

Quantifying Background Erosion Rates in Cuba Using Cosmogenic Nuclides

A Thesis Proposal Presented

by

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1. Introduction

Soil erosion is a major issue impacting global food production and ecosystem health (Montgomery 2007). An estimated 16.4 million km² of land globally are affected by soil erosion (Dotterweich 2013) and approximately 120,000 km² of arable land becomes unproductive each year due to unsustainable agricultural practices (Pimentel et al. 1995). Although conservation agricultural practices are often implemented as a solution to these issues, and many studies demonstrate their effectiveness at the plot scale (Barton et al. 2004, Montgomery 2007), few studies have quantified their effects on a landscape scale (Schmidt and Bierman 2017). Furthermore, identifying the contribution of human actions to changing the rates and spatial distribution of erosion requires a fundamental understanding of the rate and distribution of underlying natural processes governing erosion (Dearing et al. 2006, Dotterweich 2013).

Long-term, natural rates of erosion can be quantified using measurements of cosmogenic nuclides in rock and sediment. Cosmogenic nuclides, such as ¹⁰Be and ²⁶Al, are produced at and near Earth's surface by the interaction of cosmic rays with rocks and soil (Lal 1988). Measuring these nuclides in detrital sediment yields a spatially-averaged erosion rate for the basin area upstream of the sampled location (Brown et al. 1995, Bierman and Steig 1996, Granger et al. 1996).

Although cosmogenic nuclides have been used globally to characterize the natural or background rate of erosion processes, there is a dearth of cosmogenic nuclide measurements of long-term erosion rates in tropical locales (Portenga and Bierman 2011). Because of its unique land use history, Cuba is an ideal country for comparing long-term erosion rates to modern rates that have been influenced by human actions. Cosmogenic nuclide measurements to characterize erosion rates have not been undertaken in Cuba previously.

Knowledge of background erosion rates is necessary for understanding how erosion has responded to human actions in a country that has undergone extensive changes in land use in recent history. Following colonial sugarcane production, Cuba practiced high-input conventional agriculture that was focused on crop yields, compensating for reductions in soil quality with heavy applications of fertilizers and pesticides that the Soviet Union provided (Wright 2012). The collapse of the Soviet Union and loss of associated subsidies and imports forced an abrupt shift towards sustainable soil management beginning in 1989 (Gersper et al. 1993).

My thesis research aims to characterize the background rates of erosion in Cuba using cosmogenic nuclide measurements. My data will increase knowledge of erosion in an understudied region of the globe, and will serve as a springboard for understanding how modern erosion rates resulting from a variety of land management practices compare to the rates of natural processes. I will work to develop and test a method for determining erosion rates from cosmogenic nuclide measurements of carbonate sediments, and determine the production rate of ^{26}Al in carbonate rocks of known age near our sample sites in order to calibrate this method.

2. *Background*

2.1 *Cosmogenic Radionuclides*

Cosmogenic isotopes such as ^{10}Be , ^{36}Cl , and ^{26}Al are produced by the interaction of cosmic rays with rocks and soil (Lal 1988). Minerals at the surface of the Earth are bombarded with neutrons that result from primary cosmic rays (largely protons) interacting with the Earth's atmosphere (Bierman 1994). These neutrons interact with target nuclei to produce cosmogenic isotopes *via* spallation, neutron activation, and muon capture (Lal 1991). ^{10}Be and ^{26}Al are

largely produced by spallation near the surface (Lal 1991), while ^{36}Cl is produced as a result of all three production pathways (Stone et al. 1994).

The production of cosmogenic nuclides is greatest at the surface of the Earth and decreases with depth; production rates are influenced by depth, elevation, latitude, and the strength of Earth's magnetic field (Lal 1991). Some cosmogenic nuclides are also produced in the atmosphere and are deposited on surfaces and in basins through precipitation; however separation of these meteoric inputs from cosmogenic isotopes produced *in-situ* is accomplished with laboratory cleaning methods (Kohl and Nishiizumi 1992). The concentration of cosmogenic nuclides in sediment being exported from a basin is inversely proportional to the rate at which the basin is eroding, so measuring *in situ* produced cosmogenic nuclides in detrital sediment yields a spatially-averaged erosion rate for the area of the basin upstream of the sample site (Brown et al. 1995, Bierman and Steig 1996, Granger et al. 1996).

The majority of cosmogenic nuclide analyses have focused on measuring ^{10}Be and ^{26}Al in quartz-bearing minerals, although attempts have been made to identify additional viable mineral/cosmogenic nuclide pairings (Nishiizumi et al. 1990, Braucher et al. 2005, Merchel et al. 2010). In carbonate sediments, measurement of ^{10}Be is impractical because no methods have been proven to reliably remove the meteoric ^{10}Be that is abundant in clay minerals without also losing *in-situ* ^{10}Be (Merchel et al. 2010). ^{26}Al , however, offers a viable alternative. Although the production rate of ^{26}Al in carbonates is much lower than in quartz, Merchel et al. successfully isolated ^{26}Al from well-crystallized calcite and achieved reproducible measurements across trials, demonstrating the potential of this method (Merchel et al. 2010). Further application of this method will require the determination of absolute production rates of ^{26}Al , and the adaptation of laboratory methods to account for ^{27}Al in samples with higher concentrations of clay minerals, such as sediments – research that I will undertake as part of my thesis project.

^{36}Cl has also been measured in carbonate outcrops and sediment to estimate erosion rates (Stone et al. 1994, Ryb et al. 2014), although calculating erosion rates from ^{36}Cl production in calcite can be complex due to its multiple production pathways (Stone et al. 1994). We plan on measuring ^{36}Cl in the detrital samples we collect in Cuba and in a reference core that we will use to calibrate ^{26}Al production rates in order to provide a comparison to an established cosmogenic nuclide system. Measuring ^{36}Cl in sections of a reference core that have already been dated to 110.7 ± 1 kyr to 146.0 ± 1.7 kyr using U/Th (Blanchon et al. 2009) will allow us to independently verify their ages and provide a comparison to ^{26}Al measurements in the same core.

2.2 Land Use History of Cuba

Cuba has undergone extensive land use changes. Before Spanish settlement in 1492 the native Ciboney people practiced a primitive form of agriculture, and an estimated 95% of the island was forested (CITMA 1997). Colonial, plantation-style cultivation of cash crops—primarily sugar—transformed the landscape through slash and burn agriculture, and by the end of the 18th century Cuba was producing 25% of the world's supply of sugar (Houck 2000). Following the Cuban Revolution of 1959 and the establishment of close relations between Cuba and the Soviet Union, Cuba went through a period of rapid and comprehensive agricultural development, assisted by the Soviet Union (Gersper et al. 1993). Cuba received food, agrochemicals, and farm machinery, in exchange for sugarcane, tobacco, and fruit exports (Wright 2012). Mechanization in Cuba was so advanced that Cuba was using more artificial fertilizer and running more tractors per hectare than comparable agricultural operations in the United States (Wright 2012).

The effects of this intensive industrial agriculture were predictable. Cuba was rapidly deforested: at the beginning of the 20th century, Cuba had lost an estimated 50% of its original forests, and only 50 years later forested land was reduced to 14%, largely concentrated in places

that are impractical for agriculture such as mangrove swamps and mountainous areas (CITMA 1997). In 1998, more than 75% of the land area of Cuba was affected by erosion, salinity, acidification, desertification, drainage problems, or a combination of these factors (CITMA 1998).

The collapse of the Soviet Union in 1991 brought a halt to Cuba's industrial agriculture. Previously reliant on imports from the USSR, Cuba was faced with a severe food and energy crisis (Houck 2000). Agricultural production and the availability of food fell to critically low levels, with the average caloric intake of Cuban citizens dropping by as much as 30% (Wright 2012). In response to this crisis, Cuba instituted a variety of plans to achieve domestic food security that were centered on developing ecological production techniques such as chemical-free organic agriculture, the use of bio-fertilizers and pesticides, reduced tillage methods and intercropping/crop rotation (Houck 2000). The management and restoration of soil quality is critical for organic agriculture, so soil conservation became a top priority in Cuba (Gersper et al. 1993). In only a several-year period, Cuba went from intensive industrial agriculture to soil conserving, organic agriculture featuring minimal soil tillage, the replacement of tractors with draft animals, crop rotation/intercropping, cover crops, and sustainably-produced soil amendments (Wright 2012).

This massive and rapid conversion from industrial agriculture to organic agriculture on a nationwide scale represents a unique opportunity to study the effects of agriculture on the rate and spatial distribution of erosion. Measuring the background rates of erosion is the first step towards understanding how the landscape has responded to these modern changes in land use. The cosmogenic nuclide measurements I make will be paired with existing sediment-yield data (Zorrilla and Karasik 1989) and measurements of short-lived fallout radionuclides (made at Oberlin College), allowing us to characterize erosion at multiple spatial and temporal scales.

3. Work Plan

Due to the difficulties associated with working in Cuba—a developing country that has long been closed to Americans—the nature of my thesis research may change as we determine when we will be able to collect samples and how long it will take to process them. The three main goals of my thesis: 1) measuring background erosion rates in Cuba, 2) developing a method to extract ^{26}Al from carbonate sediments, and 3) determining the production rate of ^{26}Al in carbonate rocks near my study site, will become more or less prominent pieces of my project depending on when and how many times we are able travel to Cuba. This year I have been focusing on methods development and this will continue to be the focus of my work prior to our first field season this summer. Due to the large number of samples being collected and the uncertainty of fieldwork dates/permits, it is likely that my thesis will center on samples we collect in our first field season.

3.1 Method Development

Cosmogenic nuclide analyses for determining erosion rates usually measure ^{10}Be in quartz, but much of Cuba is underlain by carbonate rocks, so I am working to develop a method for measuring ^{26}Al produced in calcite to quantify erosion rates. Collected sediments will be analyzed using a combination of ^{26}Al , ^{10}Be , and/or ^{36}Cl , as appropriate. The method we will use to clean/prepare the sediments for ^{26}Al extraction is modified from Merchel et al. (2016). We have been adding 210 ml of 3.5M acetic acid to 30 g of sediment and allowing the samples to react for 24-48 hours on a shaker table. Acetic acid is commonly used when working with clay-rich carbonate sediments, as acetic is less likely to disturb clay crystallinity and release stable, ^{27}Al (Poppe et al. 2001).

We tested other acids for this dissolution and found that acetic acid was the most appropriate choice for this procedure, because it preserved clay-mineral phases and resulted in lower amounts of stable aluminum (sourced from clays) in solution. We measured the initial aluminum concentrations in solutions of sediment dissolved with the same concentrations of acetic acid, nitric acid, and hydrochloric acid, and found that the aluminum concentrations in the nitric and hydrochloric solutions were orders of magnitude higher than in the acetic solution (Fig. 2). We determined that this difference resulted from the stronger acids dissolving a greater proportion of clay mineral phases present (Fig. 3). Clay minerals contain ^{27}Al , which increase the $^{26}\text{Al}/^{27}\text{Al}$ ratio and make measuring ^{26}Al more difficult.

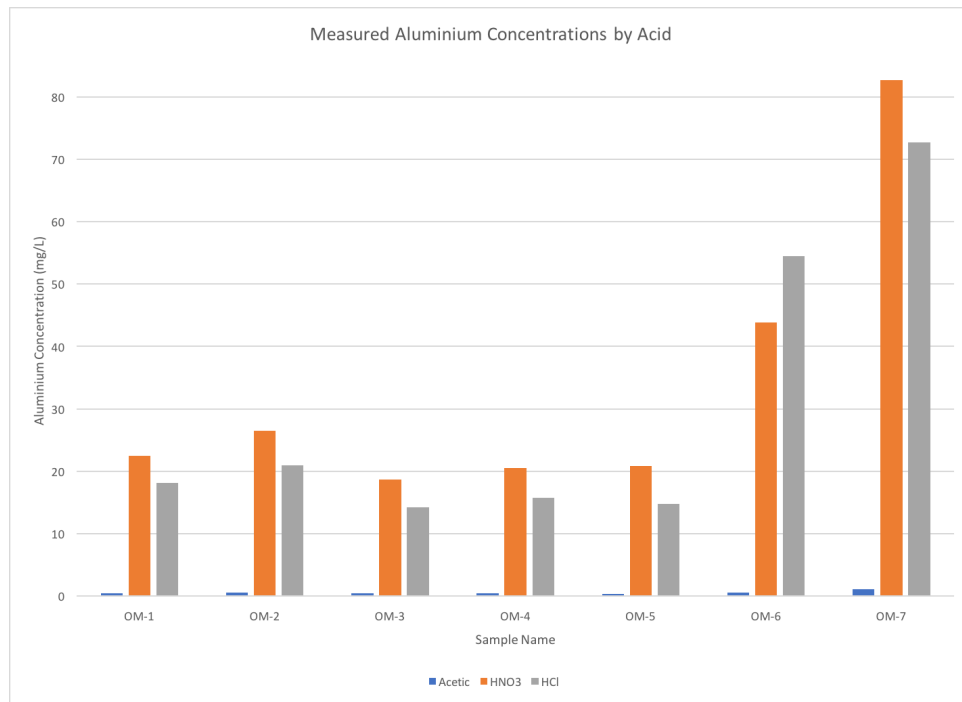


Figure 2: Measured aluminum concentrations (mg/L) in a 1:10 dilution of the dissolved solution for test CaCO_3 sediment samples dissolved with acetic acid, nitric acid, and hydrochloric acid.

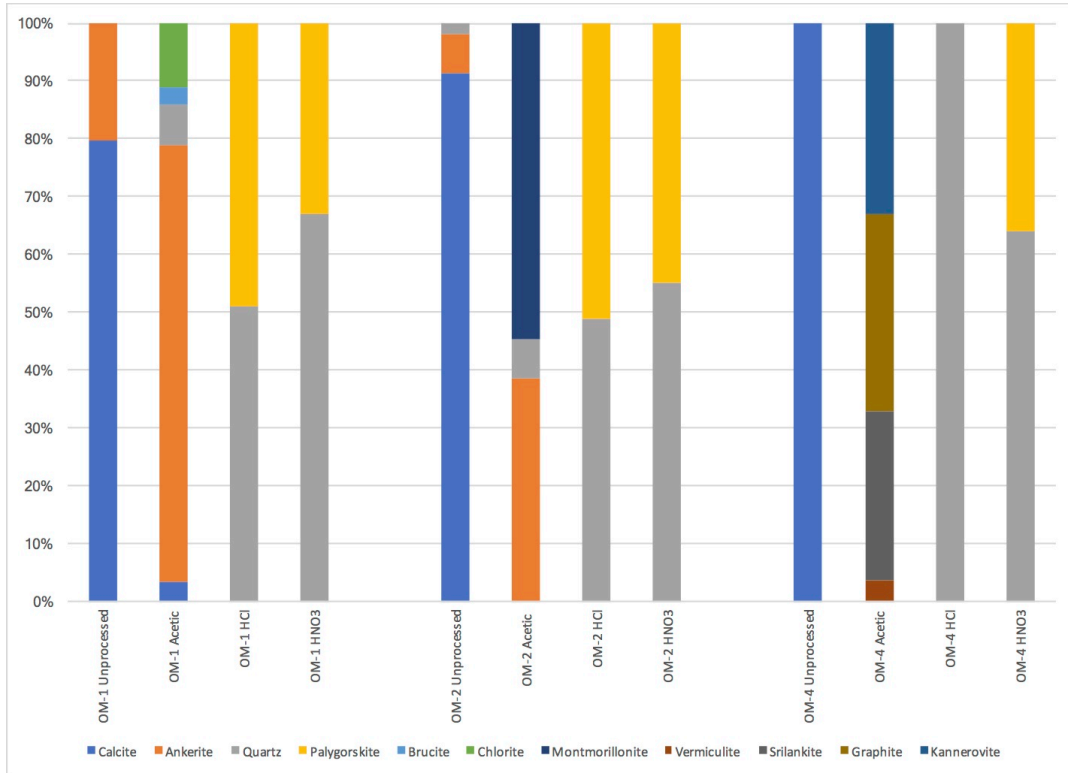


Figure 3: Comparison of the relative percentages of mineral phases identified by X-Ray Diffraction (XRD) for the initial sediments and the residual material after dissolutions. The samples dissolved with acetic acid retain a greater variety of minerals (particularly clay minerals) than the samples dissolved with nitric or hydrochloric acid.

After reacting, samples are centrifuged to separate the solution from the undissolved residue. We decant the solution, add 5 mL of deionized water to the remaining residue to wash, then centrifuge, and decant again. We dry the residue and preserve the remaining material for ^{10}Be extraction from quartz, if present. A small aliquot is taken from each solution to characterize initial aluminum yields *via* Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Aluminum is less soluble between pH 6-8 (Driscoll and Schecher 1990), so we plan on neutralizing the acetic solution to precipitate an aluminum gel, then centrifuging to separate the gel and the solution and decanting the remaining solution. After separating the aluminum gels, we will re-acidify them to get the aluminum back into solution, then pass the solution through anion and cation columns to ensure that we have completely isolated the aluminum. The

resulting aluminum hydroxide will be dried and burned to remove water and hydroxyl and converted to oxide form.

We have been testing the methodology outlined above on samples of carbonate sediments from Oman and have successfully isolated some aluminum from these samples, but we have determined that a significant amount of aluminum remained in solution. Moving forward, we plan on testing different methods of isolating aluminum, including precipitating the large amounts of calcium in solution as gypsum before attempting to isolate the aluminum, aluminum chelation, and solid-phase extraction using resins.

3.2 Calibrating ^{26}Al -Aluminum Production Rates

Production rates of ^{26}Al in calcium carbonate have not yet been established empirically, so we plan on comparing our measurements of ^{26}Al in Cuban samples to the ^{26}Al measurements we will undertake in a core sample of a fossilized coral reef from south of Cancun, Mexico, about 510 km from Havana and at approximately the same latitude. The different sections of the core were dated using ^{230}Th from 110.7 ± 1 kyr to 146.0 ± 1.7 kyr (Blanchon et al. 2009). Blanchon et al. used this core and others to constrain changes in sea level in their study area during the last interglacial period (Marine Isotope Stage 5e), placing the timing of a sea-level highstand at ~ 121 kyr. Following this highstand, relative sea level began to fall off at ~ 117 kyr (Blanchon et al. 2009), constraining the timing of when the reef rose above sea level and significant cosmic-ray dosing began. Measuring ^{26}Al in cores from this area will allow us to determine ^{26}Al production rates for our study area that can be compared to the ^{230}Th ages of the sections of the core. Once a $^{26}\text{Al}/^{27}\text{Al}$ ratio for each Cuban sample has been established and multiplied by the total ^{27}Al content in each sample to calculate the amount of ^{26}Al in atoms/g, an erosion rate for each study watershed can be determined by comparison to known ^{26}Al production rates in the carbonate core. We also plan to measure the concentrations of ^{36}Cl in the

core to cross-calibrate our measurements of ^{26}Al with an established cosmogenic nuclide method, following the methodology of Gran (2000).

3.3 Sample Collection and Processing Procedures

We will collect detrital sediment from watersheds across the island of Cuba that represent a variety of land uses, basin slopes, and average annual precipitation received to examine how erosion changes spatially and in relation to these parameters. We selected approximately 100 potential sample sites for the collection of detrital sediment by using GIS to identify watersheds representing a variety of land uses, basin slopes, and average annual precipitation (Fig. 1).

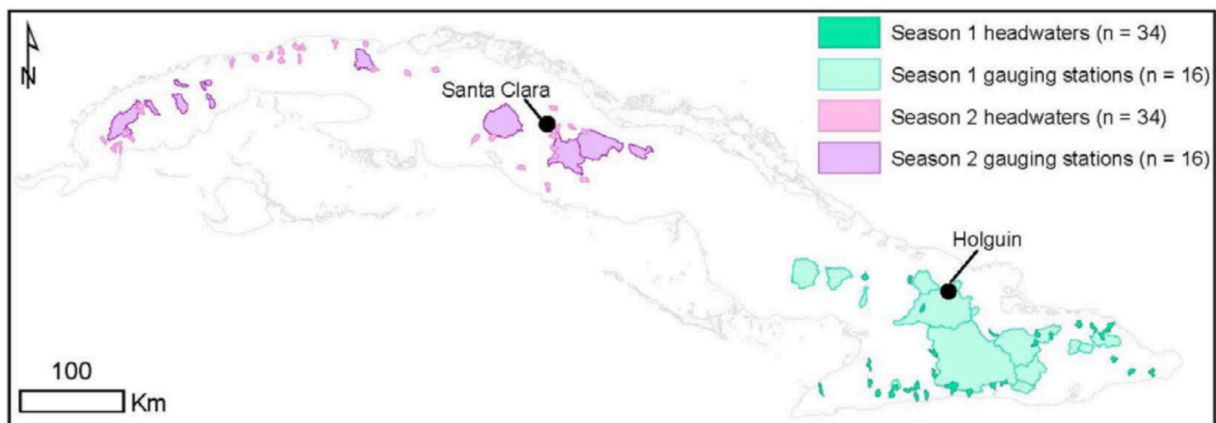


Figure 1: Map of sample watersheds from Schmidt and Bierman, 2017. Detrital sediment samples will be collected from the outlets of these watersheds.

We selected ~70 sample sites that represented a range of slopes, average annual precipitation, and land uses that were close to roads or bridges, ensuring site access. The other ~30 sites we selected are the best estimates of the locations of sediment gauging stations with up to 19 years of data that were maintained during Cuba's intensive Soviet agricultural period (Zorrilla and Karasik 1989). Sampling watersheds that represent a variety of basin slopes, precipitation, and land use will allow us to determine if these factors are controls on erosion, and sampling the gauging stations will provide us with a direct comparison to sediment yield records.

We will field-sieve detrital sediment at the selected sample points to 250-850 μm to be consistent with established procedures for ^{10}Be (Corbett et al. 2016). Once in the lab, we will wash the sediment to remove dust and organic materials and then dry it. A portion of each sample will be dissolved in hydrochloric acid to determine its quartz content. Samples that contain sufficient amounts of quartz will be purified and prepared for ^{10}Be extraction. Samples without sufficient quartz will be prepared for ^{26}Al and ^{36}Cl extraction as outlined previously. The resulting products for all isotope systems will then be mixed with appropriate binders and packed onto cathodes. The samples will be counted on an Accelerator Mass Spectrometer (AMS) at PRIME laboratory at Purdue University to determine the isotopic ratios of interest.

4. Timeline

Timeframe	Goals
Spring Semester 2018	<ul style="list-style-type: none"> • Continue to develop ^{26}Al extraction method • Begin characterization of carbonate core from reference site in Cancun, test ^{26}Al extraction on this sample • Prepare Cancun samples for ^{36}Cl extraction
Summer 2018	<ul style="list-style-type: none"> • Continue developing ^{26}Al extraction method if needed • First field visit to Cuba • Sample preparation • Begin writing introduction and background sections • Potential measurement of ^{26}Al from reference core
Fall Semester 2018	<ul style="list-style-type: none"> • Complete 2 potential additional field visits to Cuba • More sample preparation and more $^{26}\text{Al}/^{36}\text{Cl}$ extractions • Measurement of first round of ^{26}Al from initial Cuban samples • Data analysis • Begin writing methods and results/discussion • Present progress report
Spring Semester 2019	<ul style="list-style-type: none"> • Measurement of additional Cuban samples (may or may not happen in time to be included in my thesis) • Continued data analysis • Wrap up writing
Summer 2019	<ul style="list-style-type: none"> • Finish and defend

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