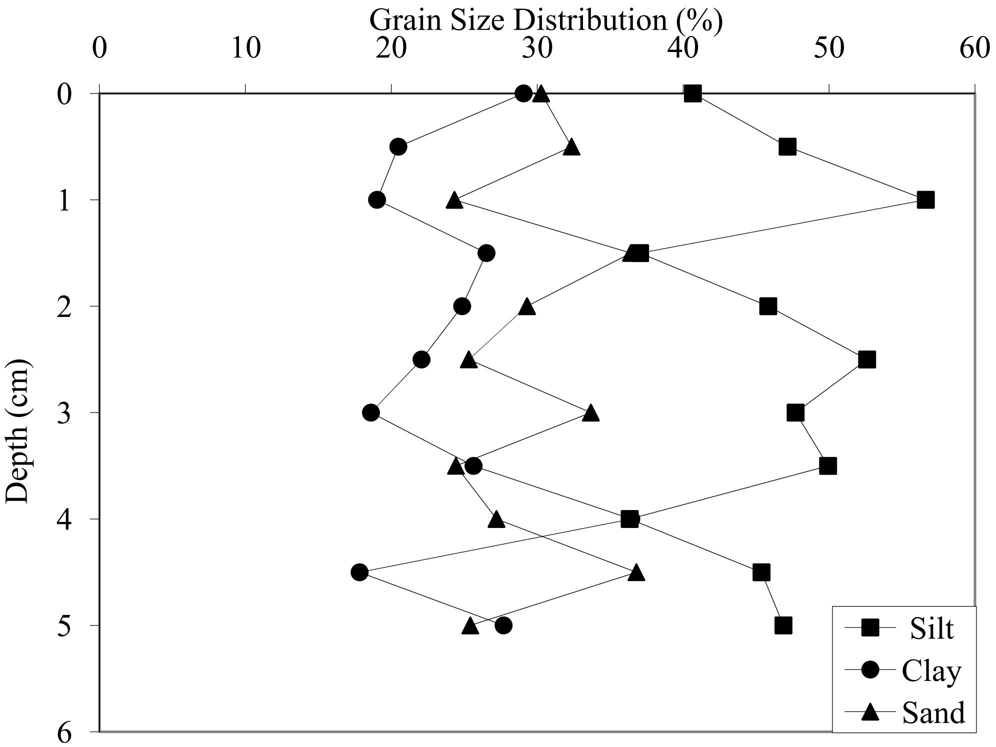


Figure 26. Grain size distributions at BONUS Area, Station 4, Rincón, PR

At the Caribbean National Forest ESE station 2, clay size particles had a fairly constant distribution that averaged 1.75 % (figure 29). The highest clay size particle distribution value at station 2 was 4 % at a depth of 6 cm and the lowest value was 0.75 % (determined at a depth of 3 cm). Silts range between 10 % to 33 % and its average distribution was 13 %. Sand was the most common particle size in the core. Its distribution range from 63 % to 88 %. The highest percentage of sand was found at 2 cm depth and the lowest value at 6 cm depth. Data for ESE station 1 were very similar for the clay distribution, but silt was the most abundant particle in this core. Average clay distribution was higher at station 1 (figure 28) with 7.6 % clay distribution. Silt's highest value was 88 % at the top of the core of station 1 and the lowest value was 59 % at 33 cm depth. Sand distribution was the lowest of those found at this location with an average of 9 %. Sand size particle distribution ranged from 2 % at 2 cm depth to 36 % in the middle part of the core.

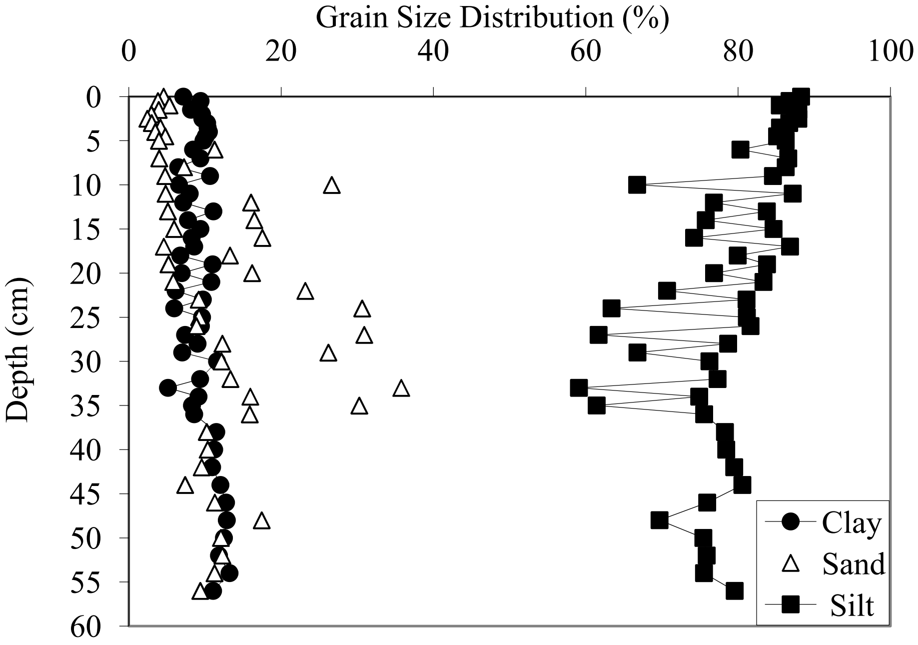


Figure 27. Grain size distribution at Espiritu Santo Estuary St. 1, Rio Grande, PR

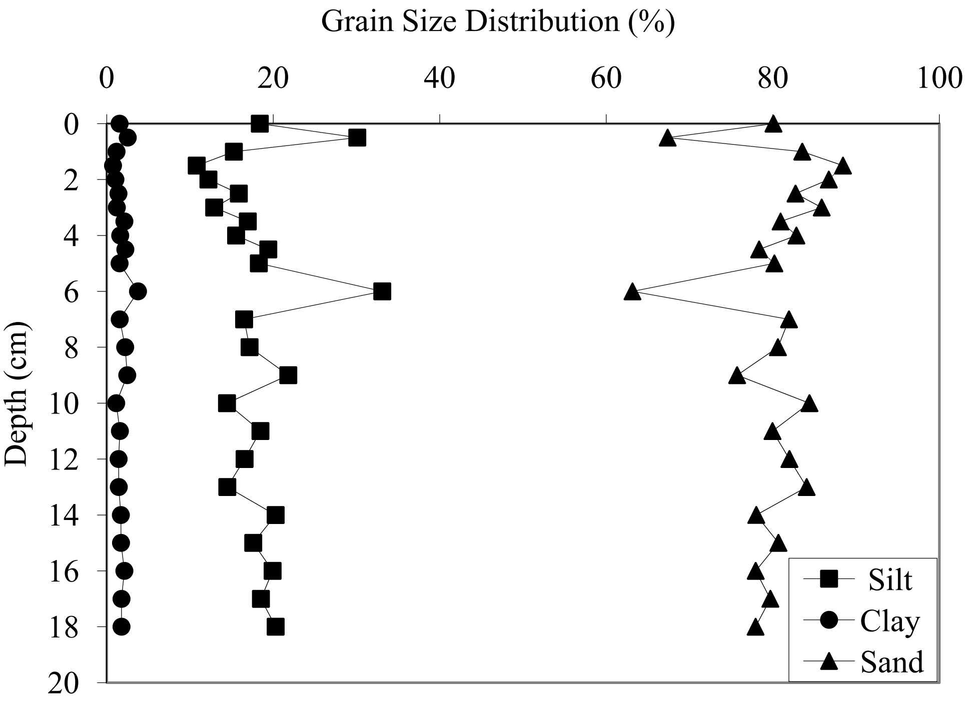


Figure 28. Grain size distribution at Espiritu Santo Estuary St. 2, Rio Grande, PR

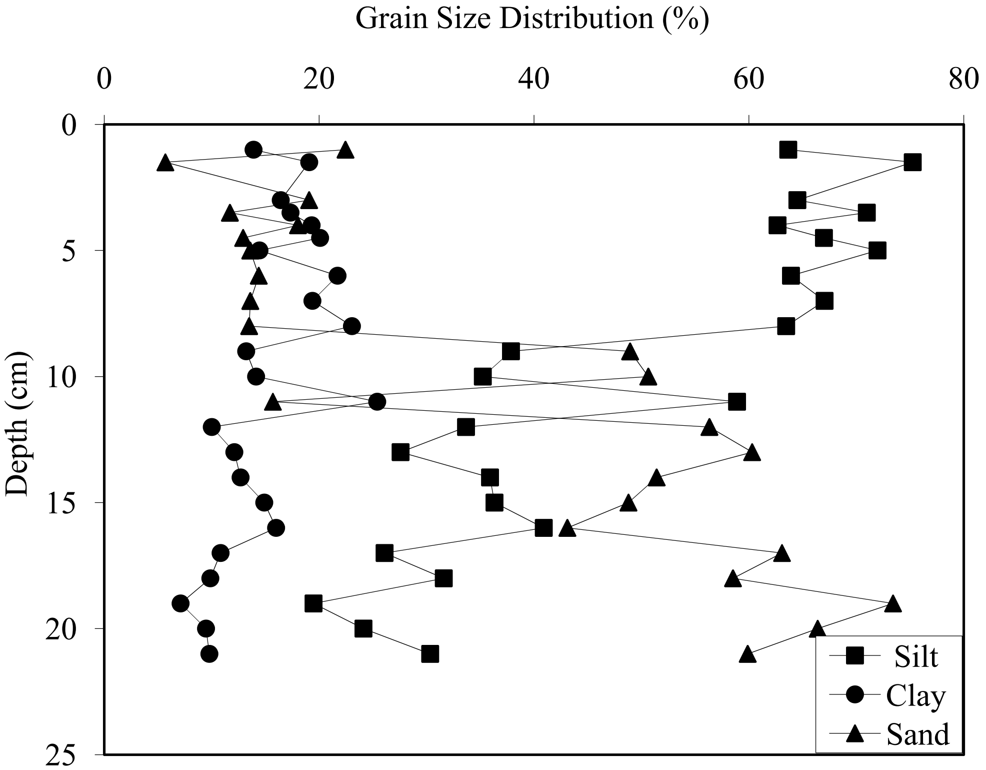


Figure 29. Grain size distribution at El Verde St. 1, Rio Grande, PR

Figure 30 displays grain size data for El Verde station 1. The size distributions for stations at higher altitude were not as constant as the estuarine stations. Silt distribution in these soil samples seemed to decrease with depth and the sand distribution increased. Clay distribution at this site ranged from 7 % to 25 %. The uneven distribution among increments was more obvious on silt and sand particles since sand distribution went from 6 % at 1.5 cm to 73 % at 19 cm depth. These values showed a slight increase with depth. However sand distribution did not constantly increase as it showed increments where its percentage went as low as 15%. In the case of silt, its distribution had some fluctuation throughout the core but a tendency to decrease as a function of depth was demonstrated.

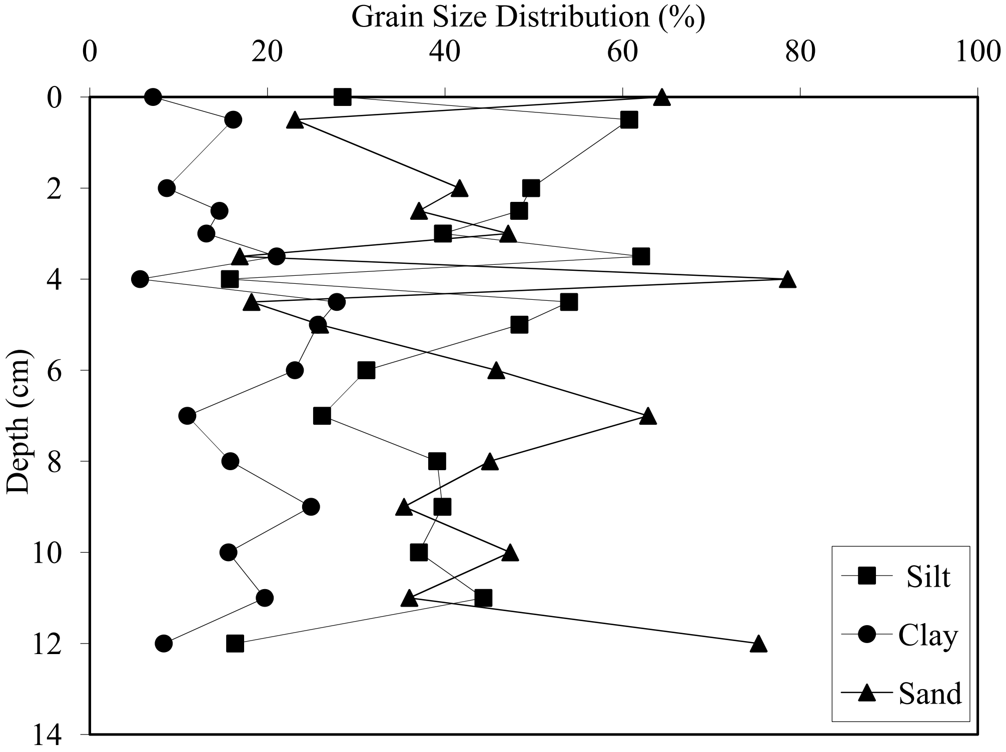


Figure 30. Grain size distribution at El Verde St. 2, Rio Grande, PR

Station 2 at El Verde (figure 31) did not possess the same pattern as station 1. Station 2 had an average clay size distribution of 16 % which was close to the distribution calculated for station 1. There was no decrease with depth at station 2, as was shown at station 1. Clay and sand seemed to follow the same decreasing trend. Average sand and silt values were 44 % and 23 % respectively. Silt ranged from 16 % to 62 %. These two values, half a centimeter apart, represent the highest and lowest values of the core. Seeing these values in such a close increments confirmed the high level of inconstancy within the soil located in the rainforest area. Sand size particle distribution ranged from 17 % to 79 %. Again these increments were just half a centimeter apart from each other.

Loss on ignition (LOI)

LOI is commonly used to estimate the percent of organic matter present in a sample (Henri, 1970). Organic matter content was analyzed to determine how Cs-137 behaved in its presence. Studies have shown that Cs-137 could be retained by organic matter (Santchi and Honeyman, 1989). The highest LOI values (e.g. organic matter concentration) were determined for Kiani Lagoon samples. A maximum of 35 % LOI was determined within the upper 5 cm of this core (Figure 32). LOI results indicated that the organic matter content at Kiani Lagoon and Mosquito Bay decreased as a function of depth. Maximum LOI values determined for Mosquito Bay were above 10 %. The highest organic matter content was found within the upper 5 cm of both cores (Figure 32).

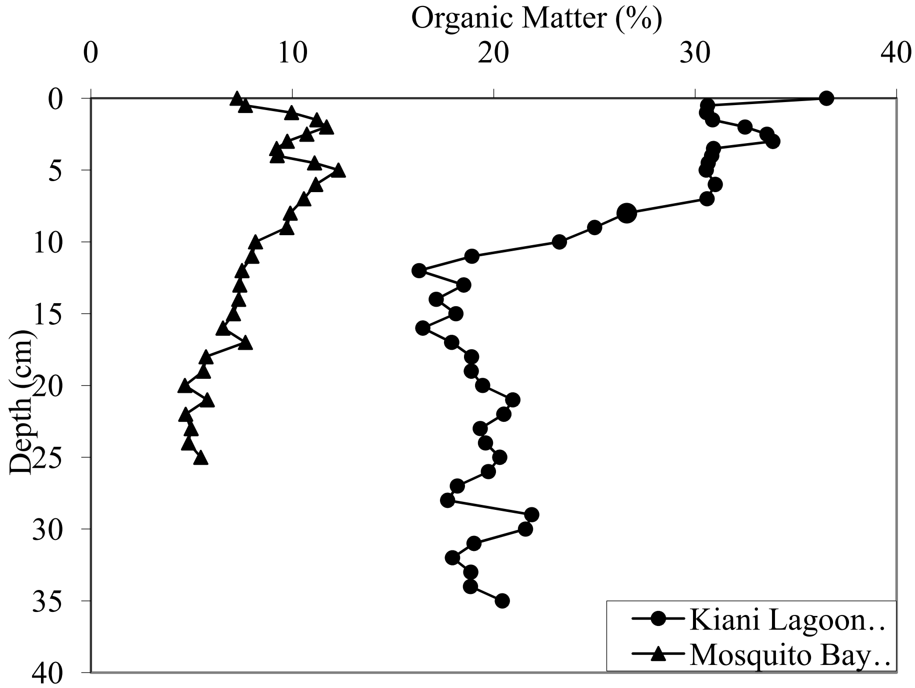


Figure 31. Organic matter percentage at Kiani Lagoon and Mosquito Bay, Vieques, PR.

The organic matter content (represented by LOI) for the BONUS facility area, figure 33 indicated a heterogeneity among samples at the study site. Organic matter content ranged from 2 % to 13 %. Station 2 presented the lowest organic matter content (ranged from 6 % at the top of the core to 3 % at the bottom). The highest organic matter content was presented at station 4, where it ranged from 11% and 13%. Organic matter content at the other two stations ranged from 2 to 10 %. The same stations that possessed higher distributions of fine grain material also possessed higher percentages of organic matter (figure 33).

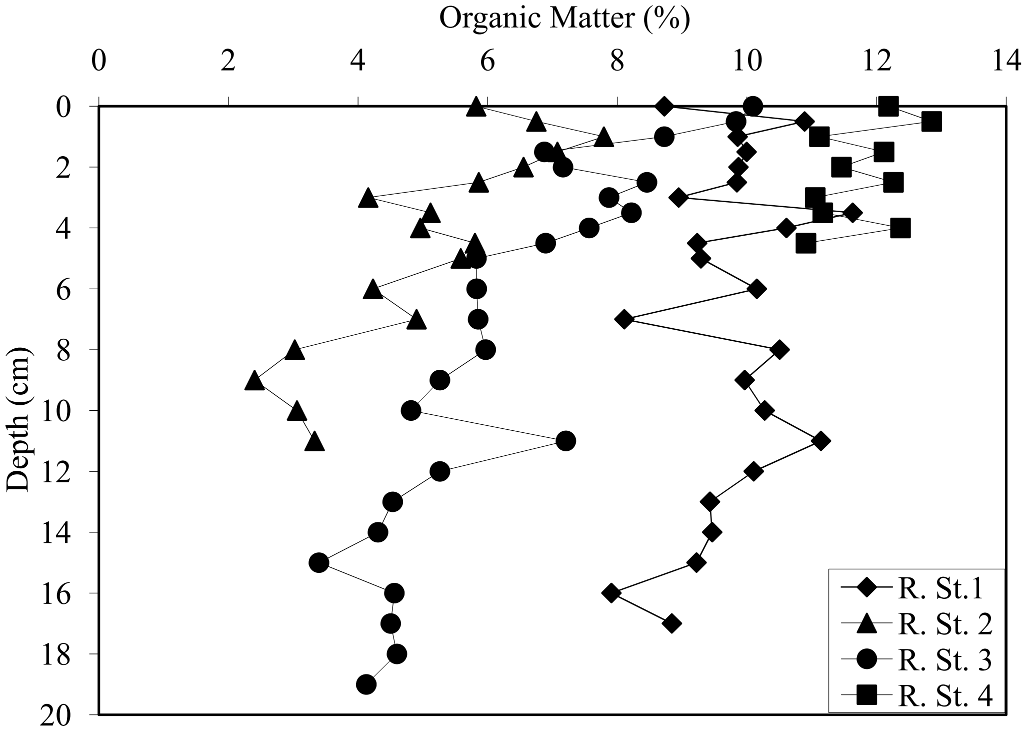


Figure 32. Organic matter percentage at BONUS Area, Rincón, PR.

Figure 34 shows results for analyzed samples at 4 stations in the tropical rain forest area and the ESE. As seen in the figure 34 the organic matter concentration ranged from less than 5 % to 35 % organic matter. Samples collected from sandy environments possessed the lowest values for organic matter and those that were collected from protected environments possessed intermediate organic matter concentrations. Samples collected from soils at the radiation center and the injection area possessed the highest LOI values. LOI values for surface samples from these latter sites ranged from 11 % to 61 % (figure 34). Station 14 (figure 34), at the radiation center, had the highest organic content of all the samples collected from the rainforest and station 5 had the lowest organic content of all samples.

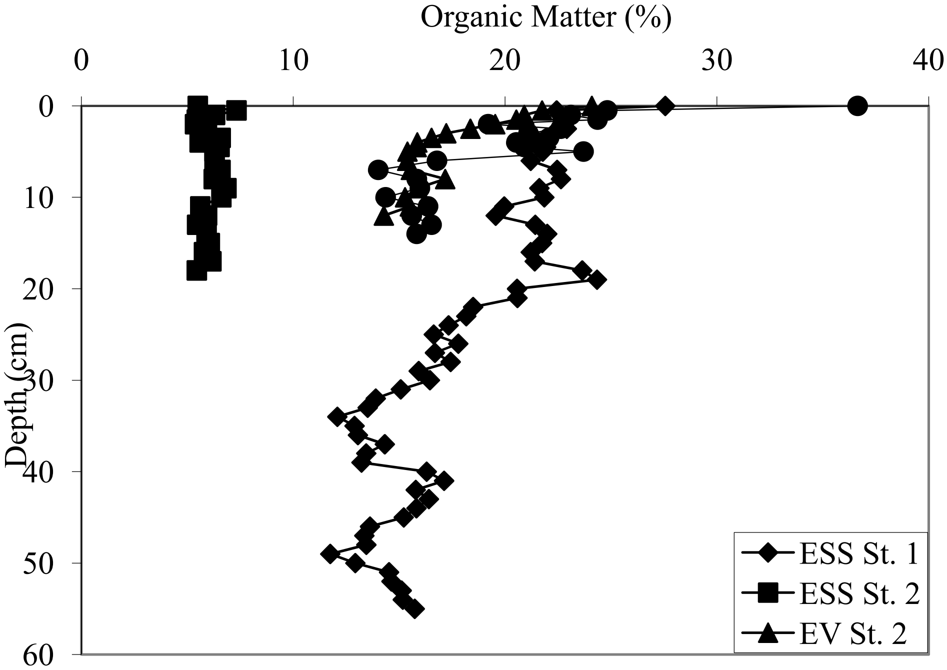


Figure 33. Organic matter in percentage at El Verde and Espiritu Santo Estuary, Rio Grande, PR.

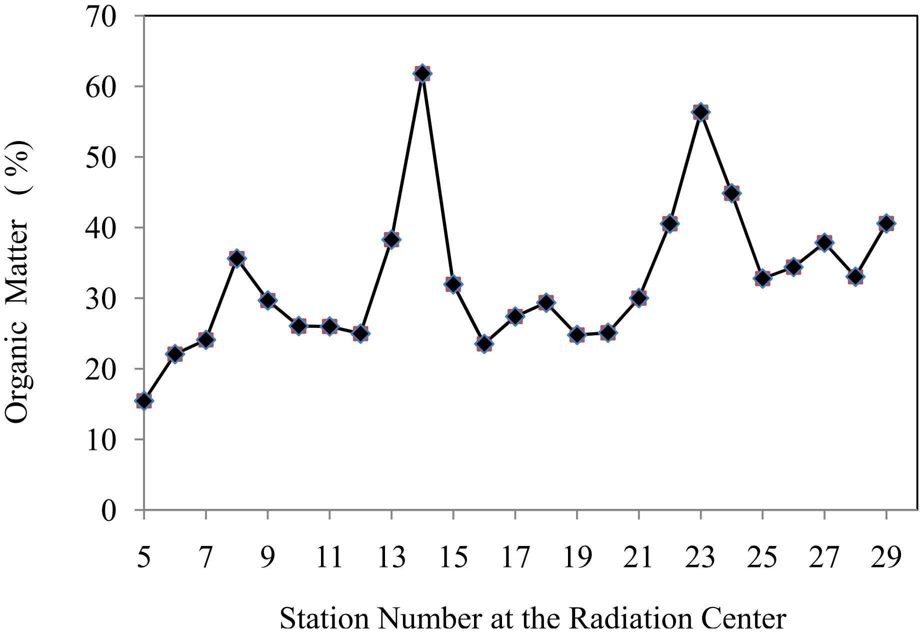


Figure 34. Organic matter in percentage at El Verde Surface Samples

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)

Results from ICP-OES provided information regarding the concentration of more than a dozen of elements that are useful to determine the oxic, suboxic or anoxic conditions of the sediments (figure 35). Samples from Mosquito Bay indicated a steady increase of Fe and Mn concentration with depth. The highest iron concentration was located at 18 cm depth, 9356 ppm. The lowest iron concentration was present at 4 cm depth, 960 ppm. Manganese concentration was consistently low throughout the length of the core when compared with iron concentrations. However, Mn concentration increased as a function of depth until the 17 cm depth where its concentration rose to 38 ppm. Below this depth its concentration decreased with depth throughout the remainder of core. In addition, there were also 5 sediment increments for which the Mn concentrations were below detection limits. Due to oxic and suboxic states within the sediments, iron concentrations ranged from 2753 ppm (at the top of the core) and 8463 ppm (at the bottom of the core) (figure 36). The Mn values ranged from 1 ppm at the top of the core to 18 ppm at the bottom of the core.

Samples analyzed from Kiani lagoon showed a constantly low manganese concentration throughout the depth of the profile and its values ranged from below detection limits to 70 ppm. Iron concentration seemed to decrease with depth with a slight elevation in concentration located near the bottom of the core (a maximum of 6086 ppm). At 3 cm and 19 cm, Fe concentrations were 25072 ppm and 20159, respectively which could be attributed to the oxic and suboxic states mentioned above (figure 36). Surface samples from Vieques (figure 38) presented the same trend in Fe and Mn concentration. Mn possessed the lowest concentration at all samples and Fe was present in higher concentration. The OP entrance station was the area where Fe had a highest concentration, 16, 033 ppm.

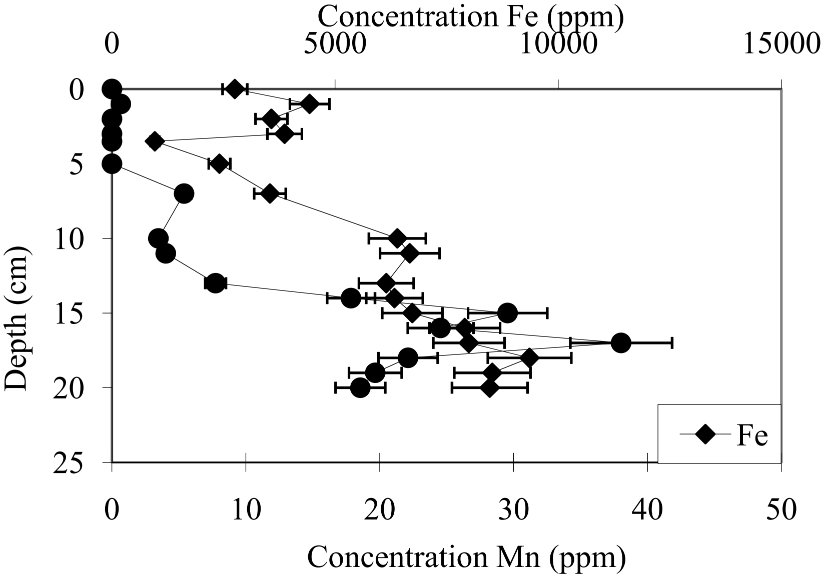


Figure 35 . Downcore concentration for Iron and Manganese at Mosquito Bay St. 1, Vieques.

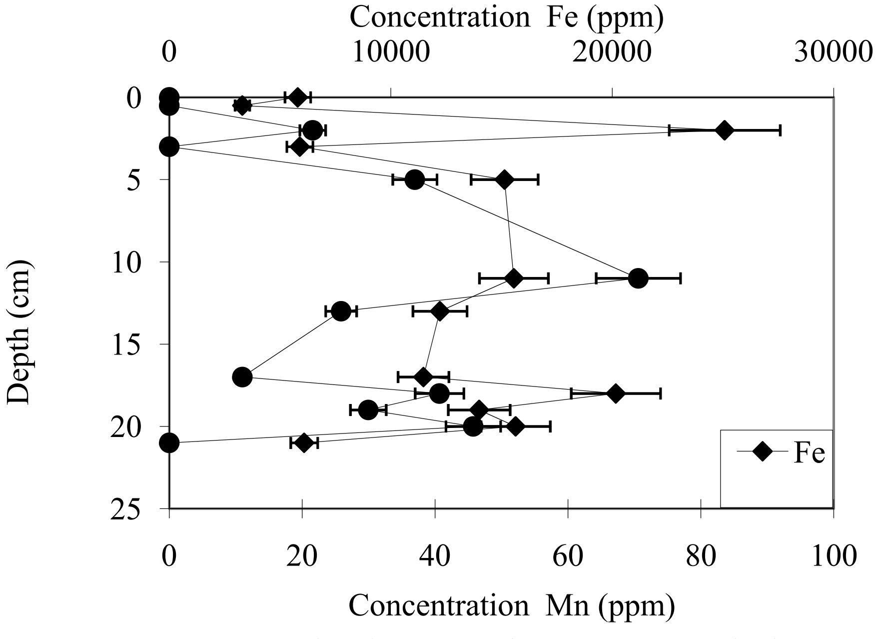


Figure 36. Downcore concentration for Iron and Manganese at Kiani Lagoon St. 1, Vieques.

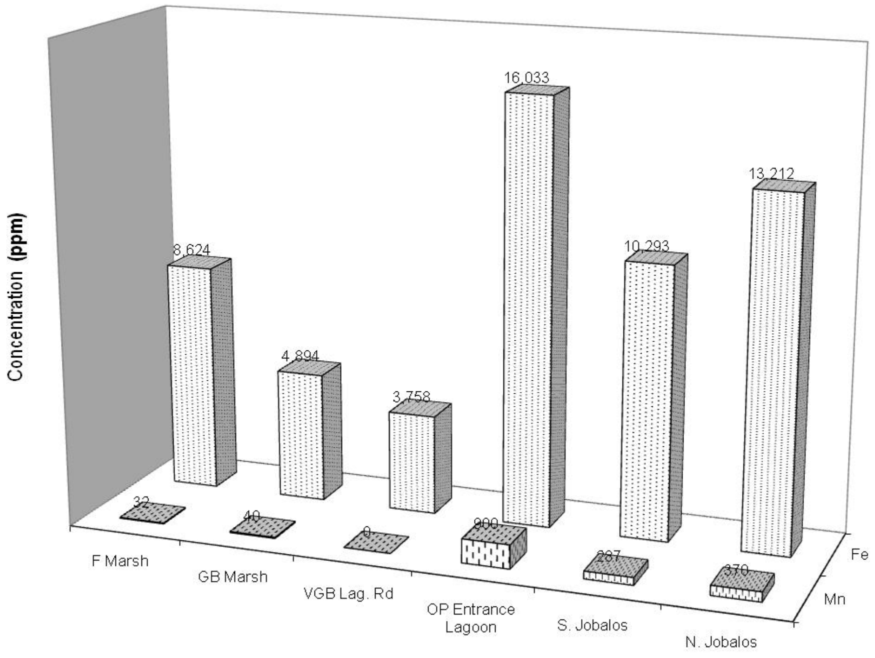


Figure 37. Iron and Manganese concentration for surface samples at Vieques National Fish and Wildlife Refuge, Vieques, PR.

ICP-OES analyzed samples are shown in figures 39-40, manganese concentrations throughout the core at all stations ranged from 0-596 ppm. The highest concentration was present at station 4 at a depth of 1.5 cm. Manganese concentration in soil samples from the BONUS area ranged from 150 ppm to almost 600 ppm.

Iron concentrations at BONUS range from around 8000 ppm to 16,000 ppm. Station 3 possessed the highest iron concentration. Higher Fe concentrations were located in the upper centimeters of the core. The highest value was 13,783 ppm at 5 cm. The average iron concentration throughout the cores was13,000 ppm. At station 3 and 4 the difference in concentrations was similar to those discussed in the previous core, however, these profiles showed similar behavior (figures 39 and 40).

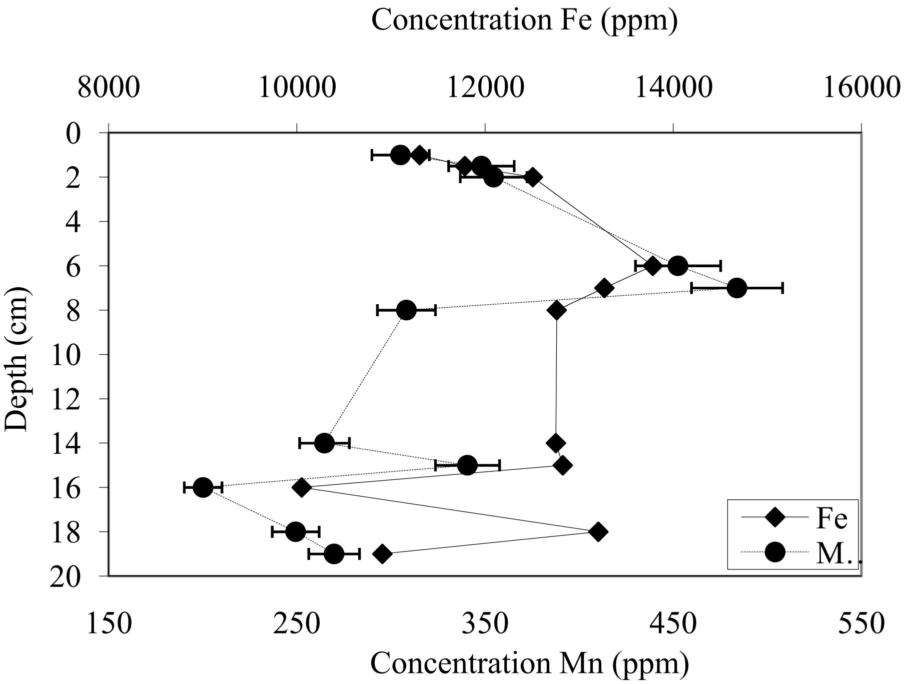


Figure 38. Downcore concentration for Iron and Manganese at BONUS Area St. 3, Rincón, PR.

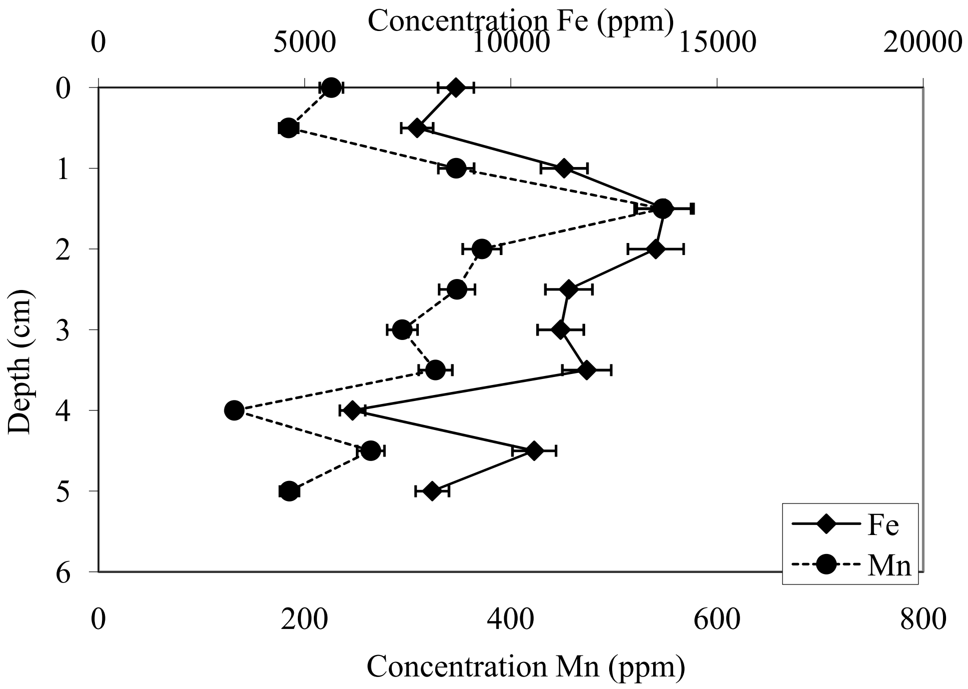


Figure 39. Downcore concentration for Iron and Manganese at BONUS Area St. 4, Rincón, PR.

Manganese and iron concentrations from the Caribbean National Forest are presented in figures 41 through 43. Manganese concentrations in soil and sediments remained consistently low. The iron concentration decreased with depth and ranged from 28,632 ppm to 15,441 ppm.

Stations at ESE showed an interesting difference in concentration levels. Fe concentrations at Station 2 were one order of magnitude smaller (3,266 ppm to 2,866 ppm) than station 1 (35,638 ppm to 21,066 ppm). However, Fe concentrations at both locations decreased with depth. Values for these stations were also higher at the top of the core in both instances.

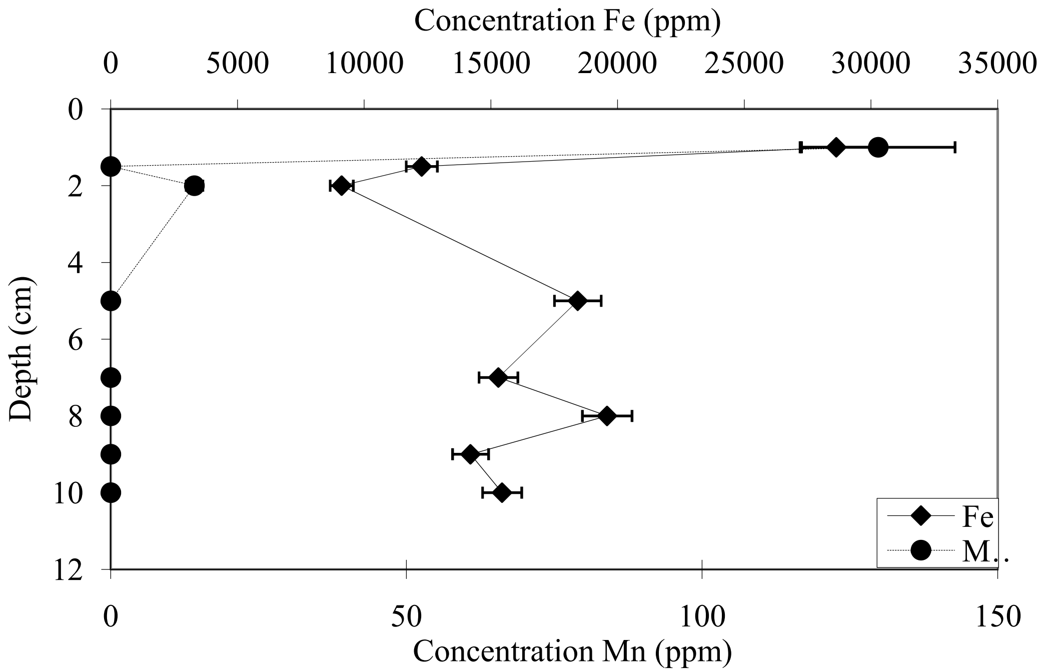


Figure 40. Downcore concentration for Iron and Manganese at El Verde St. 1, Rio Grande, PR

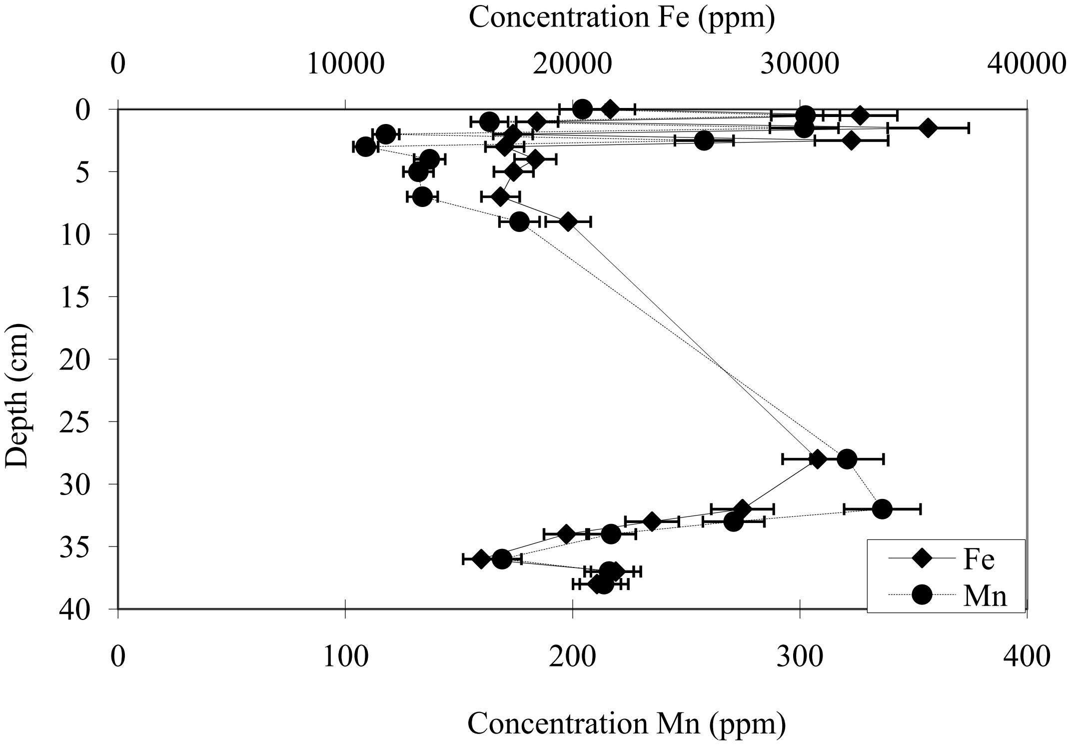


Figure 41. Downcore concentration for Iron and Manganese at Esp. Santo Estuary St. 1, Rio Grande, PR

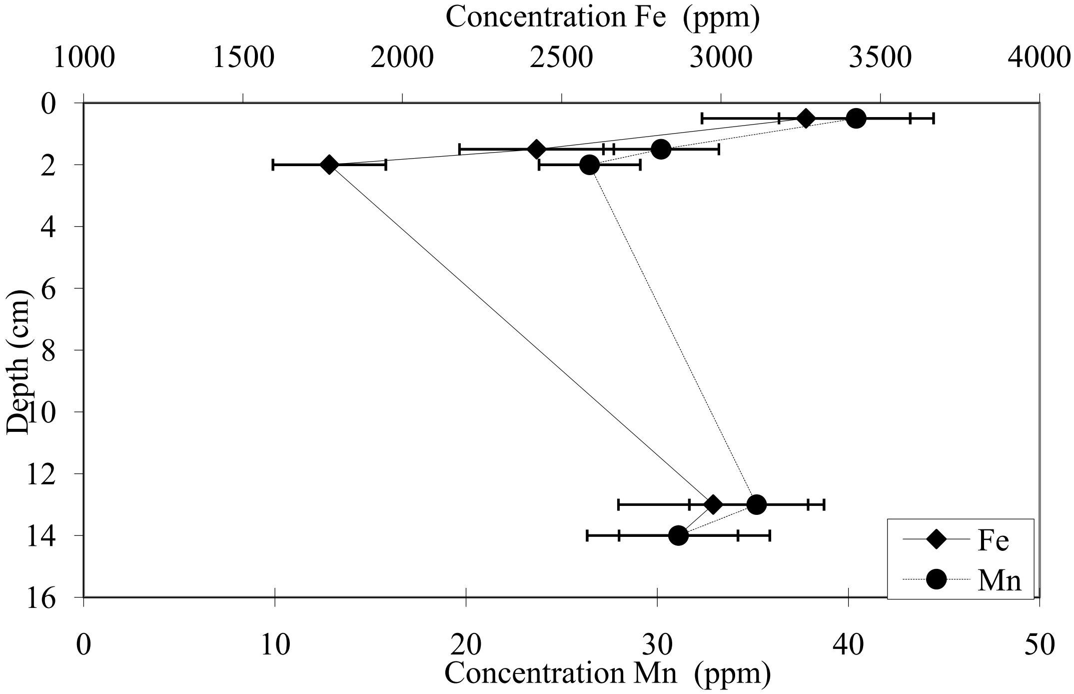


Figure 42. Downcore concentration for Iron and Manganese at Espiritu Santo Estuary St. 2, Rio Grande, PR

X-ray diffraction

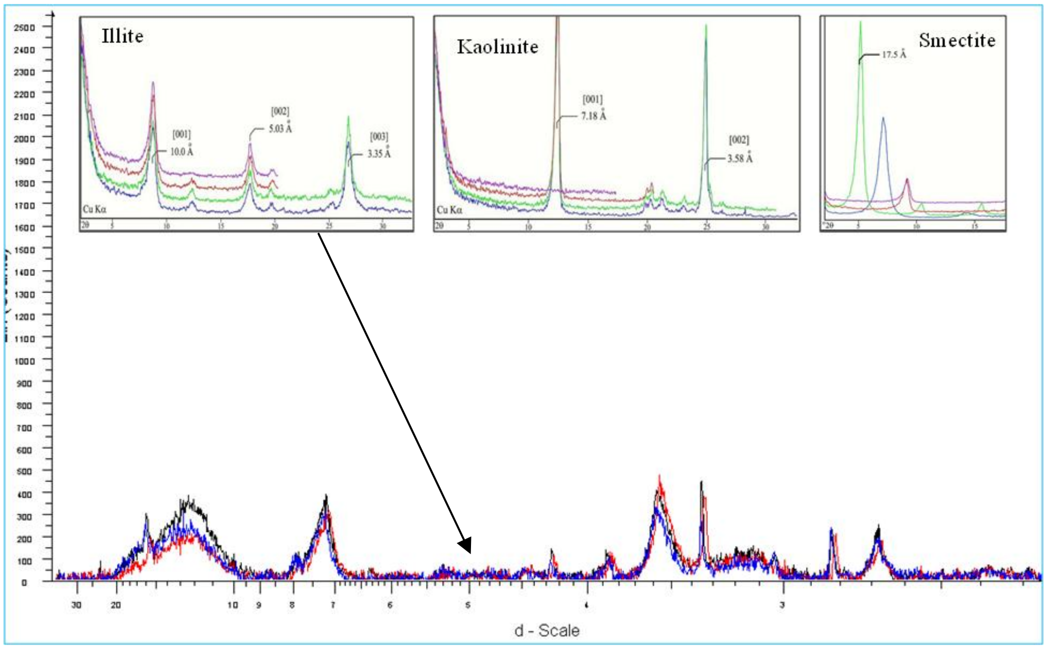


Figure 43. Mineralogical analysis of bulk samples from Vieques, PR

X-ray Diffraction (XRD) data for Mosquito Bay indicated the absence of illite at this location (figure 44). However, smectite and kaolinite were present in the majority of downcore samples collected at the site. Highest Cs-137 activities at this station were observed in samples in which kaolinite was present and illite and smectite were absent.

Surface samples collected at the different locations within the VNFWR (Figure 20) were also analyzed using the XRD technique. The XRD analysis confirmed the presence of kaolinite in all samples and the absence of illite at the study sites (figure 43).

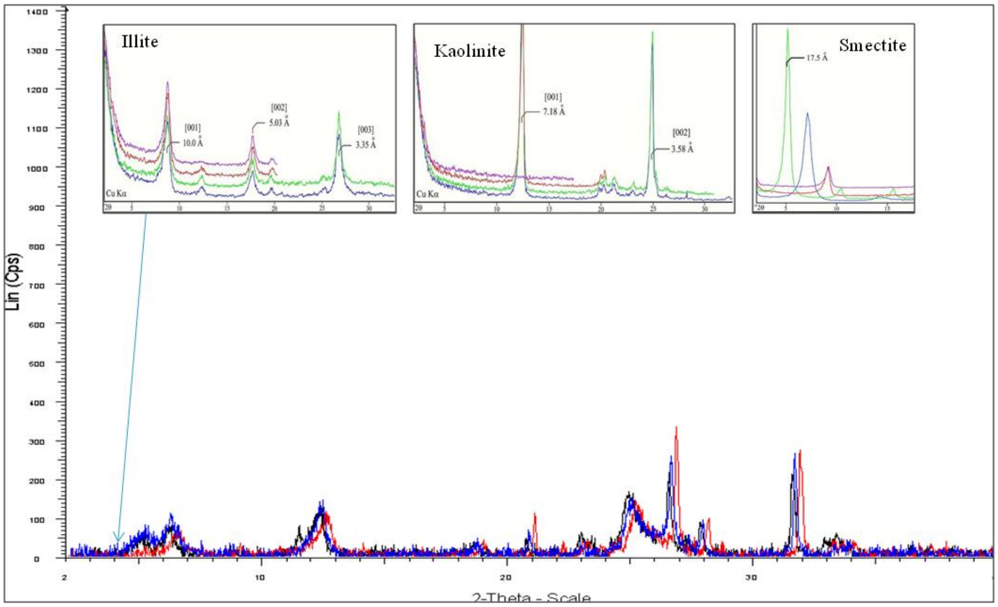


Figure 44. Mineralogical analysis of bulk samples from the BONUS area, Rincon, PR

Mineralogical analysis of the BONUS area was performed on a subset of samples that were identified based upon Cs-137 activities. Samples with the highest activities, as well as samples with the lowest activities were analyzed for the purpose of detecting the absence or presence of illite, kaolinite and smectite. Clay mineralogy results were similar for all stations at the BONUS facility area. Illite was absent throughout the cores, smectite and kaolinite were present (figure 44).

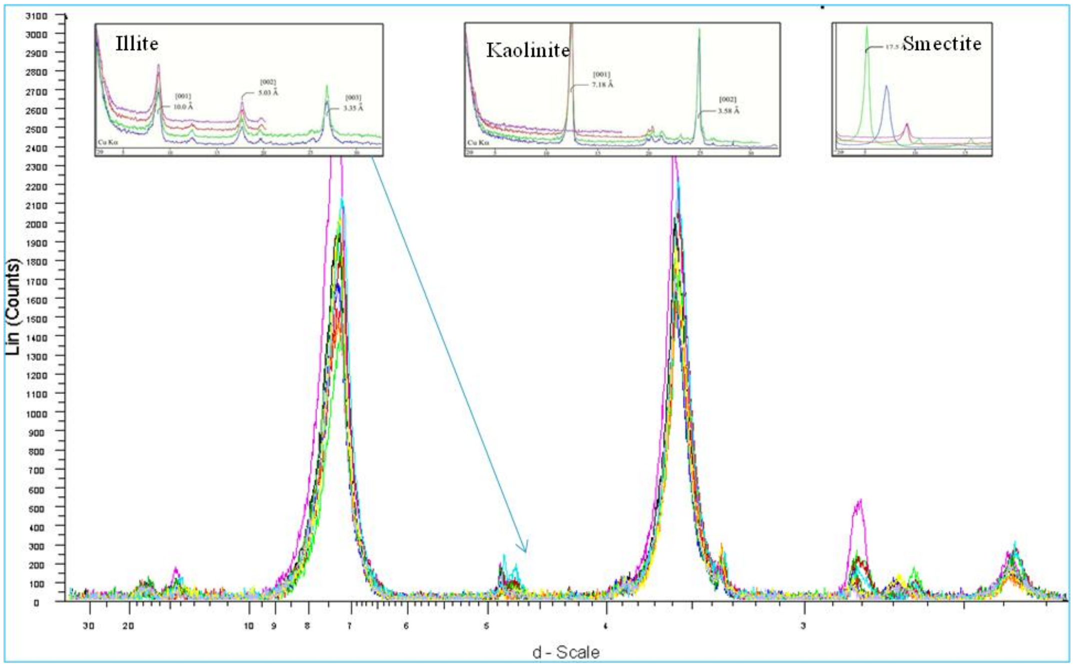


Figure 45. Mineralogical analysis of bulk samples from El Verde and Espiritu Santo Estuary

X-ray diffraction conducted at the rainforest area as well as the estuarine area is shown in figure 45. Results from the analysis revealed the absence of illite in all sample increments. The presence of smectite and kaolinite was determined for almost all analyzed samples that were collected from this study area. Samples with high Cs-137 activity at ESE Station 1 of the estuarine area possessed smectite, but did not indicate the presence of kaolinite or illite. Samples analyzed from this study site which possessed low Cs-137 activity values contained kaolinite. All samples that were analyzed from station 2 possessed kaolinite and smectite. Illite was completely absent from the soil samples collected from stations 1 and 2. Kaolinite was present at all stations.

DISCUSSION

The mineralogical composition of the study sites is a reflection of the complex nature of the tropical ecosystem. Both mineralogical analysis, X-ray diffraction and the grain size distribution, provided information that Vieques, Rincon and the El Verde Experimental Station soils are composed of clay particles that include smectite, kaolinite, chlorite and vermiculite. Illite was completely absent from the mineralogical composition of the study sites. Soils, in general, at each study site possessed a grain size distribution that could be described as constant. Downcore clay size particle distribution was fairly constant with depth at all study sites. It compresses the lowest percentage of particles sizes at all sites except for a few stations at the BONUS where clay distribution was as high as 20 %. This may be the result of the undisturbed environment from where the sample was collected. Clay distribution in the soils at the BONUS facility area was low. Since Cs-137 is generally associated with finer grain sediments this may be one of the reasons why Cs-137 does not appear to have been retained. There are only two stations at which clay size particles exceeded 10 %. Stations 2 and 4 possessed more clays than any of the other stations at the BONUS facility. Station 4 possessed Cs-137 activities that were one order of magnitude higher than station 2. Therefore, it appeared as though for this particular study site, that soil exhibiting more clay size particles did not necessarily possess higher Cs-137 activities.

Station 2 is in a protected environment surrounded by mangroves and tidal influence in which the sedimentation process generates a higher density of clays. Station

2 from Espiritu Santo Estuary would more likely retain Cs-137 coming from the slopes of the rainforest. Indeed this station is the only station where Cs-137 was found throughout the entire core. However, its clay distribution remained between 10-15 %. At the higher station of El Verde, clay distribution was higher than the distribution at the estuarine area. The difference in this fact might be due to the environmental processes such as weathering of rock in the upper elevations, which plays an important role in the formation of mineral particles. Weathering can be influenced by rain received in the area, which play a role in erosion and fluvial sediment movement.

The observed higher Cs-137 activity levels in the surface samples from El Verde were directly related to the clay content of the soil there. There was no trend in the downcore Cs-137 activities or grain size distributions determined at El Verde Experimental stations 1 and 2. The surface samples, as well as the soil samples, had a higher content of clays but there was no consistency of the composition of the soil layer. The dominant soil form was silt, which could provide binding sites for pollutants, but not to the same extent as clay sized particles.

In Vieques, clay size particles did not exceed 10 % for any sediment interval at either sample location. Downcore exPb-210 was slightly higher in the Mosquito Bay core than in the Kiani Lagoon core (figures 9-10). This was an indication of the different environments from which the samples were collected. The Kiani Lagoon is a calm aquatic environment in which the only input of water is the rainfall and some small tidal influence. The Mosquito Bay is an open coastal area in which physical processes contribute to the movement of sediment particles in the water column. Surface samples from Vieques also indicated the same pattern where clay distribution was low and silt and sand size particles dominated the local mineralogy. This is therefore indicative that although there was fewer fine size sediment particles present within the Kiani Lagoon core compared to the Kiani Lagoon core, the finer particles at the Mosquito Bay site were able to more effectively absorb Cs-137 as the result of global fallout and later introduced to Vieques' aquatic environment.

It has been shown that humic (colloidal) materials increase the retention of radionuclides in the ocean (Santschi et al; 2006). The presence of higher organic matter content (as estimated by LOI) may have increased the chance for radionuclide retention capabilities of the local sediments resulting in higher Cs-137 activities. Organic matter content was different at the different ecosystems where the study was conducted. For instance in the higher altitude of the rainforest, more dry leaves and dead trees highly increased the organic matter content of soils. However, Espiritu Santo River station 1 is located in a mangrove protected environment which promoted less input of debris and other sources that increased the organic matter. Station 2 at the Espiritu Santo River is located in an open beach environment and therefore the organic matter content there did not exceed 5 %. In a nearby protected mangrove forest, coastal influence on the accumulation of organic matter was noticeable at station 1 which organic matter content exceeded 20 %.

The estimation of the organic matter content obtained by LOI at areas such as the BONUS site also confirms that organic matter content will vary based on the ecosystem where the sample is collected. LOI samples from the BONUS areas remained fairly low. The lowest organic content was at station 2 which was closer to the shore. There the high energy waves disturbed the sediments as well as the accumulated soils. High waves also formed during cold fronts and the substrate was washed away bringing sand from beach shore to the area where samples were collected.

Organic content in samples from Vieques indicated that, at the surface of the core, higher organic content might be the result of the debris and buried shells from dead organism. Therefore Kiani has a higher organic content when compare with the Mosquito Bay area. Surface samples from Vieques had similar downcore mineralogy, but the samples collected from surface areas had higher organic content.

Atmospheric deposition of Cs-137 as a result of global fallout began in the 1950's. Cs-137 was present in the deepest sediment intervals at most sample locations, indicating that these sediments were deposited after the onset of atmospheric fallout.

As shown by gamma spectroscopy data (Figure 11-14) high to low Cs-137 activity trends were found in soils adjacent to the BONUS facility. This overall trend is likely the result of the characteristically slow mobility of Cs-137 on a substrate (Forsberg et al; 2000). Cs-137 measured in the soil collected adjacent to the BONUS facility maybe the result of global fallout and not the result of the flooding and leakage from the remains of the power plant. Although flooding occurred at the plant during hurricane George, the activity levels measured in the upper centimeters of the soil did not exceed the values measured by Alonso-Hernandez (2002, 2006) in Cienfuegos, Cuba or the fallout rate measured in Port St. Lucie, Florida (DHS, 2008). If the 1998 flooding disturbed the entombment and released a portion of the remaining Cs-137 to the adjacent area, it would be expected that higher Cs-137 activities would be present in the local soils, especially near the surface. The natural downhill slope upon which the power plant was built should also be taken into consideration. This slope would have served to facilitate the removal of the contaminants from the surface soil through runoff events.

If runoff occurred and radionuclides were transported within the sediments, it is likely that radionuclides would be transported further into the water column. It has been shown that sand does not absorb radionuclides due to its coarse grain and the high permeability of the minerals. The high energy beach adjacent to BONUS is mainly composed of sand and coarse grain material wherein radionuclides would percolate and their retention will be minimal. In the event that a leakage did occur and Cs-137 was released from the entombment to the local environment during tropical storms, it would be hard to retain Cs-137 in the soil due to the high content of sand and low clay distribution.

There are three intervals between 5 and 25 cm in which the level of Cs-137 present in the core was below detection limits for the Kiani Lagoon stations. Eight intervals within the upper 15 cm of sediment of the Mosquito Bay core exhibited either the absence of Cs-137 or the presence of Cs-137 at levels that were below detection limits. Intermittent intervals of sediment in which Cs-137 was either absent or below detection limits was likely the result of: 1) biogeochemical processes, such as Cs-137 desorption caused by cation competition resulting from anoxic conditions or salt water intrusion, or 2) the absence of permanent Cs-137 particle binding sites (e.g. interlayer position of illite).

Although sediment samples that were analyzed did not contain illite, the presence of smectite and kaolinite was detected. The surfaces of kaolinite and smectite, as well as the interlayer position of smectite potentially served as non-specific binding sites for Cs-

137. When compared to other clay minerals, smectite has the greatest ability to absorb Cs-137, as well as other cations, as a result of its expandable interlayer position. However given the fact that the absorption ability of smectite is non-selective, in the presence of increased dissolved cation concentrations (e.g. higher salinities or anoxic conditions) Cs-137 that was previously bound to smectite particles could be easily desorbed from the interlayer position and reintroduced in the dissolved phase into the local aquatic environment. Since radionuclides in Vieques are present in oxic environments, their mobility will depend on sediments and water transport. As we can see on Figure6-9, there is no evident trend on the distribution of Cs-137 in Vieques. This can be the result of sediment disturbance and mixing which was affected by the process of sedimentation. In the eventuality of a hurricane, sediment mixing will occur, making it harder to obtain a geochronology that represents the reality of the island of Vieques in terms of Cs-137 and other contaminant retention in sediments.

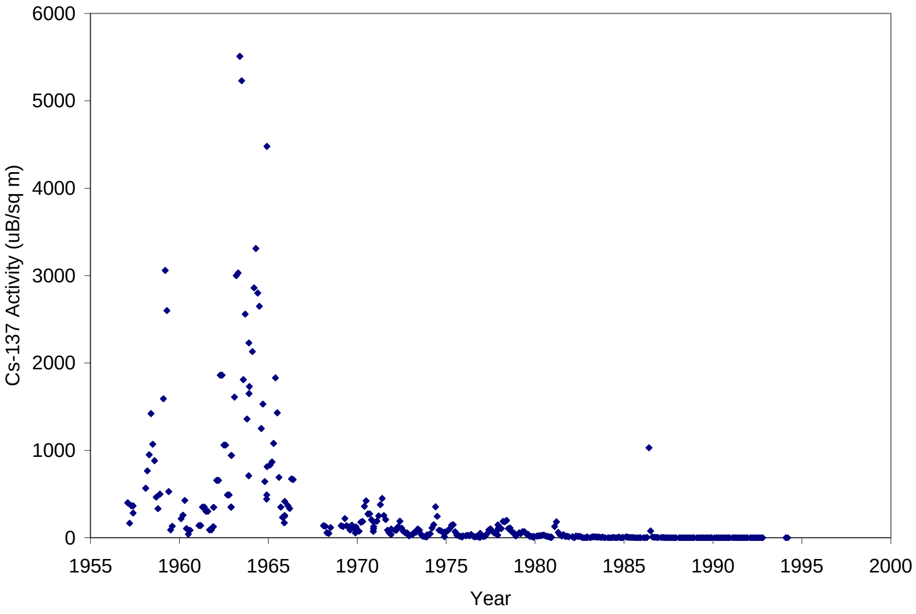


Figure 46. Cs-137 fallout record for the Miami region, adapted from Surface Air Sampling Program, Department of Homeland Security, 2008.

Cs-137 activities determined during this investigation did not exceed Cs-137 activities determined in the state of Florida. Fallout Cs-137 at Ft. St. Lucie is 29.6 μBq/m^3. Fallout data for Miami is shown in figure 47; the oscillations that were observed on the sampling sites in Miami did not match the data presented here in the current project.

Environmental conditions and exposure to tidal and weather influences definitely influence the retention capacity of the ecosystem. The inventories of station 2 are 20 times higher than the inventory from the beach ecosystem where current and deposition influence clay and organic matter accumulation.

The study sites are composed of oxic substrates where Cs-137 mobility is slow. Factors affecting the retention of radionuclides are the grain size and organic content of the substrate as well as the impact received in the environment. Due to the effectiveness of the binding site and the high cation competition for binding sites, Cs-137 is present at low concentrations at the estuary and the rainforest ecosystem of the island of Puerto Rico.

Some other factors controlling the fate and transport of Cs-137 at all study sites of this project might be the variable mixing at Vieques and the Espiritu Santo Estuary. As seen on Figures 6-9 and 15-18, gamma spectroscopy profiles confirmed the presence of Cs-137. Variable mixing enabled the sediments to be deposited in a non-uniform way, thereby providing the stratigraphic pattern we observed.

Bioturbation can also affect sediment distribution. As marine organisms live in the sediment column, they scavenge the sediments looking for their food source. As benthic fauna make their way to the top or the bottom of the sediment column, radionuclides can be moved from the depositional system. In the current study movement could have been caused by benthic organisms as they removed organic matter and clay minerals that provided the binding site for Cs-137.

Sediments coming from the rainforest area have been heavily disturbed by the development and the wide range of sedimentation rates. The Espiritu Santo Estuary has been a major location for local housing and tourist development. During the last 10 years, more than 300 hundred houses were built in the area as well as a new resort hotel complex which includes a golf course that is adjacent to the Espiritu Santo River. Urban development will increase run-off into the estuarine area which will contribute to the faster accumulation of sediments in the area. Webb and Gomez (1998) provided information on sedimentation rates for a similar area and the rates ranged from 0.24 to 3.9 cm per year of sediment. Sedimentation rates will definitely be higher at the Espiritu Santo Estuary where all the water from run-off comes to the bay. Landslides are also very common in the rainforest and as they occur, more sediment will quickly be added to the water column. As such, if Cs-137 were released to the soil, it would likely be bound to smectite or kaolinite, two clay minerals that unlike illite bind Cs-137. Given the absence of 10 Angstrom interlayer spacing of illite that represents strong irreversible Cs-137 binding sites, smectite which possesses an interlayer space of 10-18 Angstrom would likely serve as the major binding material of Cs-137 in the local environment. The presence of other elements that can out compete Cs-137 for binding site would depend on the interstitial space. Smectite, which has a larger interlayer space than illite, would facilitate the binding of other elements such as K which will then outcompeting Cs-137.

Cs-137 absorption on kaolinite is limited to the surface of this clay mineral. Like that of smectite, Cs-137 binding onto kaolinite is non-selective and can be temporary.

The ICP-OES results indicate that soils at the BONUS facility are present in a primarily oxic environment. Studies have shown that anoxic environments facilitate the mobilization of radionuclides in the substrate. When Cs-137 is present in oxic environments, its mobility will be slower compared to the anoxic environment. The presence of organic matter is higher at station 5 and the same station 5 showed the highest Cs-137 activity. Taking into consideration that illite is not present at any of the stations at BONUS and the substrate is oxic, it will be logical to infer that organic matter is playing an important role in the retention of Cs-137 at the studied sites.

This investigation provides insight into the radiogeochemistry of the rainforest and the adjacent Espiritu Santo Estuary. Gamma spectroscopy revealed the presence of Cs-137 at all sites. A difference in the Cs-137 activity levels determined at the various locations can, in part, be attributed to the different types of environments.

CONCLUSIONS

Cs-137 activities in Vieques sediments and soils vary with location. The distribution of Cs-137 in surface samples collected from mangrove forests, marsh and lagoon environments on the island range from below detection limits to 0.6 dpm/g. There is no correlation between type of environment (e.g. mangrove forest, marsh, and lagoon) and Cs-137 activity present in Vieques surface sediments and soils. Downcore data suggest that there are fine grain size particles present at both Mosquito Bay and Kiani Lagoon which are able to effectively absorb and retain radionuclides introduced into these local environments. Downcore Cs-137 activity profiles indicate the occurrence of previous sporadic episodic events (e.g. mixing, burial, erosion, bioturbation, hurricane/storm/wind precipitated particle removal, adsorption and absence of suitable particle binding sites) have transported Cs-137 laden particles away from original deposition sites.

The absence of illite may have influenced the retention capacity of Vieques sediments. The retention of Cs-137 might be influenced by the organic matter present in the analyzed samples. The presence of the clay mineral particles kaolinite and smectite, which provide a weaker binding site for Cs-137 to the sediments, was observed. Sediments in Vieques are oxic sediments which also influence the slow movement of Cs-137. Other physical and biological parameters like sediment disturbance due to hurricanes and bioturbation can affect sediment mixing.

Findings from this study provide insight regarding the extent to which radionuclides (and other contaminants) can be transported throughout Puerto Rico's various environments. Additional radionuclide, inorganic chemistry, grain size, organic matter estimates and inventories will provide further insight to determine the local capacity and ability of sediment particles to retain contaminants (e.g. depleted uranium, associated trace isotopes and heavy metals).

Analytical chemistry and clay mineralogy analyses should be undertaken to investigate additional radionuclide properties to determine the distributions of naturally occurring (Pb-210, Ra-226, and uranium isotopes) and artificially produced Pu-238, Pu-239, Pu-240, Am-241, Np-237 and Tc-99 radionuclides. Sedimentation and mixing rates should be calculated after determining downcore excess ^{210}Pb activities. Knowing these rates will provide insight regarding the geological features of sediments in the island of Vieques and how long it takes to sediment to settle. Additional radionuclide analysis should be conducted to determine the presence, distribution and concentration of depleted uranium in Vieques aquatic sediments. Determining the concentrations and distributions of these radionuclides will further assist the VNWR in their efforts to create suitable and effective practices that will help the advancement of their mission to conserve our natural resources

The data from the BONUS Area identified potential risks associated with the radionuclides left in the entombed monolith left at the facility. The low retention indicated that there is no leak of the radionuclides left in the entombed; radionuclides released during the accidents at the BONUS have been leached out from the local environment. Knowing that there is low retention is a positive feedback to thousand of surfers and consumers of the area. The downcore profiles are providing information on the land use and how radionuclides serve as tracers to identify remobilization and disturbance of the soil in which the power plant was constructed. The other aspect that we need to consider is the fact that global fallout is not a major contributor to the total inventory of Cs-137 and exPb-210.

Findings at the BONUS facility area also confirm that the absence of clays that serve as sinks for radionuclides might be another aspect contributing to the low retention of radionuclides in the area. Organic matter therefore plays an important role in the retention of radionuclides in soils; it might be possible to find higher activity levels on the crops and vegetation growing nearby the BONUS facility. The coastal water of Rincon is home of hundreds of marine and aquatic species which migrate from the cold winter to give birth and nurse their calves in the tropical region. Endangered whales and turtles utilize Dome beach and adjacent beaches as nursery and hatching grounds. Therefore, plant-to-soil-transfer analysis should be conducted.

Geochemical analysis of El Verde area and the Espiritu Santo provides information on environmental impacts that influences the retention of Cs-137. Cs-137 is present at all sampled sites. There is a difference in activity level at each site. This is likely the result of elevation, weathering, and environmental influences such as erosion, tidal processes, as well as organic matter content. Once deposited at the estuarine system, radionuclides may have been further transported by local currents and tides.

The beach area nearby the estuary is mostly composed of sand. Sand does not retain Cs-137. This study yields interesting data that can be used for better planning if more experiments such as those conducted during the Rainforest Project are undertaken in the future. All radionuclides released into the environment via tree injection and inoculation experiments must be present at some level in the soil and sediments today. Some of the radionuclides used had a short half-life. Others, like Cs-137 possess a long half-life and a fast mobility in the substrate. Vegetation at the rainforest was not sampled to study radionuclide transfer from soil-to-plants. The soil-to-plant transfer will be an important study to conduct in the near future in order to see if the radionuclides that persist in soils are carried to different trophic levels that affect food web dynamics.

Studies conducted in the late 1960's showed increased exposure of Cs-137 within the environment. These earlier studies need to be followed up with contemporary experiments conducted in the same manner. Geochemical data obtained through this research could be used to inform policy decision in the eventuality that others would propose to conduct future experiments similar to the magnitude of Rainforest Project. The absence of significant amounts of Cs-137 might be due to the fact that the sample area did not have sufficient binding sites for the pollutant released. The activity levels found at the rainforest today might be the result of atmospheric fallout resulting after the Chernobyl accident in 1986. As shown by Alonso-Hernandez (2002, 2006) the amount of Cs-137 is directly related to precipitation in Cuba and this might be the driving force in the rainforest. This statement is made after observing that the current Cs-137 activity in the rainforest does not represent the activity levels used by researchers during the RFP in the late 1960's . Poor retention can be caused by the absence of binding sites for the released pollutants.

As described in the previous text, Cs-137 retention on the island of Puerto Rico has been low and the main causes of this event in the ecosystem might be the variable sedimentation rate that has been cited by other researchers in the past as well as the absence of clay minerals. Clay minerals play a very important role in the retention and transportation of radionuclides, and on the island we only were able to document the presence of smectite and kaolinite in relatively low distribution in the soil and sediments.

CHAPTER III: ADSORPTION AND DESORPTION OF RUBIDIUM, COPPER, CADMIUM, CESIUM AND LEAD ON CLAY REFERENCE MATERIAL

INTRODUCTION

Population increases and urban development in coastal areas have impacted the aquatic and terrestrial environment in many ways. An example is the worldwide introduction of heavy metals from industrial and pharmaceutical activities (Critter and Airoldi, 2003, Bradl, 2004, Acevedo-Figueroa et al. 2006, Laing et al. 2009, Dong et al. 2009). Although many naturally occurring metals are vital for biological processes, anthropogenic activities can increase metal concentrations to levels that are deleterious. In some instances impacts can even extend to alteration of ecosystem dynamics.

Subsequent to the release of metals into the environment at elevated concentrations, their distributions, fluxes and potential for incorporation in the food chain can be influenced by many processes including aqueous chemical speciation, sorption processes and bioturbation of contaminated soils and sediments (Asci et al. 2007). One major undesirable outcome of heavy metal releases to the environment is bioaccumulation and biomagnification in the food chain. Consequently, the role of metals in food web dynamics and their mobility has become an increasingly important area of research in terms of environmental stewardship, human health, and economics (e.g., DiGiacomo, et al. 2004, Valiela & Bowen, 2002, Shriver, et al. 2002, Paul, et al. 2000).

Heavy divalent metals such as Pb, Cu and Cd are common in nature at low concentrations. At sufficiently high concentrations these metals can exert harmful effects on the ecosystem. Although Pb is found in the Earth's crust at generally small concentrations (Manahan, 2005), after the industrial revolution its use increased sharply due to mining, burning of fossil fuel, and a variety of manufacturing processes (Manahan, 2005). One major source of environmental pollution, leaded gasoline, was banned in many countries around 1995 (US EPA, 1996), and use of Pb in paint and other domestic products has also been reduced. Nevertheless, elevated lead levels in the environment continue to be a major concern (Manahan, 2005). Unlike lead, Cu is a biologically essential element for many organisms (Van Genderen et al. 2005). At sufficiently elevated concentrations, however, dissolved copper is toxic to unicellular organisms (Van Genderen et al. 2005). Anthropogenic concentrations of Cu in the environment are the result of mining (O'Brien, W. 1997, Manahan, 2005), use as a cladding on ships to reduce biofouling (Manahan, 2005) and the release of industrial effluents (Manahan, 2005). Cadmium, another heavy metal that has become problematic due to anthropogenic activities, is found in the Earth's crust at concentrations somewhat below the natural levels of Pb and Cu. It is concentrated and extracted during the production of other metals (O'Brien, W. 1997) and released into the ecosystem through municipal and industrial effluents (Manaham, S. 2005). Cd was once considered to have no known biological function in organisms (Van Genderen et al. 2005). However, at low concentrations, it provides some useful biological functions in a limited number of organisms (Van Genderen et al. 2005).

Monovalent elements can also become problematic in the environment due to human activities (Wyttenbach et al. 1995). Cs is one notable example in the form of released fission products, Cs-137 and Cs-134, from the nuclear industry (Avery, 1996; Aakrog, 1994). Cs-137 was distributed worldwide as a result of the Chernobyl nuclear accident in 1986. Subsequent to release into the environment, the propagation of elements is strongly influenced by interactions with particle surfaces (Alonso-Hernandez, 2006, Aarkrog, 2003, Moon, et. al, 2003, Livingston & Povinec, 2000, Avery, 1996, Santchi and Honeyman, 1989). As such, an understanding of metal interactions with surfaces is essential to an understanding of metal mobility in the environment.

Sorption processes in sediments and pore waters can both concentrate metals and retard their movement through the ecosystem (Fan et al. 2009, Morais-Barros et al. 2007). A variety of investigations has shown that sorption processes are strongly influenced by pH and ionic strength (Bruemmer and Herms, 1986, Bradl, 2003, Critter and Airoldi, 2003, Morais-Barros et al. 2007, Fan et al. 2009,). Metals binding to the surface of clay minerals can be especially important to the mobility of metals in the environment due to the high sorption capacity of clays and their characteristically high surface area and high surface charge (Missana et al. 2008).

Parameters of special importance to cation – clay interactions include temperature, pH, particle mass to surface area ratio, ionic strength, mineral type and porosity. Sorption is strongly promoted at high pH (Critter and Airoldi, 2003, Echevarria et al. 2005, Fan et al. 2009, Du Laing et al. 2009), and sorption decreases with increasing ionic strength (Echevarria et al. 2005). Soil type or clay mineral type also affects metal sorption because mineral structures exert a strong influence on mineral reactivity. Clays that have a double layer structure are especially strongly sorptive. Porosity also plays an important role in sorption due to its influence on water percolation through the clay matrix, and thus the extent to which water and clay surfaces can be brought into contact (Bruemmer et al. 1986).

The aim of this project is to examine the influence of pH on metal sorption by both pure mineral substrates and natural soils. The pure substrates used in this work are illite, smectite (montmorillonite) and kaolinite (kaolin). The natural substrates used in this work are soil and sediment samples from three locations in the island of Puerto Rico. This project constitutes the first examination of the influence of pH on trace metal sorption by soils from Puerto Rico. Although a few studies have described the presence of heavy metals in tropical ecosystems, including estuarine and riverine environments in Puerto Rico, none have described the influence of pH on sorption by tropical soils (Acevedo-Figueroa et al. 2006, Hunter and Arbona, 1995, Infante and Acosta, 1991).

METHODS

Smectite and illite are double layer type clays and kaolinite is a single layer type mineral. Smectite and illite consist of two tetrahedral sheets. These sheets have a negative charge that is compensated by the adsorption of cations. The interstitial space on clay minerals, specifically illite and smectite, is distinctive (table 8). The interstitial space defines the size of the ions with which each mineral will preferentially bind. In some instances the larger interstitial spacing of smectite enables favorable binding with relatively large ions such as potassium. Kaolinite has a smaller capacity for binding available cations. The mineralogy of these clays is especially effective promoting the binding of metals such as K, Na and Cs.

Table 8. Cation exchange capacity (CEC) of clay minerals (Clay Minerals Society).

Mineral	Interstitial layer	CEC	Surface Area
Kaolinite	Only one surface plate	2.0 meq/100g	10.05 +/- 0.02 m^2/g
Illite	10 Ångström	17 meq/100g	163 m^2/g
Smectite	Between 10 and 18 Ångströms	76.4 meq/100g	31.82 +/- 0.22 m^2/g

Cation binding capacity or cation exchange capacity of minerals (CEC) is highly variable. The CEC for the common minerals, illite, smectite and kaolinite, are presented in table 9. It is also the case that the interaction of natural soils with different cations is highly variable. Soils are heterogeneous natural systems composed of interacting organic and inorganic compounds. They are the final product of physical, chemical and biological weathering processes. The organic portion of soils comes from the decay of plants.

Weathering processes can create complex soil horizons, and compositions that strongly vary with depth (Manahan, 2005).

The natural soils and sediments used in this work were collected in Puerto Rico (figure 47). Soil sediment cores were collected from the area adjacent to the BONUS Plant in western Puerto Rico, and from the El Verde Experimental Station in eastern Puerto Rico. Marine sediment samples were collected from Bahia Mosquito, Vieques and from the Espiritu Santo Estuary (figure 47). Samples for these experiments were collected as described in Chapter 2 of this dissertation. Soils and sediments from bottom and top portions of the core were used to analyze any possible difference in the adsorption process as a function of core depth. The depth of the cores in soils and sediments ranged from 20cm to 62cm.

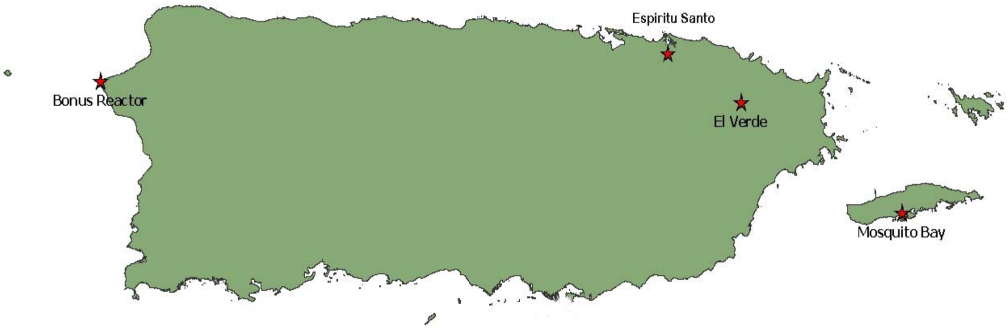


Figure 47. Sampling locations in Puerto Rico

Chemical treatments were performed in a class 100 laminar flow clean air facility (manufactured by Laminaire). Trace metal clean water (Milli-Q water) was obtained using a Millipore purification system (Bedford, MA). Teflon and polypropylene bottles, and polycarbonate filter membranes, were cleaned by soaking in HCl or HNO_3 for at least 1 week and then rinsing several times with Milli-Q water prior to use.

For all experiments, a pH 6.0 buffer solution was prepared from 50 mM 2-(n-morpholino) ethanesulfonic acid (MES, ≥ 99.5%, Sigma Aldrich) and 0.5 M NaOH. Trace Metal Grade nitric acid and certified 0.5M sodium hydroxide were purchased from Fisher Scientific (Pittsburg, PA). A metal stock solution in 2% HNO_3, containing 16.67 ppm of each metal, was prepared from single-element ICP standards (SPEX CertiPrep, Metuchen, NJ).

A pH standard (pH 3.0, 0.001 M HCl) was prepared and used to calibrate the electrode. The pH of the experimental solutions was expressed on the free hydrogen ion concentration scale. Measurements were obtained using a Ross-type combination pH electrode (No. 810200) connected to a Corning 130 pH meter in the absolute millivolt mode. Linearity and Nernstaian behavior of the electrode were verified by titrating a 0.3 M NaCl solution with concentrated HCl.

Experimental Methods

Three types of experiments were performed. In the first type of experiment, desorption of metals from minerals and soils was observed in the absence of any deliberate addition of metals to the experimental system. In the second type of experiment, rates of metal sorption by clay minerals were studied at approximately constant pH (pH~6) subsequent to addition of monovalent (Cs and Rb) and divalent metals (Pb, Cu, Cd) to the experimental system.. In the third type of experiment, the pH dependence of distribution coefficients (solid phase concentrations vs. solution phase concentrations) were determined using clay minerals (illite, kaolin, montmorillonite), terrestrials soils, and ocean sediments.

Desorption Experiments

Desorption experiments were performed over a range of pH. Solutions consisted of 5 mM MES at pH 6 added to the different types of substrates and 30µl of internal standard. Incremental additions of either 2% HNO_3 or 0.5 M NaOH were used to adjust the pH of the experimental solutions. An initial sample (5ml) of the solution was used to determine the initial concentrations of metals in each aqueous system. A 1:10 solid to solution ratio was achieved by adding 5 grams of substrate (clays or soils) to 50 ml of the aqueous solution housed in a centrifuge tube.

Experiments were conducted at room temperature t = 21 ± 0.5 °C. Samples were shaken for 24 hours on a (Eberbach) shaking table. Next, twenty-four experimental samples were centrifuged at 2000 RPM for 15 minutes in a HN-S Centrifuge (International Equipment Company). Following centrifugation, the final solution pH was measured. Two samples (5 ml each) were collected from the supernatant in the 50 ml vials for filtration. Five milliliters were used to rinse the polypropylene syringe and the Nuclepore filter (polycarbonate, 0.10 µm pore size). The syringe and the filter were then mounted on a polypropylene filter holder, and the second 5 ml from the centrifuged sample was filtered and collected in another 50 ml centrifuge tube. Samples from the desorption experiment were acidified with 10µl of concentrated HNO_3. Thirty microliters of an internal standard solution containing equal concentrations of In and Bi were then added to 5 milliliters of each acidified experimental solution.

Sorption Kinetics

Sorption kinetics experiments were performed by measuring the extent of metal sorption through time. Five hundred milliliter solutions consisting of 0.01 M ammonium nitrate, 5 mM MES (pH 6) and 100 ppb of each metal were housed. in 1L Teflon bottles An initial solution sample was collected prior to addition of 10g of solid (illite, kaolinite or montmorillonite). The contents of each bottle were stirred throughout each experiment using a (Thermolyne) magnetically-coupled stirring apparatus. Solution pH was measured and samples were taken at 10, 30, 60, 90, 120, 180, 360 minutes, 24 hrs and one week after initiation of the experiment. Two 5ml samples were taken following a protocol essentially identical to that used in the desorption experiments. However, for measurements of sorption kinetics samples were filtered but not centrifuged after each time increment. Samples were diluted 10-fold with 2% HNO_3, and 50µl of an internal standard solution containing equal concentrations of In and Bi was added to the solutions prior to analysis

Sorption Experiments

Sorption experiments were performed over a range of pH. Solutions contained 0.01 M using ammonium nitrate (99.999%, Sigma-Aldrich), 5 mM MES, and 100 ppb of each metal. The overall experimental protocol, sample preparation and processing was similar to that used in desorption experiments. The only distinction between the desorption and sorption experiments was the addition of metals in the latter. The concentrations of individual elements ranged between 0.48 and 1.17 µM depending on each element's atomic mass (see table 9). The sum concentration of all added elements in each experimental system was 4.87 μM. Prior to analysis, samples were diluted 10-fold with 2% HNO_3, and 50µl of an internal standard solution that contained equal concentrations of In and Bi was added.

Table 9. Initial concentration of metals added to adsorption experiment

Metal	Initial concentration
Pb	483.6 nM
Cu	1.57 μM
Cd	889.6 nM
Cs	752.4 nM
Rb	1.170 μM

Analysis

Acidified samples were analyzed with an Agilent Technologies 7500cx inductively-coupled plasma mass spectrometer (ICP-MS). Solutions were introduced into the ICP-MS with a Micro Mist concentric nebulizer and a double-pass (Scott-type) quartz spray chamber that was Peltier-cooled to t = 2°C. During instrument tuning, the formation of oxide and double-charged ions was minimized with a 1 ppb Ce solution. MO^+ and M^{2+} peaks were always less than 1.5% and 2% of the corresponding M^+ peak, respectively, and correction for this effect proved unnecessary. Metal concentrations were calculated from linear regressions of five standards (0.5, 1, 2, 5, and 10 ppb). A 2% HNO_3 solution was run before and after the calibration line, to serve as a blank and to rinse the instrument after the highest standard. In addition, after each autosampler position, Milli-Q water was aspirated for 5 s followed by a 2% HNO_3 wash solution for 60 s, in order to rinse the outside of the autosampler probe and the sample introduction system. All standards and solutions were injected in triplicate. Ion counts were corrected for minor instrument drift by normalizing ^{65}Cu, ^{85}Rb, ^{111}Cd, ^{114}Cd, and ^{133}Cs to ^{115}In and normalizing ^{208}Pb to ^{209}Bi. Detection limits, calculated as three times the standard deviation of 37 blanks, were estimated to be 0.01 ppb for Cd, 0.03 ppb for Cs, 0.06 ppb for Rb, 0.08 ppb for Cu, and 0.09 ppb for Pb.

Distribution coefficients were calculated by using the following equation:

$$Ks = [MS]/[M]_{final}$$

Where $[MS] = [M]_T - [M]_{final}$ = the concentration of sorbed metal and

$[M]_T = [M]_{initial} + [M]_{desorbed}$ = the total concentration of metal in each experiment.

$[M]_{final}$ = the final dissolved concentration of metal at the end of each experiment.

$[M]_{initial}$ = the initial dissolved concentration of added metal in each experiment.

$[M]_{desorbed}$ = the concentration of metal released from a substrate during desorption experiments.

RESULTS

Desorption experiments (clay minerals)

Results for the desorption of reference materials are shown in Figure 48 and summarized in Table 10. Desorption behaviors were distinctive for all 3 types of clays. Cu and Rb are extensively desorbed from all clays. Kaolin and montmorillonite produced relatively low concentrations of Cu and Rb (≤ 200 nM), while illite produced Rb concentrations on the order of 2, 500 nM. Rb concentrations produced by desorption from illite are more than twice as large as initial Rb concentrations produced by deliberate metal additions in sorption experiments (table 10). Illite produced moderate concentrations of Cs (~ 225 nM), whereas for kaolin and montmorillonite, released Cs concentrations are relatively low (<11nM). Pb and Cd show the smallest extent of desorption from all clays (<2nM). Figure 48 also shows, for all metals, that the extent of desorption is not strongly dependent on pH.

Metal desorption experiments using soils and sediments from Puerto Rico (figure 49 and table 12) show results that are similar to those obtained using pure clay minerals (figure 48 and table 11). In general high desorbed concentrations of Cu (≤ 660 nM) were observed at all study sites. High desorbed concentrations of Rb were observed at all sites except for the El Verde area where desorption of Rb is ≤120 nM. Pb, Cd and Cs exhibit relatively minor extents of desorption (≤10 nM) from soils at all of the study sites. The soils from El Verde are the only samples that show a decrease in desorption with increasing pH (figure 49). Desorption at all other sites appears to be independent of pH.

Desorbed concentrations of Cu and Rb vary from site to site but have concentrations generally similar to those produced by desorption from montmorillonite and kaolin. Desorbed Cs concentrations were generally low for all minerals, soils and sediments with the exception of Illite, which produced Cs concentrations one to two orders of magnitude higher than was observed for other solids. Desorbed Cd concentrations were low for all solids, but were generally higher for soils and sediments than was observed for clays minerals. Pb concentrations were low for clay minerals and generally only slightly higher in soils and sediments.

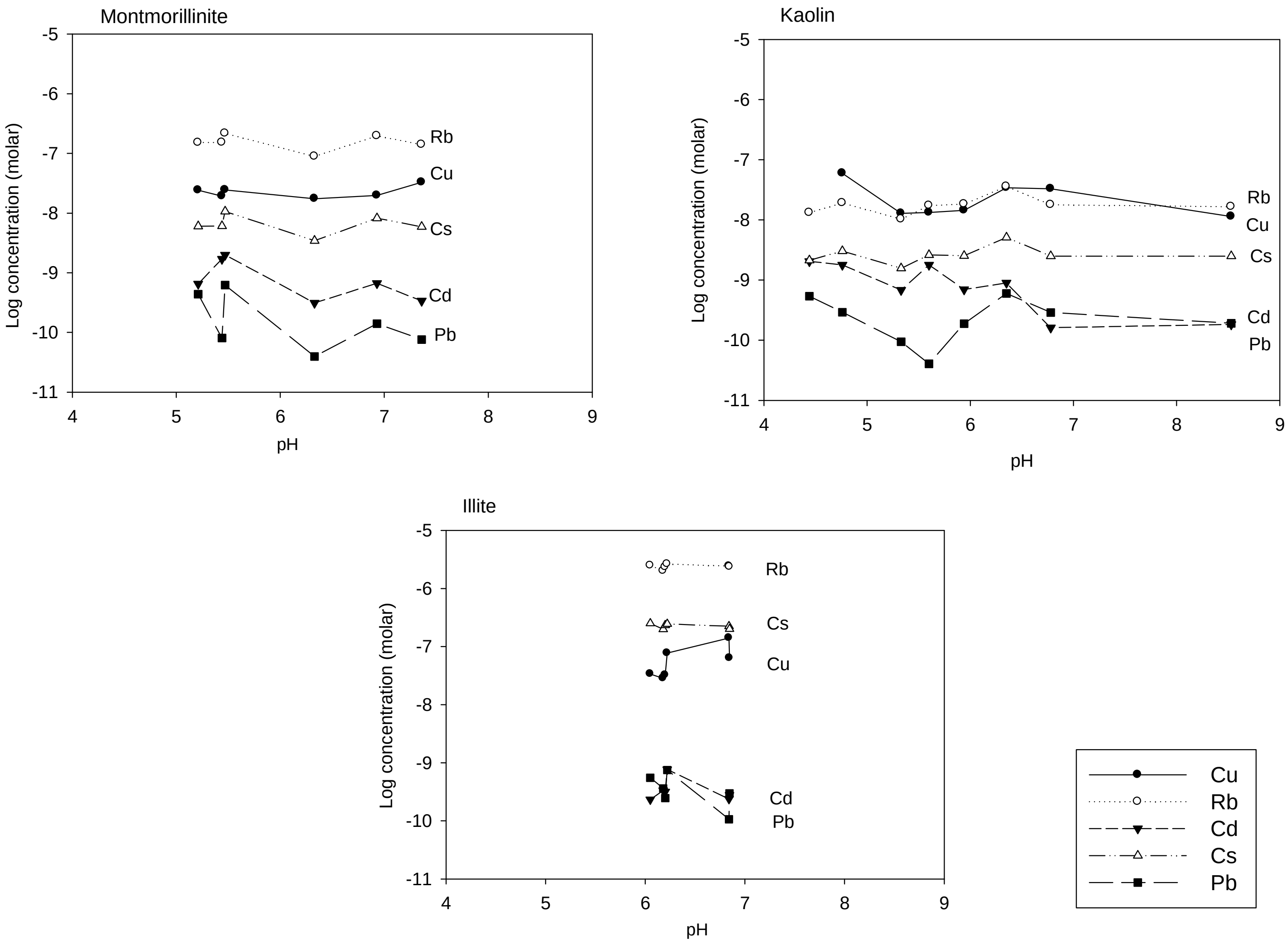


Figure 48. Desoption experiment in clay minerals.

Table 10. Summary of results of desorption experiments on clay minerals

Element Desorption on Illite	Average concentration (nM)	Standard Deviation	Highest concentration (nM)	Lowest concentration (nM)
Pb	0.40	0.23	0.55	0.11
Cu	62.60	42.82	140.26	28.29
Cd	0.40	0.20	0.77	0.23
Cs	225.20	21.94	249.88	198.17
Rb	2376.7	209.7	2630.2	2006.60

Element Desorption on Montmorillonite	Average concentration (nM)	Standard Deviation	Highest concentration (nM)	Lowest concentration (nM)
Pb	0.23	0.24	0.62	0.04
Cu	22.97	5.60	32.87	17.40
Cd	0.94	0.72	1.98	0.31
Cs	6.70	2.44	10.62	3.436289
Rb	157.34	44.66	216.10	88.88

Element Desorption on Kaolin	Average concentration (nM)	Standard Deviation	Highest concentration (nM)	Lowest concentration (nM)
Pb	0.24	0.18	0.60	0.04
Cu	25.54	17.95	59.70	11.40
Cd	1.15	0.66	2.05	0.16
Cs	2.84	1.10	5.11	1.57
Rb	19.31	7.85	35.84	10.27

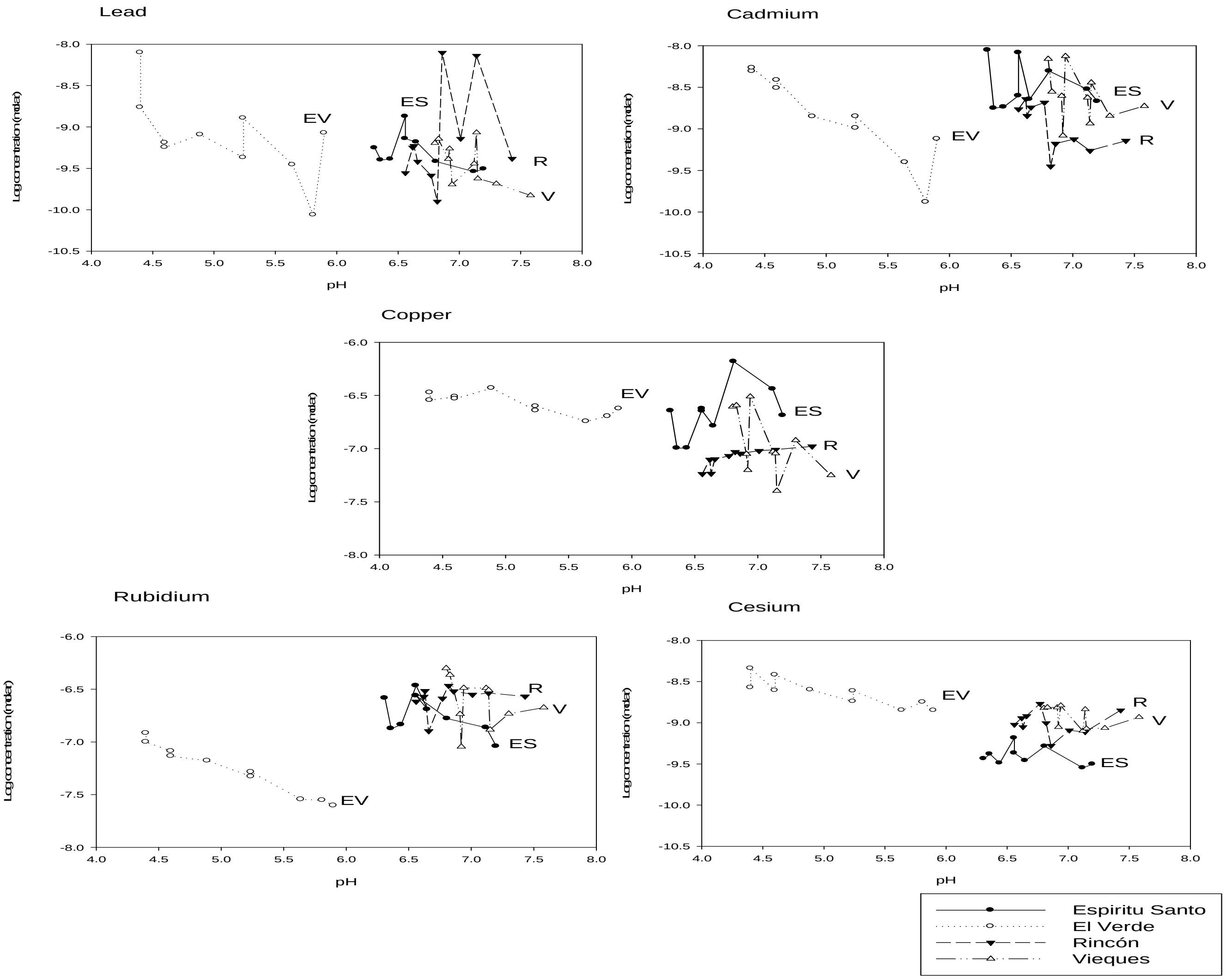


Figure 49. Desorption experiments on soils and sediments from Puerto Rico

Table 11. Summary of results of desorption experiments for soils and sediments in Puerto Rico.

Element Desorption at Espiritu Santo	Average concentration (nM)	Standard Deviation	Higher concentration (nM)	Lower concentration (nM)
Pb	0.56	0.33	1.34	0.29
Cu	253.67	171.55	659.36	101.14
Cd	3.95	2.79	8.87	1.77
Cs	0.41	0.12	0.65	0.28
Rb	194.94	81.88	342.11	90.83

Element Desorption at El Verde Exp. Station	Average concentration (nM)	Standard Deviation	Higher concentration (nM)	Lower concentration (nM)
Pb	0.75	0.50	7.91	0.09
Cu	269.16	58.73	370.13	180.34
Cd	2.24	1.78	5.41	0.14
Cs	2.47	1.08	4.58	1.41
Rb	55.73	26.49	121.33	24.89

Element Desorption at BONUS Area Rincon	Average concentration (nM)	Standard Deviation	Higher concentration (nM)	Lower concentration (nM)
Pb	1.97	3.20	7.90	0.03
Cu	84.19	13.74	105.12	57.89
Cd	1.24	0.73	2.29	0.35
Cs	1.05	0.36	1.70	0.53
Rb	272.29	59.79	341.53	126.93

Element Desorption at Vieques	Average concentration (nM)	Standard Deviation	Higher concentration (nM)	Lower concentration (nM)
Pb	0.39	0.27	0.86	0.15
Cu	136.33	93.61	308.91	40.00
Cd	3.094	2.00	6.92	0.83
Cs	1.19	0.35	1.63	0.85
Rb	243.59	110.48	500.66	130.70

Equilibration kinetics (clay minerals)

Several sorption experiments were performed over time (Figure 50) at constant pH (~6) to determine an optimum sampling period for sorption experiments that were performed over a range of pH. These experiments, conducted using the clay reference materials, showed that equilibrium between the solutions and all clay minerals (illite, kaolin and montmorillonite) was attained on short time scales. Only small changes in concentration were observed after 120 minutes (figure 50). The equilibria between sorbed and dissolved metals can be summarized as follows: Pb and Cu were sorbed to the greatest extent, Cd was sorbed to a lesser extent, and Cs and Rb were adsorbed to much lower extents than the divalent elements. The solution concentrations of all metals except Rb decreased sharply within the first 10 minutes of each experiment. For Rb this decrease was observed only in the case of Montmorillonite. Due to strong desorption, Rb concentrations actually increased through time

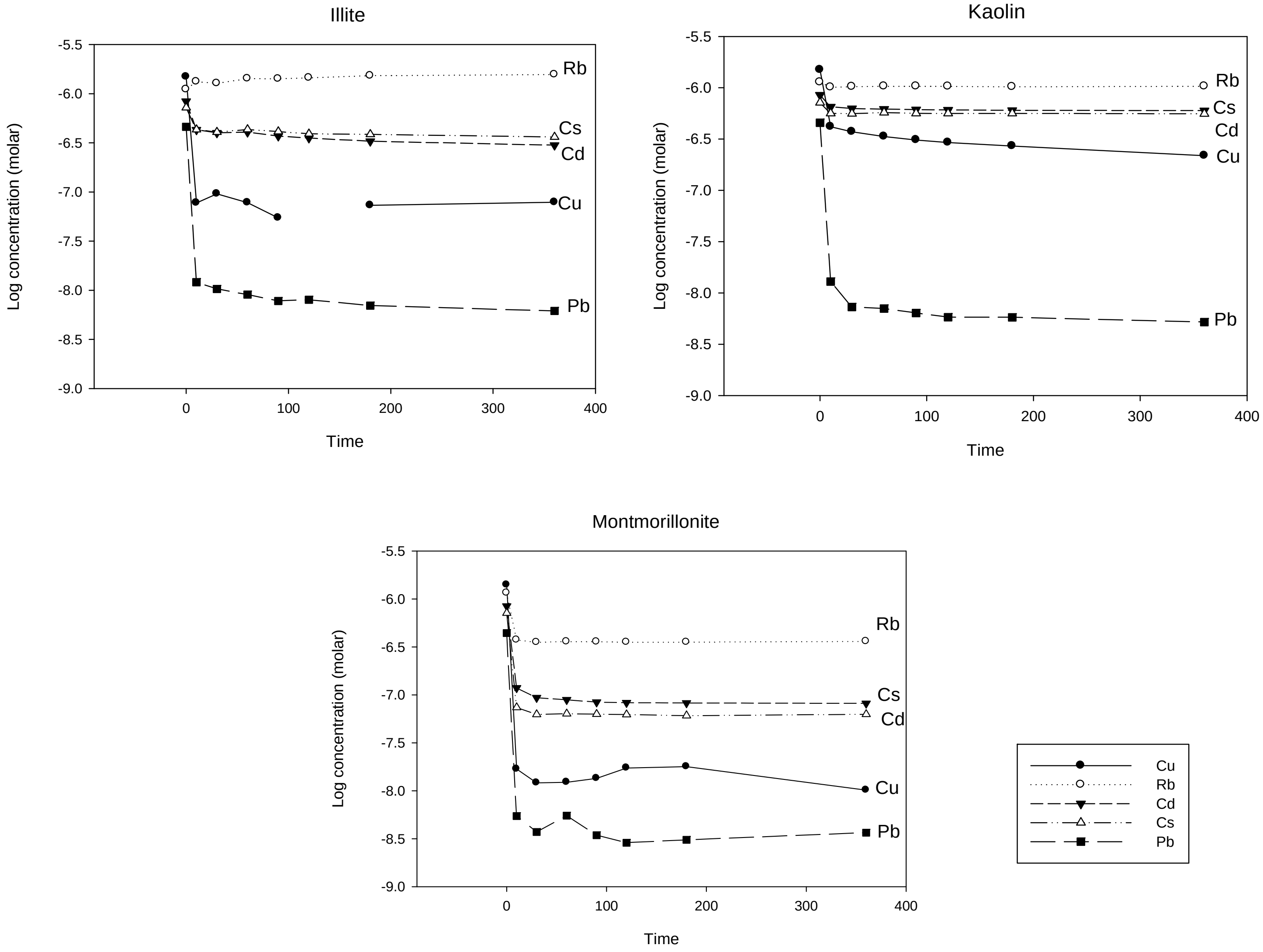


Figure 50. Element concentration over time on clay minerals

Sorption on reference material

Figure 51 shows results clay minerals adsorption experiments performed using illite, kaolin and montmorillonite, and Table 12 provides log K_s averages and standard deviations Figure 51 demonstrates that the extent of adsorption is not strongly dependent on pH for the metals and clays used in this study. Distribution coefficient values ranged over two to three orders of magnitude. The highest average log K_s values were observed for Pb (log K_s (Pb) ~ 2.7) and the lowest values were observed for Rb on Illite (log K_s (Rb) = -0.55). Observed average log K_s values had the following order Pb > Cu > Cd > Cs > Rb.

The average distribution coefficients observed (Table 13) for two of the divalent cations, Pb and Cu, were quite consistent for all clay mineral substrates ((log K_s (Pb) ~ 2.7 and log K_s (Cu) ~ 1.6). For the remaining elements, distribution coefficients were increasingly variable between the substrates, and the extent of variability increased in the order Cd < Cs < Rb. Average distribution coefficients for Cd were as low as log K_s (Cd) ~ 0.7 (kaolin) and as high as log K_s (Cs) ~ 1.3 (montmorillonite). Cs and Rb log K_s averages were even more variable between the three types of clay minerals: Average log K_s values for Cs were as low as 0.27 (kaolin) and as high as 1.5 (montmorillonite) Average log K_s values for Rb ranged between -0.55 (illite) and 0.73 (montmorillonite).

For Cd, Cs and Rb, the highest average distribution coefficients were always observed for montmorillonite. The lowest average distribution coefficients for Cd and Cs were observed for kaolin and the lowest log K_s value for Rb was obtained for illite, the clay mineral that produced net desorption in the Figure 50 evaluation of sorption kinetics.

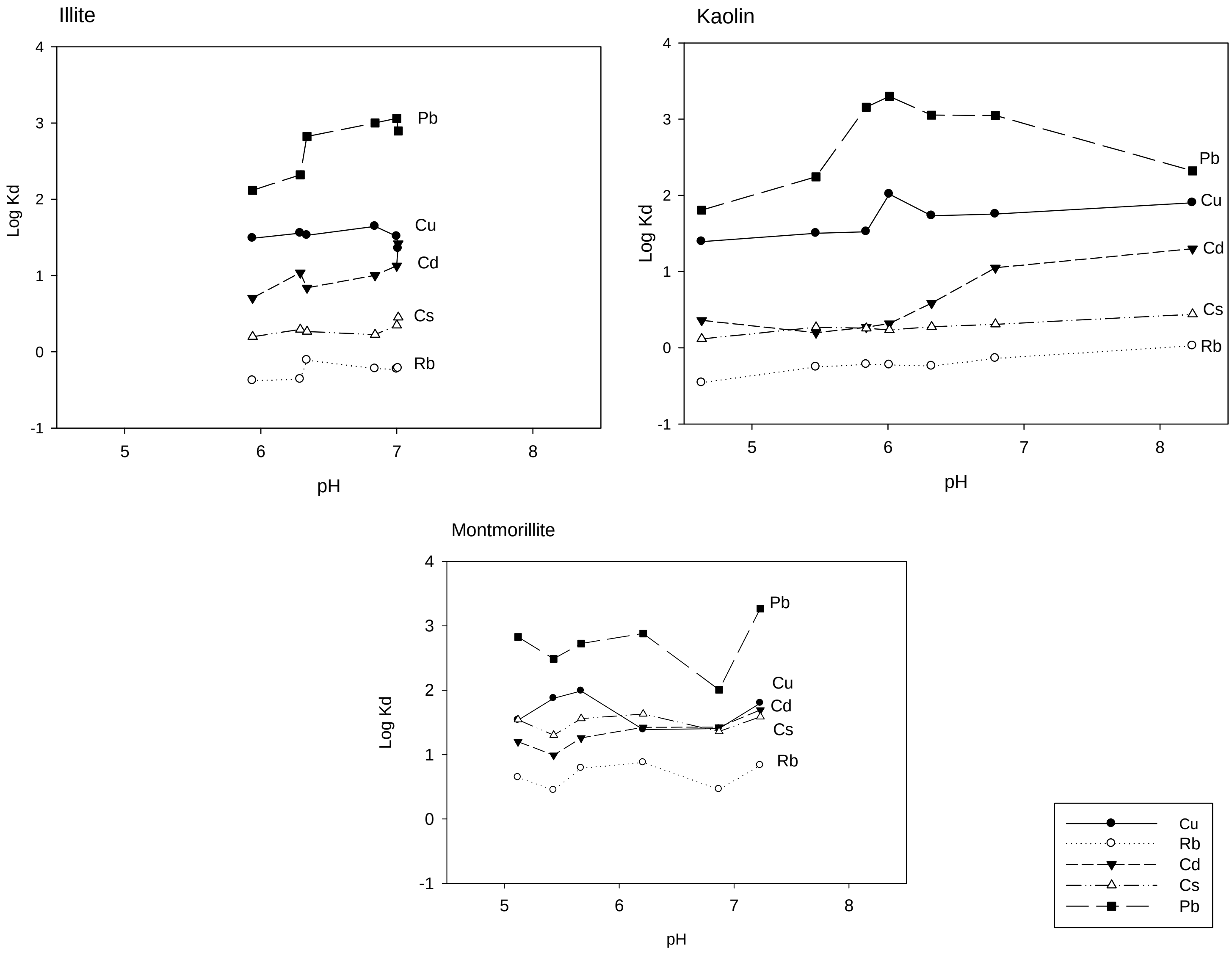


Figure 51. Metal adsorption on clay mineral

Table 12. Summary of results of adsorption experiments on clay minerals

Element Adsorption Illite	Average log K_s	Standard Deviation	Highest value	Lowest value
Pb	2.70	0.39	3.06	2.19
Cu	1.53	0.098	1.67	1.37
Cd	1.03	0.24	1.42	0.71
Cs	0.45	0.07	0.55	0.33
Rb	-0.55	0.41	0.02	-1.16

Element Adsorption Montmorillonite	Average log K_s	Standard Deviation	Highest value	Lowest value
Pb	2.70	0.42	3.27	2.00
Cu	1.67	0.26	2.00	1.39
Cd	1.33	0.24	1.70	1.00
Cs	1.50	0.13	1.63	1.30
Rb	0.73	0.16	0.90	0.53

Element Adsorption Kaolin	Average log K_s	Standard Deviation	Highest value	Lowest value
Pb	2.70	0.56	3.30	1.81
Cu	1.70	0.19	2.04	1.40
Cd	0.68	0.46	1.30	0.20
Cs	0.27	0.10	0.44	0.12
Rb	-0.20	0.15	0.04	-0.43

Sorption on soils and sediments in Puerto Rico

Metal sorption experiments on soils and sediments from the island of Puerto Rico are shown in figure 52. Table 15 shows sorption comparisons for all four soils and sediments at the study sites. As was observed using the pure clay minerals, the most strongly sorbed metal was Pb and the least strongly sorbed metal was Rb. In contrast to the order of log K_s.values observed for the pure clay minerals, Cd was sorbed more strongly than any metal other than Pb, and Cs was sorbed more strongly than Cu at all sites except the BONUS site at Rincon.

As in the case of the experiments performed using pure clay experiments, pH adjustments were performed in the experiments with soils and sediments. The pH ranges in these experiments are shown in Table 14. Soils from El Verde Experimental Station (EV) had the lowest pH of all samples, starting with a pH of 4.4. Even though the soil from El Verde ES was treated with 0.5 M NaOH to gradually increase the pH, the treatment only increased pH by 1.4 units to a maximum value of 5.8. All soils had a substantial buffer capacity, similar to that seen in experiments with illite. Samples from Rincon exhibited a change of only 0.6 pH units after addition of 2% HNO_3. The pH of sediments from the Espiritu Santo River and Mosquito Bay (Vieques) changed by only 0.7 units and 0.6 units after similar treatments. For all soil types except El Verde, there was no easily discernable trend of log K_s values with pH. For the acidic El Verde soils, log K_s generally increased with increasing pH. The strongest increase was observed for Cd sorption, and only in the case of Cu was there no observed trend at this site.

Results from the clay mineral experiments can be compared and contrasted with the results obtained using soils and sediments. Distribution coefficients observed for Pb in both pure clay minerals and the natural soils were closely comparable. Average log K_s values obtained with soils and sediments ranged between 2.45 and 2.84 compared to an average of 2.70 for the pure clay minerals. In the case of Cu, Average log K_s values obtained using soils and sediments ranged between 0.56 and 1.12. These values are substantially smaller than the range of values observed using pure clay minerals ($1.53 \leq \log K_s \leq 1.70$. In contrast to the lower log K_s values for Cu observed using natural samples, average log K_s (Cd) values obtained for natural soils and sediments ($1.11 \leq \log K_s(Cd) \leq 2.02$) are substantially higher that those observed using pure clay sediments ($0.68 \leq \log K_s(Cd) \leq 1.33$). Distribution coefficients for Cs and Rb obtained using natural samples were broadly comparable to those observed using pure minerals: $1.05 \leq \log K_s(Cs) \leq 1.58$) vs. $0.27 \leq \log K_s(Cs) \leq 1.50$) and $-0.50 \leq \log K_s(Rb) \leq 0.42$) vs. $-0.55 \leq \log K_s(Rb) \leq 0.73$)

Table 13. Experimental pH for each soil type

Sample	Lowest pH	Highest pH	Sample type
Mosquito Bay, Vieques	6.85	7.60	Ocean Sediment
Espiritu Santo, Rio Grande	6.3	7.12	Ocean Sediment
El Verde Experimental Station, Rio Grande	4.36	5.81	Soil
Area adjacent to BONUS Power Plant, Rincon	6.66	7.22	Soil

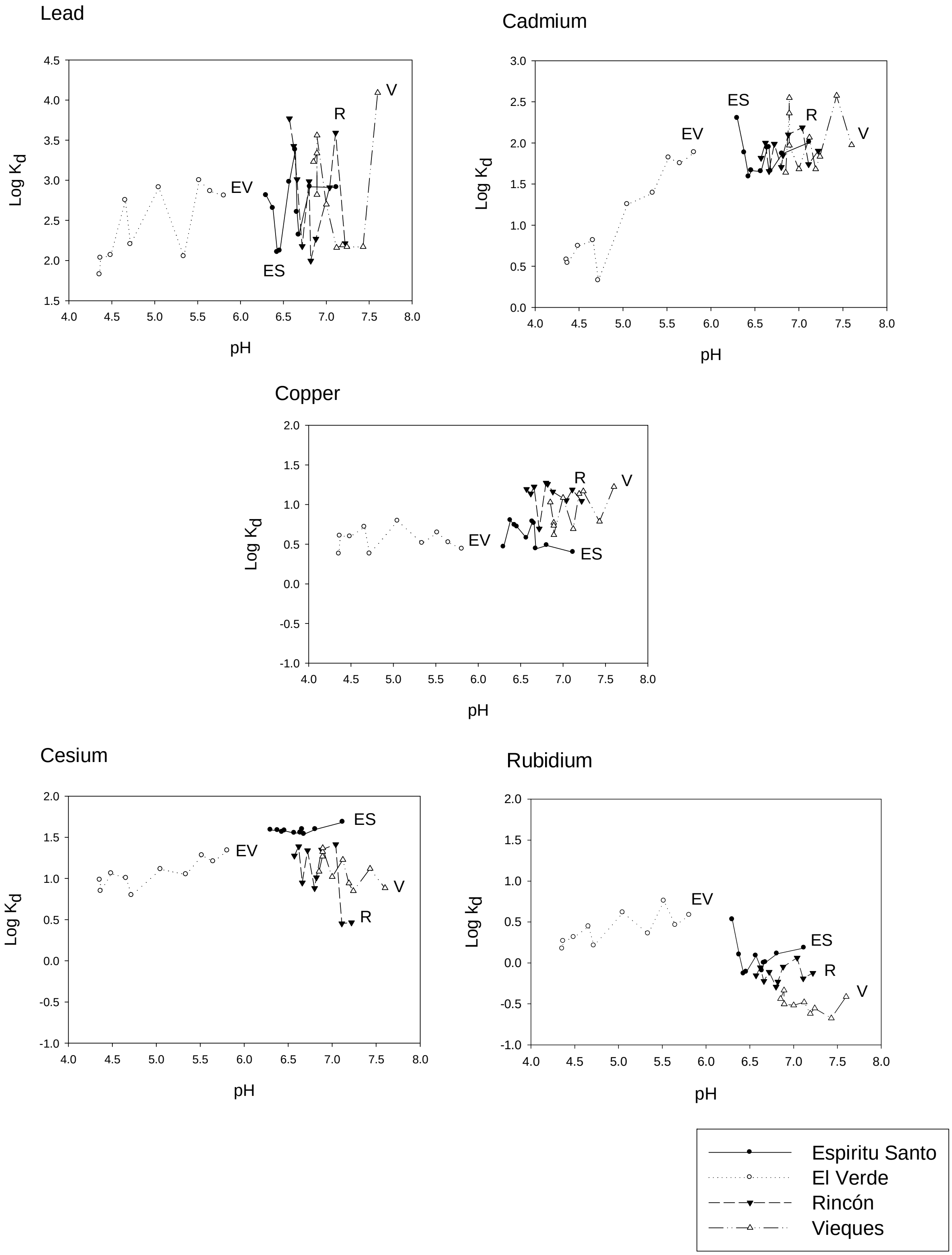


Figure 52. Metal behavior in soils and sediments from different study sites.

Table 14. Summary of result of adsorption experiments for soils and sediments in Puerto Rico.

Element Adsorption at El Verde Exp. Station	Average log Ks	Standard Deviation	Highest value	Lowest value
Pb	2.45	0.45	3.00	1.82
Cu	0.56	0.14	0.71	0.38
Cd	1.11	0.58	1.88	0.33
Cs	1.07	0.17	1.34	0.79
Rb	0.42	0.19	0.76	0.17

Element Adsorption at BONUS Area Rincon	Average log Ks	Standard Deviation	Highest value	Lowest value
Pb	2.84	0.64	3.77	2.00
Cu	1.12	0.17	1.27	0.70
Cd	1.89	0.17	2.19	1.66
Cs	1.05	0.37	1.42	0.45
Rb	-0.14	0.10	0.06	-0.29

Element Adsorption at Espiritu Santo	Average log Ks	Standard Deviation	Highest value	Lowest value
Pb	2.68	0.41	3.38	2.10
Cu	0.62	0.16	0.80	0.40
Cd	1.85	0.22	2.30	1.59
Cs	1.58	0.04	1.68	1.54
Rb	0.07	0.19	0.53	-0.001

Element Adsorption at Vieques	Average log Ks	Standard Deviation	Highest value	Lowest value
Pb	2.84	0.69	4.09	2.16
Cu	0.92	0.23	1.22	0.62
Cd	2.03	0.35	2.57	1.64
Cs	1.11	0.19	1.37	0.85
Rb	-0.50	0.10	-0.68	-0.33

DISCUSSION

The soils and sediments from Puerto Rico do not contain illite at any study sites. However, kaolinite and smectite are present at all stations. Samples from the BONUS site are approximately 20% clays as a mixture of kaolinite and smectite. Soil at El Verde Experimental Station consists of approximately 15% clay, principally in the form of kaolinite. Sediment at the Espiritu Santo Estuary is approximately 10% clay in the form of smectite and kaolinite. An understanding of soil composition is important to interpretation of sorption properties with respect to the contributions of the clay minerals studied in this investigation.

Samples from the BONUS site have both comparatively high Ks values and comparatively high clay content. Samples from other sites in the island have similar fractions of smectite and kaolinite. Clay mineralogy in Puerto Rico is a likely controlling factor for metal mobility. Based on observed Ks values, Pb is likely to have a comparatively slow mobility and high retention in the soils and sediments of Puerto Rico. Accordingly, the mobility of Cu, Cd, Cs, Cd and Rb will be substantially faster than Pb because the lower log Ks of these metals..

Soil pH does not strongly affect the sorption of metals for most of the investigated clays, soils and sediments. This trend is generally observed except for Kaolin and the acidic soils from El Verde Experimental station. The influence of increasing pH, on the log Ks of Cd is especially notable. The observations of comparative Pb and Cd sorption obtained in this work are consistent with those of Appel and Ma (2002) who reported that a variety of tropical soils types, Oxisol, Ultisol and Mollisol, have a preference for Pb sorption relative to Cd. The Ks values for Cu sorption by soils are smaller than those obtained in the clay mineral experiments. This behavior might be due to the nature of Cu complexation and speciation in sediments. Delgadillo et al. 2008, states that up to 80% of the total dissolved Cu in surface waters can be organically complexed. As such, its sorption availability would be reduced. This explanation for the behavior of Cu in soil sorption studies would require that organics present in the soils were released into solution during the sorption experiments. This is consistent with the observation that the samples demonstrating unusual adsorption of Cu are the samples from the comparatively organic-rich rainforest ecosystem and its estuary.

The results obtained in sorption experiments help in interpreting comparative retention of metals and radionuclides in soils and sediments from Puerto Rico. Pb-210 concentrations in most cases are higher than Cs-137 concentrations. Since distribution coefficients are highest for Pb for all soils and sediments, it expected that Pb-210 will not travel far in the sediment column before being sorbed by the substrate. Cs distribution coefficients are much smaller. Therefore Cs is likely to be far more mobile in the soils and sediments in the island. After governmental activities in which the amount of Cs-137 introduction was extremely large, the observed amounts of Cs-137 in the Puerto Rican environment today are comparable to the fallout Cs-137 contribution in this region of the hemisphere. Nevertheless, the soil composition of Puerto Rican soils can have a significant impact on Cs-137 environmental activity. At the rainforest study site where most samples are especially rich in smectite, Cs-137 inventories are higher than at any other location within the area.

This study furthers an understanding of geochemical processes in Puerto Rico through investigations at four different ecosystems on the island. Ecosystems such as the tropical rainforest receive more than 500 cm of rain a year, commonly causing floods and landslides. Puerto Rico is also one of the primary areas where hurricanes develop and, on decadal scales, cause major ecosystem destruction. The mobility and soil-retention of metals such as Pb, Cd, Cu, Cs and Rb examined in this study will help to provide an understanding of ecosystem interaction in these extreme, but natural events.

CHAPTER IV: GEOCHEMICAL FACTOR S AFFECTING RESULTS AND MAJOR CONCLUSIONS

GEOCHEMISTRY OF THE STUDY SITES AND HOW THEY IMPACT CURRENT RESULTS

Resource managers and policymakers often rely on environmental studies and monitoring efforts conducted by researchers in order to implement effective manage practices designed to preserve natural resources. Although hypotheses frequently guide scientific investigations, outcomes of some investigations can be surprising and do not always support the original hypothesis. For this environmental assessment project, the working hypothesis was that Cs-137 activity of soil and sediments would be elevated within three study sites in Puerto Rico as a result of local military and federal government activities. However, samples analyzed during this study indicate that Cs-137 (and Pb-210) activity does not appear to be particularly elevated at any of the three study sites.

The sorption and retention of Cs-137 depends on various geochemical properties and environmental conditions. Clay mineralogy influences the sorption and retention ability of sediments and soils. Illite and smectite, in particular, provide effective Cs-137 binding sites due to the interstitial spaces of these two clay minerals. Particle size, water and in-situ chemistry also influence the ability of Cs-137 to be absorbed and retained in sediments and soils (Johnson-Pyrtle and Scott, 2001). Results of this investigation indicate that, in general, there appear to be particles of suitable size for Cs-137 sorption and retention size throughout all three study sites (see figures 22-31). During this investigation it was determined that clay mineralogy of the study sites, particularly the limited presence and/or absence of illite and smectite, contributed to the soil and sediment's inability to effectively retain locally introduced Cs-137.

Salinity also affects the retention of Cs-137. At higher salinities Cs-137 will be desorbed from fluvial sediments due to cation competition reactions (Avery, 1996). Of the various ecosystems sampled during this investigation only three of the study sites, Mosquito Bay and Green Bay (Kiani Lagoon) at Vieques, and/or Espiritu Santo River area's Coco Beach might have been affected by changes in porewater and surface salinity. All other samples examined during this investigation are either soils or were collected from freshwater systems. Consequently, changes in salinity are not factors for absorption and retention of Cs-137 at the majority of the sites that were examined during this investigation.

Physical processes and events also influence the retention of Cs-137 in sediments and soils. In addition to experiencing major storms on an annual basis, and frequent hurricane events, various regions of Puerto Rico are also subject to flash floods, landslides and particle erosion. All of these natural physical processes, in addition to anthropogenic activity, have the ability to influence the retention of Cs-137 by removing and transporting Cs-137 laden particles away from their original introduction site, beyond the local study sites and potentially offshore.

Cs-137 activity was expected to be higher in the study sites based on the initial activity that was released at each site. As mentioned previously, the amount of Cs-137 that was irradiated at the El Verde Experimental Station was 10^{14} Bq and the estimated amount of Cs-137 that remains in the entombed monolith at the BONUS facility is 2.088 x 10^{7} Bq (see chapter 2 for details). Cs-137 has not been locally introduced at Vieques.

As such it is anticipated that the sole source of Cs-137 present in Vieques is from is global fallout. The Cs-137 activity of samples collected from Vieques is comparable to activities determined for all of the other study sites, indicating that the majority of Cs-137 present on the island of Puerto Rico is the result of global atmospheric fallout. Furthermore, the average Cs-137 activity determined for each of the three study sites is comparable to Cs-137 activities in other regions of the Caribbean. The closest study (in terms of proximity to Puerto Rico) was performed in Cienfuegos, Cuba. There Alonso-Hernandez et al. (2006) indicated that the average atmospheric deposition of Cs-137 in the region was 14 dpm m^{-2}. A radionuclide assessment study was also performed for the Costa Rican tropical ecosystem. This Costa Rican investigation, which was conducted after the Chernobyl accident, revealed that mean Cs-137 activity of 35,000 dpm/m^{-2} (Bossew and Strebl, 2001). LeBrecque and Cordoves (2001) found that Cs-137 activities in tropical soils of two Venezuelan rainforests range from 120 to 600 dpm/m^{-2}. Cs-137 activities were also determined for the Miami, Florida area. As previously mentioned in Chapter 2 (see figure 47), the Miami, Florida area received Cs-137 as a result of global atmospheric fallout. The Cs-137 activity peaks determined in the Miami, Florida area coincide with periods of nuclear weapons testing and the Chernobyl accident. Cs-137 deposition in the Miami, Florida area has decreased continuously following the Chernobyl accident.

Cs-137 activity present in the Caribbean appears to primarily be the result of global fallout. Although the amount of activity in the region varies, it should be noted that the values determined during this investigation are comparable to those that were determined elsewhere in the Caribbean, specifically in Cuba (Alonso-Hernandez, 2006).

The variations identified throughout the Caribbean are likely the result of environmental influences and geochemical properties. The average Cs-137 activity for the BONUS, Vieques and El Verde Experimental Station sites were 0.94 dpm/g, 0.15 dpm/g and 2.93 dpm/g, respectively.

This investigation represents the first time a radionuclide assessment project has been undertaken at multiple locations throughout the island of Puerto Rico. The fact that this investigation revealed the low retention of Cs-137 in local soils and sediments is an important research finding. Results presented in Chapters 2 and 3 of this dissertation indicate that to some extent the local ecosystems have the ability to retain Cs-137 and Pb-210. Findings from this investigation (see chapter 3 for details) reveal that all soils and sediments collected during this study were able to retain Cs and Pb. (Actually Pb was the most common metal sorbed during the adsorption experiment.)

MAJOR CONCLUSIONS

The results of this investigation indicate that the Cs-137 present in Puerto Rican soils and sediments is the result of fallout occurring in the Caribbean region. Highest Cs-137 activity was found in surface samples collected from the rainforest at the El Verde Experimental Station. The higher elevation and precipitation at this study site as well as soil composition might be the contributing factors to the activity in the site. This Cs-137 activity is similar to what was reported by Alonso-Hernandez et al. (2002, 2006). They conducted a series of experiments in Cienfuegos, Cuba in which they reported a direct relationship between precipitation and Cs-137 activity. In addition, it should also be noted that LaBrecque et al. (2001) found that Cs-137 activity was higher in the Venezuelan cloud forest compared to nearby study sites at lower elevations. The cloud forest is the highest ecosystem in the tropical rainforest and the elevation of El Verde experimental station is located at a proximity close to the cloud forest.

As shown in Chapter 3 of this dissertation the distribution coefficients for Cs and Pb are different and the soils of the ecosystem favors the adsorption of Pb to a greater extent when compare with Cs. For most of the cores on the island, Pb-210 has a higher activity than Cs-137. It might be proposed that Pb-210 input in the island is higher than the input of Cs-137. Since Cs-137 is an anthropogenic radionuclide, and Pb-210 is a natural occurring radionuclide we will need to analyze for the balance in the uranium decay series, which produce Pb-210.

It is well known that after the Chernobyl accident, Cs-137 regional fallout depended on wind force. Therefore another possible explanation to the minimum activities of Cs-137 in the island is that the Caribbean region did not receive the same activity that was received in the mainland of the US and the European continent. We have evidence in this dissertation that Cs-137 is present at low levels at all sampling locations, therefore the governmental activities and accidental release by the BONUS Power Plant had no effect on the current activity level in the island.

In terms of mineralogy, the substrate provided suitable binding sites although illite is not present at any of the study sites. Smectite and kaolinite content at all study sites was relatively low when compared to the amount of sand present at each site. High fine particle size content is related to higher Cs-137 retention potential. Sand does not retain radionuclides as efficiently. It has been demonstrated by many researchers that the presence of fine grain clay minerals is vital for Cs-137 binding in substrates. Illite formations depend on the weathering of rocks and the resulting residual soils. There are 215 soil types in Puerto Rico and all study sites are located in different geological formations. Therefore the absence of illite can be attribute to ecosystem characteristics. For instance, the BONUS area is located within a limestone formation. pH range among the soils and sediments went from 4 to 8. Binding with other clay particles would be possible since there are other clay minerals such as vermiculite, saprolite, chlorite and muscovite but the binding would not be as strong and Cs-137 would be released after its binding.

Organic matter can also facilitate Cs-137 retention. The organic matter content at the study sites went from low to intermediate. The higher organic matter content in the rainforest might be due to the degradation of leaves and debris. For instance, Arctic sediments, where intentional release of radionuclides also occurred, showed activity levels 10 times higher than what we found at the rainforest. Another factor we should take into consideration is the fact that according to the ICP-OES analysis, the substrate was oxic, which implies that Cs-137 mobility is low in the sediments. Cation competition is another factor that adversely influences the competition for binding sites among pollutants. At study sites, binding seems to be low and the presence of potassium as well as other elements might outcompete Cs-137 for binding the analyzed substrate.

Results indicate that although intentional release of radionuclides occurred in two of the study sites of Puerto Rico, Cs-137 activity is not residual activity from the governmental activities and is more likely the result of global fallout. Due to environmental conditions, once introduced, a portion of the Cs-137 may have been transported away via erosion, as well as runoff, currents, and tide induced water movement. Fluctuations in Cs-137 downcore profiles were the result of fluctuations in global fallout and local substrate disturbance, such as remobilization, hurricanes and other atmospheric events as well as bioturbation. At the rainforest, high precipitation may have served to move the soils form one site to the other via a variety of particle movement mechanisms, including landslides that commonly occur in the area.

The Rainforest Project (Odum and Drewry, 1970), construction of the prototype BONUS power plant and the Ammunition facility in Vieques are notable events in the island's history. However, Puerto Rico has been fortunate to have not experienced major disasters associated with these activities. After completing the BONUS reactor and El Verde experiments, no further studies were preformed to monitor the long term effects of the associated radio-pollution. Investigating the long-term effects of these experiments is vital to understand the effect of the introduction of radionuclides into the ecosystem. Dr. Ariel Lugo, the director for the International Institute for Tropical Forestry, stated that the "irradiated forest was studied for twenty three years, until 1988; at that time it had not fully recovered" (Interview by Suzanna Engman, 2007).

The current investigation provides radiogeochemical data that will be useful to policy makers in determining whether or not to authorize similar types of experiments in the future. Gamma spectroscopy has yielded information to analyze doses at which the human population could be exposed. Dose rates at the rainforest went from 5 r/hr (before the late 1960's experiments) to 200 r/hr which represent an enormous increase that can adversely affect human health. In Vieques cleanup work is still in progress and finding the missing ammunitions is important. Potential pollutants can be stored in these ammunitions and after their explosion sediments can serve as the sink for anthropogenic elements used during the military practices, further affecting human and environmental health. A program on open explosion has been recommended by the US Department of Defense and it is estimated that all related environmental clean-up work will last another 14 years. Information provided by this investigation should prove beneficial when designing additional studies at the VNWR. One such study should be conducted at the target facility, which could not be accessed during this investigation due to its closure by the Nuclear Regulatory Commission.

An in-depth analysis of the erosion and sedimentation at the three study sites is recommended in order to further understand where the sediments are being transported. At the rainforest, a long-term study should be undertaken to analyze the soil to plant transfer factor in the area, and see if that is the cause of the slow growth of the vegetation located at the irradiated and injection areas (Odum and Drewry, 1970). An investigation of soil to plant transfer of radionuclides should also be conducted at the BONUS facility area in order to determine the potential impact of radio-pollution in the event that radionuclides present at this facility are accidentally released into the environment.

REFERENCES

Aarkrog, A. (2003) Input of anthropogenic radionuclides into the World Ocean. Deep-Sea Research II. 50, 2597–2606

Aarkrog, A. (1994) Radioactivity in Polar Regions - main sources. J. Environ. Radioactivity. 25, 21-35

Acevedo-Figueroa, D., B.D. Jimenez, and C.J. Rodriguez-Sierra. (2006) Trace metals in sediments of two estuarine lagoons from Puerto Rico. Environmental Pollution. 141, 336-342

Alonso-Hernandez, C.M., M. Diaz-Asencio, A. Munoz-Caravaca, R. Delfanti, C. Papucci, O. Ferretti, et al. (2006) Recent changes in sedimentation regime in Cienfuegos Bay, Cuba, as inferred from Pb-210 and Cs-137 vertical profiles. Continental Shelf Research. 26:2, 153-167.

Alonso-Hernández, C.M., H. Cartas-Águila, M. Díaz-Asencio, A. Muñoz-Caravaca, J. Martín-Pérez, & R. Sibello-Hernández. (2006) Atmospheric deposition of 137Cs between 1994 and 2002 at Cienfuegos, Cuba. Journal of Environmental Radioactivity. 88:2, 199-204.

Alonso-Hernandez, C., M. Diaz-Asencio, A. Munos-Caravaca, E. Suarez-Morell, R. Avila-Moreno. (2002) 137Cs and 210Po dose assessment from marine food in Cienfuegos Bay (Cuba). Journal of Environmental Radioactivity. 61:2, 203-211.

Anoruo, A. O., C. H. Jagoe, J. I. Blake, F. C. Anoruo and J. D. Salley. (2002). Long-term effects of radiocesium (Cs-137) on forest growth and development. Journal of Environmental Monitoring and Restoration. 1(1):1-13

Appel, C. and L. Ma (2002). Concentration, pH, and Surface Charge Effects on Cadmium and Lead Sorptionin Three Tropical Soils. Journal of Environmental Quality. 31, 581–589.

Arapis, G.D. & M.G. Karandinos. (2004) Migration of Cs-137 in the soil of sloping semi-natural ecosystems in Northern Greece. Journal of Environmental Radioactivity. 77 (2), 133-142.

Aşçi, Y., M.Nurbas and Sağ Açikel. (2007) Sorption of Cd(II) onto kaolin as a soil component and desorption of Cd(II) from kaolin using rhamnolipid biosurfactant, Journal of Hazardous Materials. B139 50–56.

Augustin, J. and R. Zedja. (1991) Cancer incidence and geochemical factors in the environment. The Science of The Total Environment. 106:1-2, 155-163.

Avery, S. (1996) Fate of cesium in the environment, distribution between the abiotic and biotic component of aquatic and terrestrial ecosystem. Journal of Environmental Radioactivity. 30 (2), 139-171

Ayala, C and V. Carro. 2005."Expropiations and Displacement of Civilians in Vieques, 1940-1950." In Puerto Rico under Colonial Rule: Political Persecution and the Quest for Human Rights, edited by R. Bosque Pérez and J. Colón Morera Baqar, R., Zaidi, L. M. Hinkey, N. R. Rodriguez, Nadathur S., G. Syed & H. Imam. (2003) Biodegradation of toxic chemicals in Guayanilla Bay, Puerto Rico Marine Pollution Bulletin. 46, 418–423

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. Journal of Colloid and Interface Science. 277, 1–18.

Bruemmer, G.W. J. Gerth and U. Herms. (1986) Heavy metal species, mobility and availability in soils. Journal of Plant and Soil Science. 149:4, 382-398

Bossew, P. and F. Strebl. (2001) Radioactive contamination of tropical rainforest soils in Southern Costa Rica. Journal of Environmental Radioactivity. 53:2, 199-213.

Charmasson, S. (2003) Cs-137 inventory in sediment near the Rhone mouth: role played by different sources. Oceanologica Acta. 26(4), 435-441.

Ciffroy, P., G. Durrieu, and J.-M. Garnier. (2009) Probabilistic distribution coefficients (Kds) in freshwater for radioisotopes of Ag, Am, Ba, Be, Ce, Co, Cs, I, Mn, Pu, Ra, Ru, Sb, Sr and Th – implications for uncertainty analysis of models simulating the transport of radionuclides in rivers. Journal of Environmental Radioactivity. 100, 785–794.

Claval, D., L.Garcia-Sanchez, J. Real, R. Rouxel, S. Mauger and L. Sellier. (2004) Erosion of atmospherically deposited radionuclides as affected by soil disaggregation mechanisms. Journal of Environmental Radioactivity. 77, 47-61.

Critter, S.A.M., and Claudio Airoldi. (2003) Adsorption–desorption processes of calcium on Brazilian soils. Geoderma. 111, 57–74.

Dean, W.E., Jr. (1974) Determination of Carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. Journal of Sedimentary Petrology. 44, 242-248.

Desmarais, A. P. and B. Helmuth. (1970) A tropical rainforest; A study of irradiation and Ecology at El Verde, Puerto Rico. Oak Ridge, TN: Atomic Energy Commission

Díaz, E. and A. Massol-Deyá. 2003. Trace element composition in forage samples from military target range, three agricultural areas, and one natural area in Puerto Rico. Caribbean Journal of Science. 39 (2), 58-63.

Dong, D., X., Zhao, X. Hua, J. Liu, M. Gao. (2009) Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China. Journal of Hazardous Materials. 162, 1261–1268.

Du Laing, G., J. Rinklebe, B. Vandecasteele, E. Meers, and F.M.G. Tack. (2009) Trace metal behavior in estuarine and riverine floodplain soils and sediments: A review. Science of the Total Environment. 40:7 3972-3985.

Echeverria, J.C., I. Zarranz, J. Estella, and J. J. Garrido. (2005) Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of lead on illite. Applied Clay Science. 30, 103–115.

Eisenbud, M and T. Gessel. (1997) Environmental Radioactivity. San Diego CA: Academic Press.

Fan, Q., Z. Li, H. Zhao, Z. Jia, J. Xu and W. Wu (2009) Adsorption of Pb(II) on palygorskite from aqueous solution: Effects of pH, ionic strength and temperature. Applied Clay Science. 45, 111–116.

Fanning, K., R. Byrne, J. Breland II, P. Betzer, W. S. Moore, R. Elsinger et al. (1981) Geothermal springs of the West Florida continental shelf: Evidence for dolomatization and radionuclide enrichment. Earth Planetary Science Letters. 52, 345-354.

Farai, I.P; R.I. Obed and N.N. Jibiri. (2006) Soil radioactivity and incidence of cancer in Nigeria. Journal of Environmental Radioactivity. 90:1, 29-36.

Forsberg, S., K. Rosén, V. Fernandez and H. Juhan. (2000) Migration of 137Cs and 90Sr in undisturbed soil profiles under controlled and close-to-real conditions. Journal of Environmental Radioactivity. 50:3, 235-252.

Fox, R.L., 1982. Some highly weathered soils of Puerto Rico, 3. Chemical properties. Geoderma. 27: 139--176.

Heiri, O., Lotter, A.F. and Lemcke, G. (2001) Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology. 25, 101-110.

Hunter, J. M. and S. I. Arbona. (1995) Paradise Lost: an introduction to the geography of water pollution in Puerto Rico. Soc. Sci. Med. 40 (10), 1331-1355.

Jackson M.L. (1958) Soil Chemical Analysis-Advanced Course, published by the author, Madison, Wisconsin.

Jibiri, N. (2001) Assessment of health risk levels associated with terrestrial gamma radiation dose rates in Nigeria. Environment International. 27:1, 21-26.

Johnson-Pyrtle A. (1999) Distribution of ^{137}Cs in the Lena River estuary-Laptev Sea system as evidenced by marine, estuarine and lacustrine sediments. PhD Thesis, Texas A&M University, College Station, TX. 206p.

Johnson-Pyrtle, A., M. Scott, T. Laing and J. Smol. (2000) Cs-137 Distribution and Geochemistry of Lena River (Siberia) Drainage Basin Lake Sediments. The Science of the Total Environment. 255(1-3), 145-159.

Johnson-Pyrtle, A. and M. Scott. (2001) Distribution of Cs-137 in the Lena River Estuary-Laptev Sea System. Marine Pollution Bulletin. 42(10), 912-926.

Infante R. and I. L. Acosta. (1991) Size distribution of trace metals in Ponce. Puerto Rico Air Particulate Matter. Atmospheric Environment. 25B:1, 121-131.

LaBrecque, J.J., P.A. Rosales and P.R. Cordoves. (2001) Anomalously high values of cesium-137 in soils on the Peninsula de Paraguana (Venezuela). Journal of Radioanalytical and Nuclear Chemistry. 247 (3), 563-566.

LaBrecque, J. J. and P. R. Cordoves. (2004) The spatial distribution of cesium-137 in surface soils in the Gran Sabana and Sierra de Pacarima (Venezuela). Journal of Radioanalytical and Nuclear Chemistry. 262:2, 375-381.

Larsen, M.C., Simon, A., 1993. Rainfall-threshold conditions for landslides in a humid-tropical system, Puerto Rico. Geography Annotaded. 75A 1–2., 13–23.

Larsen, M.C., Parks, J.E., 1997. How wide is a road? The association of roads and mass-wasting disturbance in a forested montane environment. Earth Surface Processes Landforms. 229., 835–848.

Larsen, M.C. and A. J. Torres-Sanchez. (1998) The frequency and distribution of recent landslides in three montane tropical regions of Puerto Rico. Geomorphology. 24, 309–331.

Larue, D.K. (1994) Puerto Rico and Virgin Island, Chapter 8. Caribbean Geology: An Introduction. U.W.I. Publisher Association, Kington. pp151-165

Lindsay-Poland, J. (2001) Environmental impacts of Navy training, Vieques Issue Brief [on-line] http://www.forusa.org/Programs/PuertoRico/Envirobrief1101.html

Livingston, H.D. & P.P. Povinec. (2000) Anthropogenic marine radioactivity. Ocean and Coastal Management, 43, 689-712

Manahan, S., (2005) Environmental Chemistry 8th ed. CRC Press LLC. Printed in the United States. 783 pp.

Micromeritics Instrument Corporation. 2003. Saturn DigiSizer 5200, Operator's Manual.

Missana, T., M. Garcia-Gutierrez, and U. Alonso. (2008) Sorption of strontium onto illite/smectite mixed clays. Physics and Chemistry of the Earth. 33, S156–S162.

Moon, D.S., Hong, G.H., Kim Y.I.; Baskaran, M.; Chung, C.S., Kim, S., et al. (2003) Accumulation of anthropogenic and natural radionuclides in bottom sediments of the Northwestern Pacific Ocean. Deep Sea Research II. 50, 2649-2673.

Montgomery, J.R. and R.J. Santiago. (1978) Zinc and Copper in 'Particulate' Forms and 'Soluble' Complexes with Inorganic or Organic Ligands in the Guanajibo River and Coastal Zone, Puerto Rico. Estuarine and Coastal Marine Science. 6, 111-116.

Morais Barros, A.J., S. Prasad, V. Duarte-Leite and A. Gouveia-Souza. (2007). Biosorption of heavy metals in upflow sludge columns. Bioresource Technology. 98, 1418–1425.

Myasoedov, B. F. (2000) Century of radiochemistry: history and future. Journal of Nuclear and Radiochemical Sciences.1, 23-26.

O'Brien, W. (1996) Bronze Age Copper Mining in Britain and Ireland. Shire Archaeology. Princes Risborough, 64pp.

Odum H. (1970) Puerto Rico Nuclear Center, Annual Report. The rainforest project, annual report, operated by the University of Puerto Rico under contract with the US Atomic Energy Commission, Rio Piedras, Puerto Rico.

Odum, H. & G. Drewry. (1970) A tropical rainforest; A study of irradiation and Ecology at El Verde, Puerto Rico. Oak Ridge, TN: Atomic Energy Commission

Olsen, C.R, I.L. Larsen, N.H. Cutshall, J.F. Donoghue, O.P. Bricker and H.J. Simpson. (1981) Reactor-released radionuclides in Susquehanna River sediments. Nature. 294, 242 - 245

Pett-Ridge, J. C., L. A. Derry and A.C. Kurtz. (2009) Sr isotopes as a tracer of weathering processes and dust inputs in tropical granitoid watershed, Luquillo Mountains, Puerto Rico. Geochimica et Cosmochimica Acta. 73, 25–43.

Poppe, L.J., V.F. Paskevich, J.C. Hathaway, and D.S. Blackwood. (2001) A Laboratory Manual for X-Ray Powder Diffraction. U. S. Geological Survey Open-File Report 01-041. 88p

Puerto Rico Nuclear Center. 1970. The rainforest project, annual report, operated by the University of Puerto Rico under contract with the US Atomic Energy Commission

Puerto Rico Nuclear Center. 1969. The rainforest project, annual report, operated by the University of Puerto Rico under contract with the U.S. Atomic Energy Commission

Puerto Rico Nuclear Center. 1968. The rainforest project, annual report, operated by the University of Puerto Rico under contract with the U.S. Atomic Energy Commission

Renken, R., W.C. Ward, I.P. Gill, F. Gomez-Gomez and J. Rodriguez-Martinez. (2000) Geology and Hydrogeology of the Caribbean Islands Aquifer System of the Commonwealth of Puerto Rico and the U.S. Virgin Islands. Professional Paper 1419, 148p.

Robinson W. and V. E. Noshkin. (1999) Radionuclide characterization and associated dose from long-live radionuclides in close-in fallout delivered to the marine environment at Bikini and Enewetak Atolls. The Science of the Total Environment. 237/238, 311-327.

Sadasivian, S, V.K. Shukka, S. Chinnaesa and S.J. Sartandel. (2003) Natural and fallout radioactivity measurements in Indian soils. Journal of Radioanalytical and Nuclear Chemistry. 256 (3), 603-607.

Santchi, P.H. & B.D. Honeyman. (1989) Radionuclides in aquatic environment. Rad. Phys. Chem. 34(2), 213-240

Santschi, P., J.W. Murray, M. Baskaran, C.R. Benitez-Nelson, L.D. Guo, C.C. Hung, et al. (2006) Thorium speciation in seawater. Marine Chemistry. 100, 250–268.

Scatena, F.N., and Larsen, M.C., 1991. Physical aspects of Hurricane Hugo in Puerto Rico. Biotropica. 23 4A, 317–323.

Takeda, A., H. Tsukada, Y. Takaku, S. Hisamatsu, & M. Nanzyo (2006) Accumulation of uranium derived from long-term fertilizer applications in a cultivated Andisol. Science of The Total Environment. 367:2-3, 924-931.

Tyler, A. N., S. Carter, D. A. Davidson, D. J. Long and R. Tipping. (2001) The extent and significance of bioturbation on Cs-137 distributions in upland soils. Catena. 43, 81–99.

United Nations Scientific Committee on the Effects of Atomic Radiation. (1982) Ionizing Radiation: Sources and Biological Effects Report.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). (2000) The 2000 report to the General Assembly with scientific annexes. New York.

United Nations Scientific Committee on the Effects of Atomic Radiation . (2001) Report to the General Assembly.

US Agency for Toxic Substances and Disease Registry. (2002) Drinking water supplies and groundwater pathway evaluation, Isla de Vieques bombing range, Vieques, Puerto Rico. [on-line]: http://www.atsdr.cdc.gov/HAC/pha/vieques/vie_p1.html

US Department of Agriculture, National Forest Service. (2004) History of the Caribbean National Forest. Retrieve on April 20, 2008. http://www.fs.fed.us/r8/caribbean/about/history.shtml

US Department of Homeland Security (1999) Surface Air Sampling Program. Retrieve on January 10,2008 http://www.eml.st.dhs.gov/databases/sasp/sasp_sample_search.cfm

US Department of Energy. (2003) DOE/EA-1394: Public access to the BONUS facility environmental assessment for authorizing the Puerto Rico Electric Power Authority (PREPA) to allow public access to the boiling nuclear superheat (BONUS) reactor building, Ricon, Puerto Rico [online].10-58 http://tis.eh.doe.gov/nepa/ea/EA1394/eafinal.pdf

U.S. Department of Energy, Office of Legacy Management. (2005) Long-term surveillance and maintenance plan for the Boiling Nuclear Superheated (BONUS) Reactor Facility, Rincon, Puerto Rico. Stoller Corporation, Colorado.

US Environmental Protection Agency, 1996, Urban soil lead abatement demonstration project. Volume 1: EPA Integrated Report, National Center for Environmental Assessment Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC.

US Environmental Protection Agency. (2001) Final Master Work Plan, Atlantic Fleet Weapons Training Facility. [On-line]: http://www.epa.gov/region02/draftfinal_projmanplan.pdf

US Navy. (2002) Expenditure of depleted uranium (DU) rounds at Vieques Inner Training Range, Puerto Rico [on-line] www.deploymentlink.osd.mil/du_library/statements/vieques_brief/index.htm

US Natural Resources Conservation Services (2003) Soil Survey of Caribbean National Forest and Luquillo Experimental Forest,Commonwealth of Puerto Rico. 182pp.

US Nuclear Regulatory Commission, Office of Nuclear Materials Safety and Safeguards. 2000. Environmental Survey Report for Vieques Island - Meetings and Press Conference. [On-line] http://www.nrc.gov/reading-rm/doc-collections/commission/secys/2000/secy2000-0206/2000 0206scy.html#ENCLOSURE%20A

US Nuclear Regulatory Commission, Office of Nuclear Materials Safety and Safeguards. (2001) Materials Licenses in 10 CFR Part 20 for the University of Puerto Rico, Río Piedras Campus (NRC License 52-01986-04).

Uyttenhove, J., M. Lemmens & M. Zizi. (2002) Depleted Uranium in Kosovo: results of a survey by gamma spectrometry on soil samples. Health Physics 83, 543-548.

Valiela, I., and J.L. Bowen. (2002) Nitrogen sources to watersheds and estuaries: role of land cover mosaics and losses within watersheds. Environmental Pollution. 118, 239–248.

Van Genderen E.J., A.C. Ryan, J. R. Tomasso, and S. J. Klaine (2005). Evaluation of acute copper toxicity to larval fathead minnows (Pimephales promelas) in soft surface waters. Environmental Toxicology and Chemistry. 24:2, 408-414.

Webb, Richard M.T. and Gómez-Gómez, Fernando. (1998) Synoptic Survey of Water Quality and Bottom Sediments, San Juan Bay Estuary System, Puerto Rico, December 1994-July 1995: U.S. Geological Survey Water Resources Investigations Report 97-4144. 69 p.

World Health Organization. (2001) Depleted Uranium: Sources, Exposure and Health Effects. WHO/SDE/PHE/01.1. Geneva, April 2001, http://www.who.int/ionizing_radiation/pub_meet/ir_pub/en/

Wyttenbach, A., V. Furrer and L. Tobler. (1995) The concentration ratios plant to soil for the stable elements Cs, Rb and K. The Science of the Total Environment. 173/174, 361-367.

Yarrow, M. (2000) History of the U.S. military in Puerto Rico: The U.S. Military in Latin America after the Cold War, American Friends Service Committee Latin

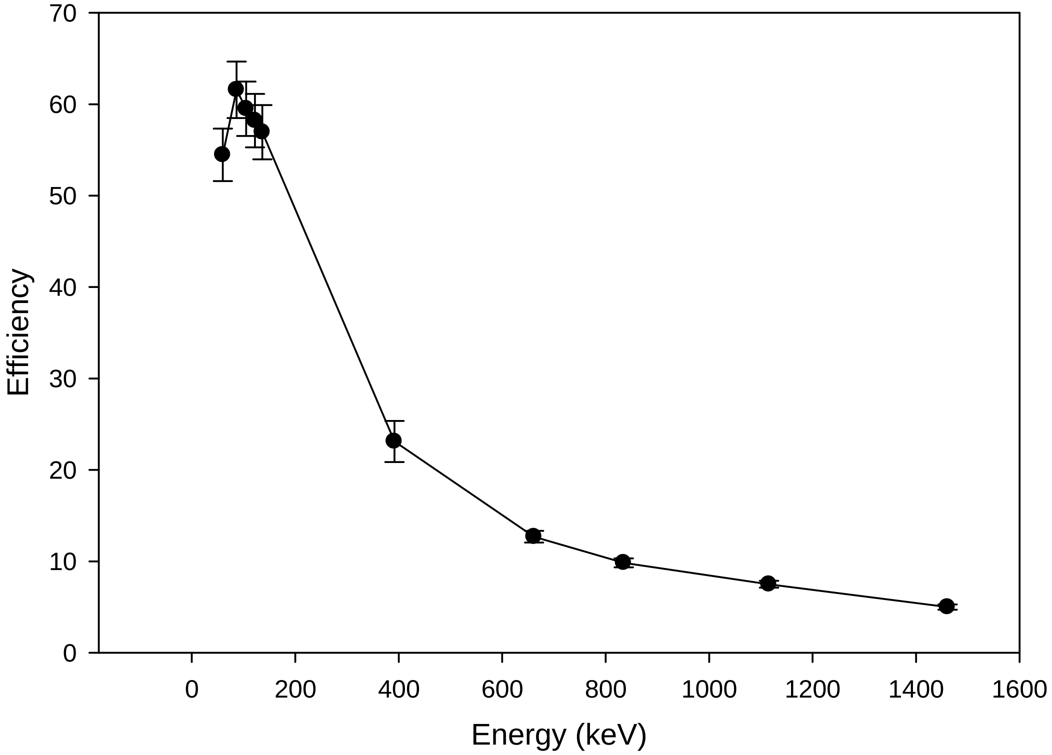
American and Caribbean Peace Building Program. pp. 12 [on-line] http://www.afsc.org/latinamerica/peace/strings/pricorep.pdf

Zhiyanski, M., J. Bech, M. Sokolovska, E. Lucot, J. Bech and P.M. Badot. (2008) Cs-137 distribution in forest floor and surface soil layers from two mountainous regions in Bulgaria. Journal of Geochemical Exploration. 96:2-3, 256-266.

Zikovsky, L. (2006) Alpha radioactivity in drinking water in Quebec, Canada. Journal of Environmental Radioactivity. 88:3, 306-309.

APPENDICES

Appendix A. Gamma Spectrometry Calibration

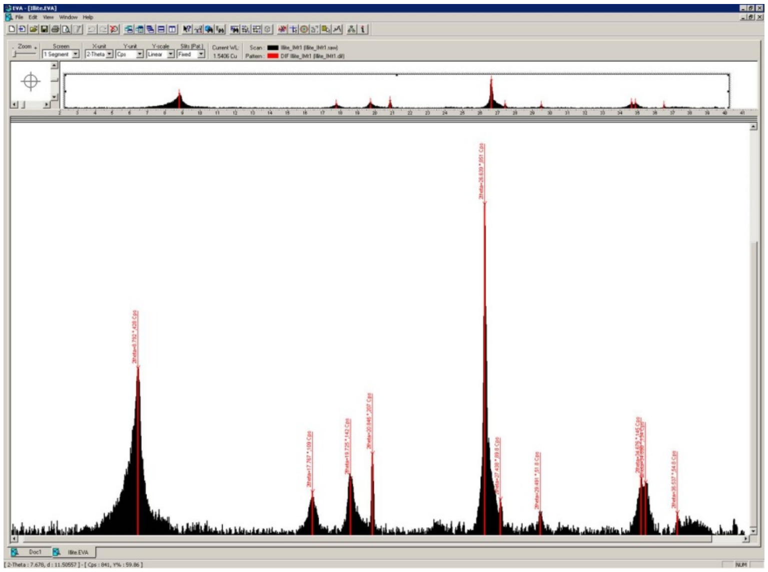


Gamma calibration was performed using NIST 4357 Standard multiline.

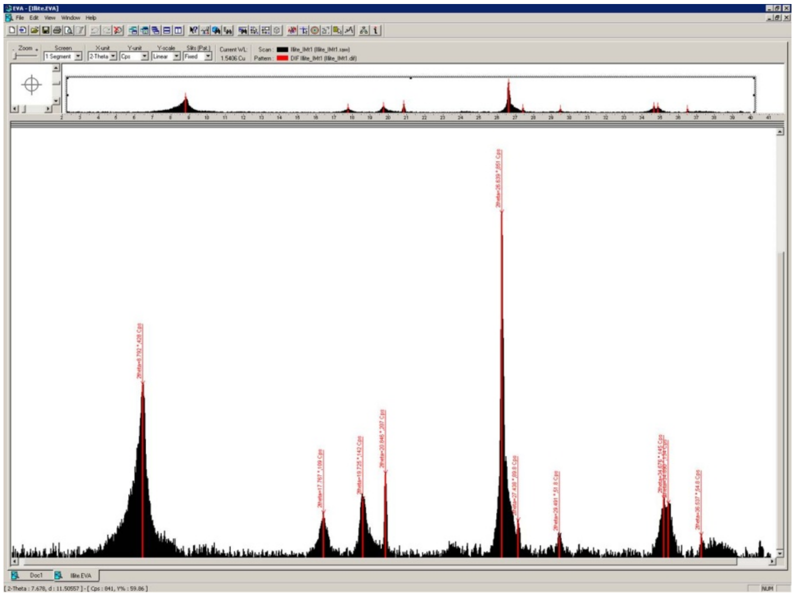
Energy (keV)	Efficiency (%)	Error	Computed	Error	Difference
60.01	54.45	2.88	54.69	2.89	-0.24
86.54	61.57	3.08	60.30	3.33	1.28
105.31	59.50	2.98	60.48	3.13	-0.97
122.06	58.20	2.91	58.79	2.97	-0.60
136.48	56.94	2.97	56.52	3.00	0.42
391.70	23.11	2.25	22.31	2.38	0.80
661.66	12.69	0.63	12.72	0.64	-0.03
834.83	9.84	0.49	10.04	0.53	-0.20
1115.55	7.49	0.38	7.32	0.41	0.17
1460.75	5.00	0.29	5.05	0.29	-0.05

Appendix B. X-Ray Diffraction Calibration Curves

Calibration curve for XRD was performed using reference material from the Clay Mineralogical Society.



Illite Calibration



Kaolinite Calibration Curve

Appendix C. Loss on Ignition Protocol (Heiri et al. 2001; Dean, 1974)

Step 1: Finely grind sediments and homogenize by either stirring by hand or shaking in a closed container.

Step 2: Oven dry powdered samples in a pre-weighed crucible (or container used for the heating) at 105 degrees Celsius for a time period between 12- 24 hours.

Step 3: Cool to room temperature in desiccator (s) and weigh both samples and crucible to obtain the dry weight for the sample (DW_{105}) in grams.

Step 4: Return sample to furnace and heat between 500-550 degrees Celsius for about 4hrs (when using mixed sediment samples). By heating the samples for 4hrs, the differences between weight losses between the samples are small enough that it may not be regarded as significant.

Step 5: Cool to room temperature in desiccator (s) and weight sample in crucible to obtain the dry weight of sample (DW_{550}) in grams.

Step 6: Calculate Loss on Ignition using equation below.

$LOI_{550} = ((DW_{105} - DW_{550}) / DW_{105}) * 100$

Suggested sample weight of about 1-2 grams. However, when conducting this analysis it is important that all samples are approximately the same weight. This is to further reduce the difference between weight loss between the samples due to positional heating influence on the sample.

Heated and cooled crucibles should be handled with thongs preferably.
Sample spreadsheet setup for recording data.

Crucible weight (grams)	**Sample weight (grams)**	**Dry Weight at 105˚ (grams)**	**Dry Weight at 550˚ (grams)**	**LOI Organic Matter (%)**

* A sample ID column will be added to the actual table

Appendix D. EPA Methods 3050b for ICP Analysis

The recommended determinative techniques for each element are listed below:
FLAA/ICP-AES

Aluminum
Magnesium
Antimony
Manganese
Barium
Molybdenum
Beryllium
Nickel
Cadmium
Potassium
Calcium
Silver
Chromium
Sodium
Cobalt
Thallium
Copper
Vanadium
Iron
Zinc
Lead
Vanadium

This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

Summary of Method

For the digestion of samples, a representative 1-2 grams (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide 3
(H_2O_2).

For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

If required, a separate sample aliquot shall be oven-dried for a total percent solid determination.

Apparatus and Materials

- Digestion Vessels - 250-mL
- Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system)
- Drying ovens - able to maintain 30EC + 4EC.
- Temperature measurement device capable of measuring to at least 125EC with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)
- Filter paper - Whatman No. 41 or equivalent.
- Centrifuge and centrifuge tubes
- Analytical balance - capable of accurate weighing to 0.01 g.

- Heating source - Adjustable and able to maintain a temperature of 90-95EC. (e.g., hotplate, block digesters, microwave, etc.)
- Funnel or equivalent.
- Graduated cylinder or equivalent volume measuring device.
- Volumetric Flasks - 100-mL.

Reagents Needed

- Reagent grade chemicals shall be used in all tests.
- Reagent Water
- Nitric acid (concentrated), HNO_3
- Hydrochloric acid (concentrated), HCl
- Hydrogen peroxide (30%), H_2O_2

CAUTION: Wear goggles and gloves at all times!!!! Lab coat is recommended.

Procedure:

1. Mix sample to homogeneity and sieve using a USS Standard #10 (2mm) sieve. For each sample, weight to the nearest 0.01 g (1-2 g of wet sample and 1 g of dry sample).

2. Add 10 mL 1:1 HNO_3 (1 part DI water to 1 part conc. HNO_3), mix and cover with a watch glass or vapor recovery device.

3. Reflux (stir using glass rod or magnetic stirrers). Heat at $95^oC \pm 5^o$ without boiling for 10 to 15 minutes, and allow sample to cool.

4. Add 5 mL conc. HNO_3.

5. Replace the cover and reflux for 30 minutes at $95^oC \pm 5^o$.

6. If brown fumes are generated (indicating oxidation of the sample by HNO_3) repeat this step by adding 5 mL of conc. HNO_3. Repeat as needed until NO brown fumes are given off by the sample (indicating a complete reaction with HNO_3).

7. Return sample to hotplate and allow sample to evaporate to approximately 5 mL by heating at 95^oC max, without boiling, for two hours. Maintain a covering of solution over the bottom of the vessel at all times. DO NOT allow complete evaporation or drying.

8. Allow sample to cool to room temperature. Add 2 mL of water and 3 mL of 30% H_2O_2. Cover with watch glass and warm to about 60^oC with hotplate.

9. CAREFULLY continue to add 1mL aliquots of 30% H_2O_2 until bubbling subsides. DO NOT add more than 10 mL of 30% H_2O_2 TOTAL.

10. Cover the sample with a ribbed watch glass and continue heating (max of 95^oC) until the volume has been reduced to approximately 5 mL.

11. Add 10 mL Conc. HCl to the sample.

12. Cover and reflux (stir using glass rod or magnetic stirrers) for 15 minutes.

13. Filter the sample through a pre-weighed and pre-labeled Whatman No. 41 filter paper and collect filtrate liquid in 100 mL volumetric flask.

14. Dry filter paper. After drying weigh filter paper plus residue subtracting original weight of paper to find residue weight.

Steps 15-26 may be used to improve the solubilities and recoveries of Antimony (Sb), Barium (Ba), Lead (Pb), and silver (As) when necessary.

*Heat 1L of hot water to 95°C and sit aside.

15. Add 2.5 mL conc. HNO_3 and10 mL conc. HCl to 1-2 g wet weight or 1g dry weight) sample and cover with watch glass.

16. Place sample on heat source at 95°C, reflux (stir using glass rod or magnetic stirrers) for 15 minutes.

17. Filter the digestate through Whatman No. 41 filter paper and collect filtrate in 100 mL volumetric flask.

18. Wash filter paper while still in the funnel with no more than 5 mL hot (95°C) HCl, then with 20 mL hot (95°C) DI water.

19. Collect washings in the same 100 mL flask containing previous filtrate.

20. Remove filter paper and residue from the funnel, and place both the filter paper w/ residue back into the vessel (beaker).

21. Add 5 mL conc. HCl and heat at 95°C until filter paper dissolves.

22. Remove vessel from heat source and wash the cover and sides with DI water.

23. Filter the residue and collect the filtrate in same 100 mL volumetric flask used for previous filtrate.

24. Allow filtrate to cool, then dilute to volume. If precipitate occurs in the flask upon cooling, DO NOT dilute to volume.

25. If precipitate forms add up to 10mL HCl to dissolve the precipitate.

26. Dilute to volume needed for analysis. (100 ml)

Appendix E. Sample preparation for XRD Analysis

Removal of CaCO3 & Mg CO3 with NaOAc buffer

1. Amount of sediment start with depends on composition of sample (mostly sand or clay) = 20g sample needed
2. Separate sample into amounts of 5g & put each in a 100mL centrifuge tube (if highly calcareous 10-20% CaCO3, or sandy soil & shell, treat in beaker instead of centrifuge tubes.
3. Add 50mL of NaOAc buffer- pH5 to each 5g sample of soil.
4. Stir with rubber tipped rod.
5. Digest in near boiling bath for 30 minutes with intermittent stirring.
6. Centrifuge until supernatant liquid is clear, liquid is decanted & discarded.
7. 2 more washing with 1N NaOAc are done & centrifuge if sample is nearly calcareous, repeat water bath also

Removal of Organic Matter MnO2 by H2O2

1. With sample from above (that's still wet with NaOAc buffer) transfer sediment from centrifuge bottle to beaker (600mL) using a rubber policeman. Try to use as little water in transferring as possible.
2. Add 5mL 30% H2O2.
3. Stir & cover with watchglass. Watch carefully to prevent bubbling over. If bubbling over, squirt with DI water or stir in cold water bath to control reaction.
4. Once reaction has subsided, place on hotplate for few minutes & watch closely.
5. Stir & rinse sides of beaker with 5mL of H2O2.
6. After reaction is stable add 10mL more of H2O2 & cover glass. Let digest on hotplate for 2-4 hours covered.
7. Repeat 6 as needed until complete digestion of O.M. is complete (black to grayish white).
8. When the dark color of O.M. has largely disappeared, wash soil 3 times with NaOAc centrifuge & decant. Wash once with 95% methanol, centrifuge & decant.

Removal of free Ferric Iron

1. Using sample from before (5-10g) place in centrifuge 100mL centrifuge bottle.
2. Add 40mL of 0.3 M Na-citrate & 5mL of 1 M NaHCO3
3. Place in hat water bath at Between 75-80 degrees Celsius (not more)
4. Add 1 g of solid Na2S2O4 using spoon & stir for 1 minute then occasionally for 5 minutes.
5. Add 2nd amount of 1g Na2S2O4 & stir
6. Add 3rd amount of 1g Na2S2O4 at end of 2nd 5 minute period.
7. Heat aver burner for 15 minutes between 75-80 degrees Celsius.
8. Add 10mL of NaCl & 10mL of methanol.
9. Mix, warm, & centrifuge for 5 minutes at 1600-2200rpm

10. Decant & save supernatant in 500mL volumetric flask.
11. If brown or red color persists, repeat treatment. Then treat with 1N NaCl, centrifuge & decant. Add 10mL methanol, mix & warm in water bath (do not let boiling occur). Centrifuge for 5 minutes.

Appendix F. Data from adsorption/desorption experiments

Metal desorption on clay minerals. Concentration express in nM.

Illite

pH	Cu	Rb	Cd	Cs	Pb
6.05	33.87	2494.51	23.40	249.88	0.06
6.18	28.29	2006.60	0.33	198.17	0.36
6.20	32.31	2331.87	31.63	233.25	0.02
6.22	77.22	2630.23	-0.08	245.59	0.75
6.84	140.26	2427.81	0.24	223.24	0.11
6.85	63.53	2368.90	0.28	201.05	0.30

Kaolin

pH	Cu	Rb	Cd	Cs	Pb
4.44		1.12	0.31	0.33	-0.27
4.76	1.78	1.28	0.25	0.48	-0.54
5.33	1.11	1.01	-0.17	0.20	-1.03
5.6	1.12	1.24	0.25	0.42	-1.40
5.94	1.16	1.26	-0.16	0.40	-0.73
6.35	1.53	1.55	-0.05	0.71	-0.22
6.78	1.52	1.25	-0.80	0.40	-0.54
8.53	1.06	1.22	-0.74	0.40	-0.72

Montmorillonite

pH	Cu	Rb	Cd	Cs	Pb
5.21	24.17	151.29	0.65	6.01	0.44
5.44	19.31	151.64	1.70	6.07	0.08
5.47	24.38	216.10	1.98	10.62	0.62
6.33	17.39	88.88	0.31	3.44	0.04
6.93	19.72	195.75	0.66	8.19	0.14
7.36	32.87	140.40	0.34	5.88	0.08

Metal desorption by site, concentration express in nM.

Espiritu Santo Estuary

pH	Cu	Rb	Cd	Cs	Pb
6.31	226.92	260.80	20.87	18.37	0.56
6.36	101.14	133.73	1.77	0.42	0.40
6.44	101.23	146.02	1.83	0.32	8.41
6.56	237.62	342.12	2.50	0.65	1.34
6.56	163.50	274.84	8.24	10.43	0.72
6.65	225.19	203.12	2.26	0.35	0.66
6.81	659.36	166.26	4.95	0.52	0.38
7.12	363.36	136.78	2.99	0.28	0.29
7.2	204.73	90.83	2.14	0.31	8.31

El Verde Experimental Station

pH	Cu	Rb	Cd	Cs	Pb
4.4	337.08	121.33	4.92	2.68	7.91
4.4	227.87	46.97	5.41	4.58	1.72
4.6	285.15	99.98	3.08	2.47	0.65
4.6	249.74	51.79	3.84	3.81	0.57
4.89	180.34	28.51	1.40	2.51	0.81
5.24	307.34	81.81	1.02	1.82	0.43
5.24	201.43	28.00	1.41	2.43	1.28
5.64	294.75	73.29	0.40	1.42	0.35
5.81	237.78	24.89	0.13	1.78	0.09
5.9	337.08	121.33	4.92	2.68	7.91

BONUS area, Rincon

pH	Cu	Rb	Cd	Cs	Pb
6.56	93.30	341.53	1.72	0.95	0.03
6.62	57.89	242.43	2.29	1.14	0.57
6.63	90.03	303.04	1.43	0.89	0.06
6.66	78.93	269.67	1.81	1.21	0.38
6.77	58.24	305.61	2.07	1.70	0.26
6.82	95.27	282.09	0.04	0.99	0.13
6.86	97.90	290.99	0.66	0.53	7.90
7.01	105.12	271.21	-0.08	0.81	0.72
7.14	79.78	126.93	0.55	0.77	7.29
7.43	93.30	341.53	1.72	0.95	0.03

Vieques

pH	Cu	Rb	Cd	Cs	Pb
6.8	93.62	323.98	6.92	1.51	0.64
6.83	248.01	500.66	2.79	1.54	0.72
6.91	255.09	432.56	2.49	1.53	0.41
6.92	88.96	183.34	0.83	0.88	0.55
6.94	90.17	309.47	7.48	1.62	0.20
7.12	62.82	90.08	2.37	0.80	8.36
7.14	308.91	325.62	1.16	1.45	0.86
7.15	40.00	130.69	3.60	0.85	0.24
7.3	119.60	185.03	1.43	0.86	8.05
7.58	93.62	323.98	6.92	1.51	0.64

Distribution coefficient for equilibrium kinetics experiments on clay minerals, express in nM.

Illite

Time	Cu	Rb	Cd	Cs	Pb
0	1482.55	1102.99	837.02	718.78	460.28
10	77.44	1325.65	429.23	431.14	12.10
30	95.88	1271.82	400.32	406.38	10.31
60	77.85	1419.25	405.65	432.11	9.03
90	54.45	1412.23	370.34	411.65	7.80
120		1446.16	353.35	390.35	8.01
180	73.05	1519.87	328.08	385.46	6.98
360	78.57	1561.99	299.04	362.44	6.16

Montmorillonite

Time	Cu	Rb	Cd	Cs	Pb
0	1401.66	1155.41	841.95	711.56	441.22
10	16.87	373.24	118.27	73.76	5.45
30	12.09	352.65	93.41	62.50	3.71
60	12.27	357.91	88.90	63.50	5.49
90	13.46	357.56	83.88	62.76	3.44
120	17.28	354.05	82.79	62.28	2.87
180	17.83	353.93	82.32	60.63	3.08
360	10.13	360.72	81.55	62.60	3.65

Kaolin

Time	Cu	Rb	Cd	Cs	Pb
0	1495.45	1131.42	848.72	714.87	455.69
10	417.49	1010.91	650.51	563.11	12.93
30	372.64	1024.95	627.30	559.87	7.31
60	334.88	1032.32	618.49	573.19	7.04
90	310.48	1033.02	611.19	561.75	6.39
120	291.91	1028.93	607.73	563.41	5.81
180	270.51	1021.91	601.45	561.91	5.79
360	217.64	1031.85	598.78	557.32	5.20

Distribution coefficient for adsorption experiments on clay minerals, express as the log K_s.

Illite

pH	Cu	Rb	Cd	Cs	Pb
5.94	1.50	-1.16	0.71	0.33	2.12
6.29	1.57	-0.46	1.05	0.47	2.32
6.34	1.54	-0.78	0.85	0.43	2.82
6.84	1.67	-0.62	1.00	0.42	3.00
7	1.54	-0.30	1.13	0.47	3.06
7.01	1.37	0.02	1.42	0.55	2.90

Montmorillonite

pH	Cu	Rb	Cd	Cs	Pb
4.79	1.54	0.73	1.20	1.55	2.83
5.13	1.88	0.54	0.99	1.30	2.49
5.46	1.99	0.82	1.26	1.56	2.73
6.14	1.39	0.90	1.42	1.63	2.88
6.88	1.41	0.53	1.43	1.36	2.01
7.31	1.80	0.85	1.69	1.59	3.27

Kaolin

pH	Cu	Rb	Cd	Cs	Pb
4.86	2.04	-0.21	0.32	0.24	3.30
5.59	1.53	-0.21	0.20	0.26	3.16
5.94	1.74	-0.22	0.27	0.28	3.05
6.06	1.76	-0.11	0.59	0.31	3.05
6.4	1.40	-0.43	1.05	0.12	1.81
6.89	1.52	-0.23	1.04	0.27	2.24
8.34	2.04	-0.21	0.32	0.24	3.30

Distribution coefficient for adsorption experiments at the study sites in Puerto Rico, express as the log K_s.

Espiritu Santo

pH	Pb	Cu	Cd	Cs	Rb
6.30	3.38	0.85	1.94	1.55	0.13
6.38	2.65	0.45	1.88	1.58	0.23
6.43	2.11	0.77	1.59	1.56	-0.02
6.46	2.12	0.75	1.66	1.58	-0.01
6.57	2.93	0.55	1.87	1.60	0.17
6.64	2.92	0.82	1.61	1.59	0.04
6.66	3.38	0.85	1.94	1.55	0.13
6.81	2.65	0.45	1.88	1.58	0.23
7.12	2.11	0.77	1.59	1.56	-0.02

El Verde

pH	Pb	Cu	Cd	Cs	Rb
4.36	1.83	0.50	0.58	0.98	0.25
4.37	2.03	0.68	0.54	0.85	0.29
4.49	2.06	0.68	0.74	1.06	0.36
4.66	2.75	0.77	0.81	1.00	0.46
4.72	2.20	0.51	0.33	0.80	0.25
5.05	2.91	0.86	1.25	1.11	0.63
5.34	2.05	0.61	1.39	1.05	0.40
5.52	3.00	0.72	1.82	1.28	0.77
5.65	2.86	0.62	1.75	1.20	0.49
5.81	2.81	0.57	1.88	1.34	0.61

Rincon

pH	Pb	Cu	Cd	Cs	Rb
6.57	3.77	1.22	1.82	1.28	0.08
6.62	3.43	1.16	2.00	1.39	0.13
6.66	3.01	1.24	1.66	0.95	-0.03
6.72	2.18	0.73	1.99	1.34	0.09
6.80	2.99	1.29	1.71	0.88	-0.04
6.82	2.00	1.28	1.85	1.01	-0.02
6.88	2.28	1.19	2.10	1.35	0.14
7.04	2.91	1.08	2.19	1.42	0.21
7.11	3.60	1.21	1.74	0.45	-0.67
7.22	2.22	1.08	1.90	0.47	-0.48

Vieques

pH	Pb	Cu	Cd	Cs	Rb
6.85	3.23	1.06	1.64	1.08	-0.13
6.89	2.17	0.81	2.58	1.12	-0.39
6.89	2.82	0.81	2.55	1.32	-0.10
6.89	3.56	0.70	1.97	1.37	-0.06
7.00	2.70	1.11	1.68	1.02	-0.19
7.12	2.17	0.71	2.07	1.23	-0.36
7.19	2.19	1.15	1.68	0.94	-0.42
7.24	2.18	1.20	1.83	0.85	-0.32
7.43	3.34	0.86	2.36	1.27	-0.08
7.60	4.09	1.24	1.97	0.88	-0.20

Appendix G. Self-adsorption and weight corrections

In order to verify the radionuclide activities determined during this investigation, a subset of samples were analyzed utilizing two gamma detectors with different configurations. Activity values reported in chapter 2 were obtained utilizing a gamma detector with a well configuration. Both the gamma well and planar detectors were calibrated using the same calibration standards. In addition, self-adsorption curves were calculated as a function of the weight of each standard.

Determining the self-adsorption characteristics and efficiencies of both detectors allowed for the verification of Cs-137 activity values determined during this investigation. Environmental samples tend to have low levels of radioactivity. As such it is important to be able to accurately determine the efficiency of each detector, particularly at 100 keV and below for this study. Figure 53 and 54, shows the self-adsorption trend and weight correction factors for samples analyzed using the planar detector. The full energy peak efficiencies are affected by the high self-absorption of the gamma rays emitted, which strictly depend on the energy of the gamma-ray considered as well as on the composition and apparent density of the analyzed sample. As the total weight of the sample increase self-adsorption chances will increase. Figure 53and 54 shows that correlation and how using samples in a range of weights that were from 1gram to 11grams, will allow us to correct for the transmission received by planar detector as a function of sediment weight.

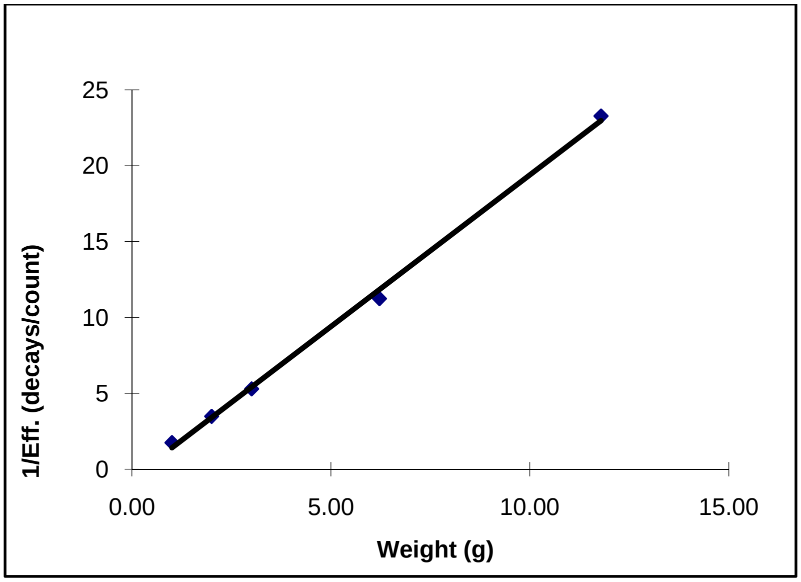


Figure 53. Pb-210 self adsorption correction on planar detector, R squared is equal to 0.99.

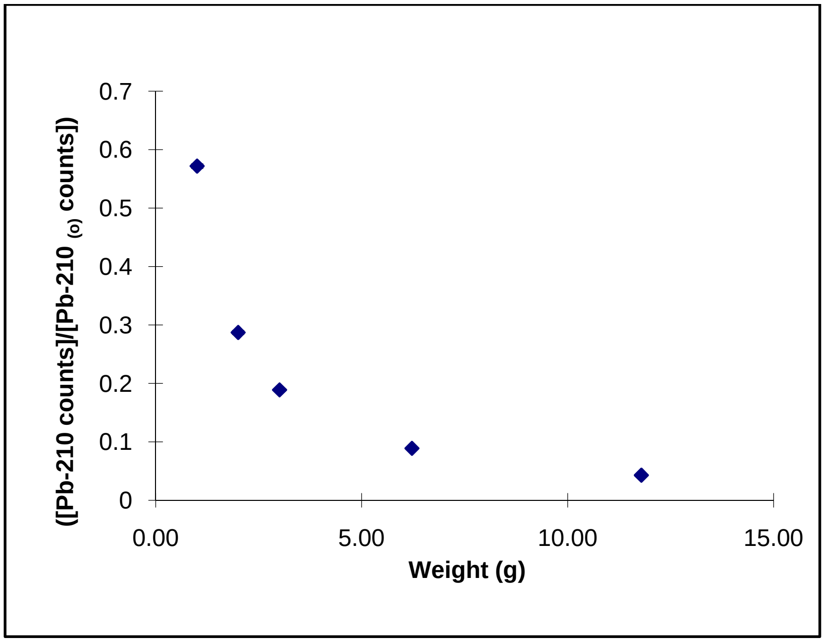


Figure 54. Pb-210 weight vs. efficiencies on planar detector. Pb-210 transmission received by planar detector as a function of sediment weight.

Well detector efficiency is plotted in figure 55. Efficiency of the well detector is greater at lower energy levels.

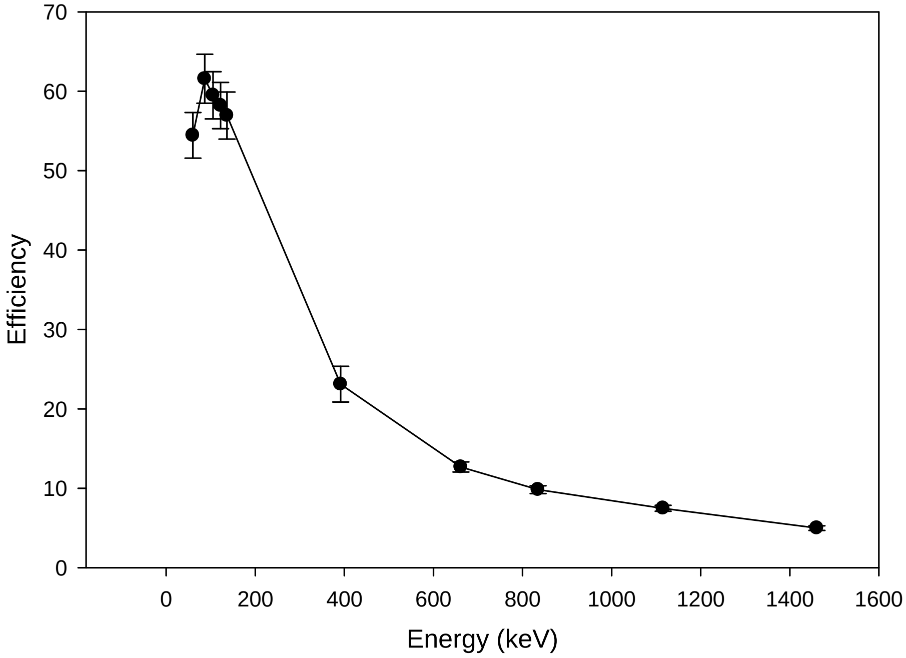


Figure 55. Energy Efficiency calibration for Germanium well detectors

Self adsorption directly affects the counting of samples since the adsorption is a function of sample density (Cochran et al. 1998). Therefore environmental samples need to be normalized in order to eliminate variations in density which affects transmission to the detector (Cochran et al. 1998). This normalization is performed using the same geometry, realizing that although the geometry and volume of a sample can be controlled, the density of a sample varies according to the composition of the sample. Environmental samples are a mix of organic matter, different soil types, mineral content, as well as various other parameters (including moisture content) that can easily change during dry seasons, storms or other weather-related events. Because the island of Puerto Rico has a tropical climate, storms, hurricanes, wave action, etc. can directly impact the chemical, biological and geological composition of environmental samples.

Samples from Vieques were measured for Pb-210 activity utilizing both the gamma well and planar detectors (figure 56). Activity values determined varies throughout the core, and decreases from zero to 16 cm and increases again in deeper sediments. The consistency between the two detectors is strong and serves to validate the acceptable usage of both detectors during this investigation.

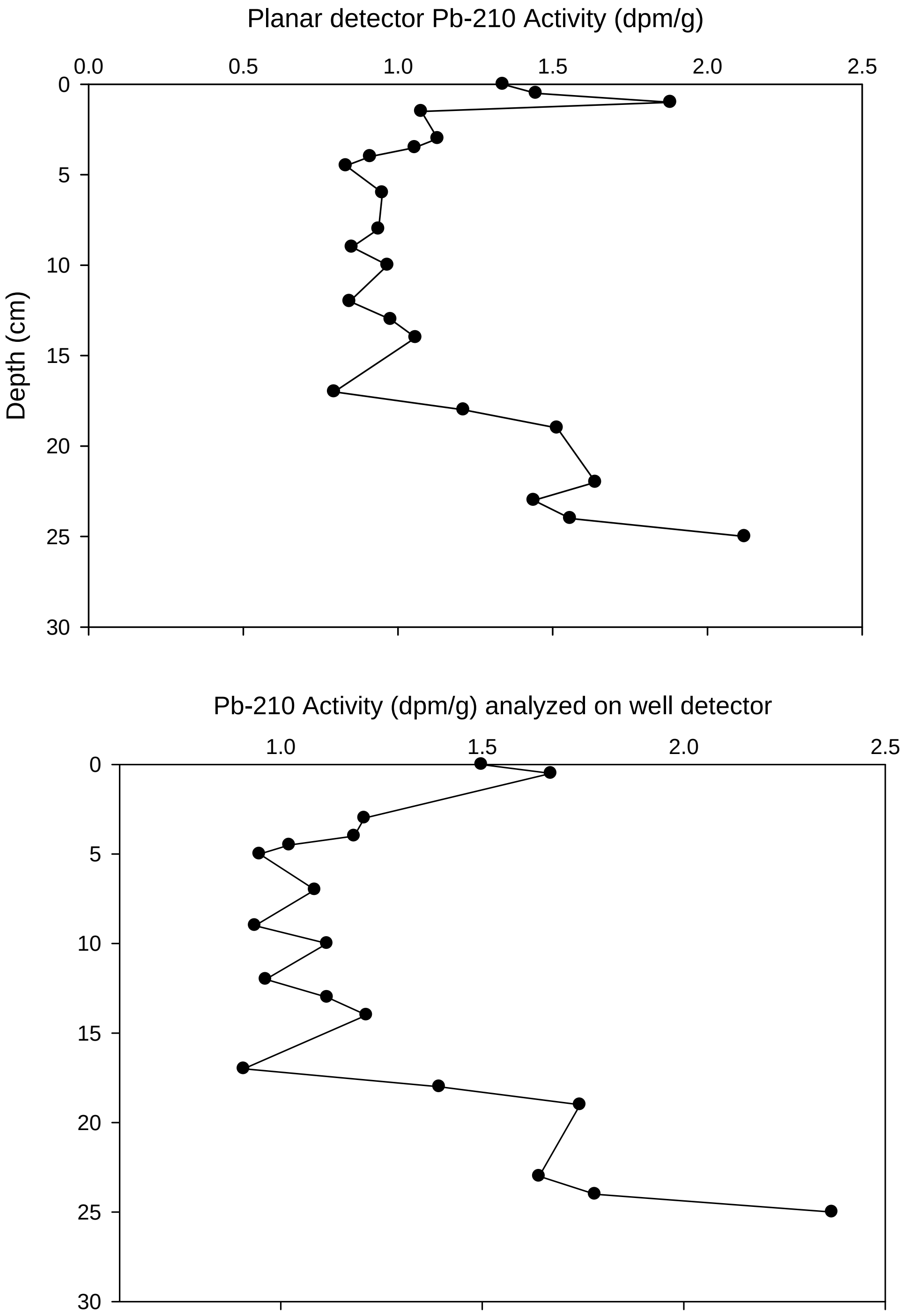


Figure 56. Result comparison of Pb-210 activity in samples from Mosquito Bay performed on well and planar detector.

ABOUT THE AUTHOR

Warner Ithier-Guzman was born in Mayaguez, Puerto Rico. He has a B.S. Degree in Biology from the Inter-American University-San German, a M.S. Environmental Protection and Evaluation from Inter-American University-Metropolitan Campus. As a doctoral student he conducted research on radiogeochemistry and work at the Environmental and Occupational Safety and Health Office at the University of Puerto Rico-Rio Piedras. He received the NSF Bridge to the Doctorate Fellowship as well as the OCEANS Fellowship. Some of the specialized course work on his curriculum includes special seminars from the Vespucci Institute and the Radiation Safety Officer Certification from Harvard University. He has been appointed to various committees including the Advancing Science in Limnology and Oceanography local organizing committee held in San Juan, Puerto Rico in February 2011.