

Effects of mass wasting on fluvial sediments in Puerto Rico following Hurricane Maria

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Abstract

Mass wasting plays an important role on carbon cycling and sequestration by exposing fresh, weatherable bedrock and delivering hillslope sediments to lowlands and fluvial systems. Chemical weathering signatures of landslide-derived fluvial sediments can be used to understand linkages between hillslope and fluvial processes, and thus to characterize spatiotemporal dynamics of sediments. However, chemical signatures of fluvial sediments derived by landslides are yet to be fully understood. Here we compare the bulk chemistry, mineralogy, and grain size of fluvial sediments collected pre- and post-Hurricane Maria (landfall on Sept. 20, 2017) in the Rio Guayanés and Rio Guayabo River watersheds in southeastern Puerto Rico to help fill this knowledge gap.

Relative to fluvial muds collected before Hurricane Maria, mud samples collected after the storm exhibit higher weathering index values, but coarser grain size modes. We infer that small landslides triggered by Hurricane Maria transported slope materials from shallow depths, including weathered topsoil and saprolite, as opposed to previous deep-seated landslides which likely sampled regolith and bedrock. The variances in weathering indices observed pre- and post-hurricane do not reflect climate change, but rather subtle differences in transport mechanism which produce significant differences in weathering indices recorded by fluvial sediments. We propose that weathering indices provide a means to understand sediment dynamics in mountainous regions, particularly for sediment transported in the immediate aftermath of landslides triggered by extreme events, such as precipitation and earthquakes, and also provide important datasets required for mapping potential carbon sequestration across a landscape.

Keywords: Mass Wasting, Chemical Index of Weathering, Hurricane Maria, Fluvial Sediments, Carbon Sequestration

1. Introduction

Physiochemical characteristics of fluvial sediments have the potential to inform complex linkages among climatic, tectonic, hillslope and geomorphic processes. For example, weathering trends in fluvial sediments can shed light on rates and frequency of sediment production and transport from upland hillslopes, and thus provide a potential signature of both short- and long-term sediment transport and carbon cycling as well as a paleoclimate (White et al., 1998; White, Bullen, Vivit, Schulz, & Clow, 1999). Mass wasting is one of the major processes that deliver hillslope materials to fluvial systems in moderate - to high - relief settings. Increased mass wasting owing to climate and land-use change may increase chemical weathering rates (Moore, Buss, & Dosseto, 2019; Oliva, Viers, & Dupré, 2003), resulting in consumption of atmospheric carbon dioxide and producing a negative feedback effect for global climate change over thousands to millions of years, as well as immediately affecting stream quality and ecology (Sassa & Canuti, 2008).

Chemical weathering of fresh bedrock delivers cations into fluvial systems and draws down $p\text{CO}_2$ from Earth's atmosphere (Berner, 2003; Fernandes, da Conceição, Junior, de Souza Sardinha, & Mortatti, 2016). However, landslides may be a net source of CO_2 to the atmosphere where exposure of carbonates and sulfides result in sulfuric acid weathering of the carbonates (Emberson, Galy, & Hovius, 2018). Thus, the mineralogy of the weathering bedrock plays an important role in determining whether carbon is sequestered or released to the atmosphere.

The relative size and the frequency of the landslides also plays an important role in determining sediment volume, as well as degree of weathering, delivered to the fluvial system. For example, shallow landslides occur frequently and transport highly weathered soil and/or saprolite, whereas deep-seated landslides tend to occur less frequently, but transport large volumes of slope materials including soil, less-weathered saprolite, and deeper bedrock

(Bessette-Kirton et al., 2019; Stark & Hovius, 2001). Landslide size and frequency across a landscape is primarily governed by the spatial structure of hillslope strength variability (Bessette-Kirton et al., 2019; Varnes, 1978) which is influenced by: 1) hillslope morphology (i.e. slope, curvature, etc.) (Schmidt & Montgomery, 1995); 2) lithological characteristics, including the depth and bio-physiochemical properties of soil and underlying bedrock characteristics, including type, fracture density, and composition (Clarke & Burbank, 2011; Dixon, Heimsath, Kaste, & Amundson, 2009; Phillips, Marion, Luckow, & Adams, 2005); 3) associated surface and sub-surface hydrology; and 4) triggering mechanisms, such as precipitation, earthquakes, and anthropogenic activities (Lehmann et al., 2013; Varnes, 1978).

The impact of mass wasting on the weathering indices of sediment delivered to streams in high-relief and high-precipitation landscapes is not well known, and may provide important evidence of historical weathering trends, or could predict trends likely to occur with future mass-wasting (Bluth & Kump, 1994; Joo, Elwood Madden, & Soreghan, 2018). Mass wasting introduces a range of sediment grain sizes to fluvial systems (Larsen & Torres-Sanchez, 1998), which may also depend on several additional factors including 1) bedrock lithology (Roda-Boluda, D'Arcy, McDonald, & Whittaker, 2018), 2) rates of chemical weathering, particularly in tropical regions where more chemical weathering leads to finer grain sizes (Fernandes et al., 2016), and 3) transport mechanisms. For example, sediment supplied from gradual erosion of soil via overland flow tends to be finer grained and more homogeneous (i.e. well-sorted) (Attal et al., 2015), while sediment supplied via landslides tends to be coarser and poorly sorted, and can result in coarsening downstream, compared to the general trend of distal fining expected in a typical fluvial system (Attal et al., 2015; Roda-Boluda et al., 2018; Struck et al., 2015). In

addition, steep slopes in humid climates with abundant precipitation are more susceptible to mass wasting versus steep slopes in arid climates (Gariano & Guzzetti, 2016; Shiels & Walker, 2013).

Due to stochastic events, such as mass wasting, fluvial sediment properties can vary widely across both space and time. Anomalously low chemical index of alteration (CIA) values observed in fluvial sediments collected from the granitic watershed study area in Puerto Rico in 2014 were previously attributed to significant influence of mass wasting that tapped less-weathered regolith (Joo et al., 2018). Joo et al. (2018) posited that future climate warming and attendant increased precipitation might further stimulate delivery of mass-wasted material to streams, resulting in lower values of weathering indices in fluvial sediment. Hurricane Maria, which passed over Puerto Rico on September 20, 2017, resulted in >500 mm of rainfall within 48 hours (Silva-Tulla, Pando, Pradel, Park, & Kayen, 2020) and triggered widespread mass wasting in the study area (Bessette-Kirton et al., 2019; Keellings & Ayala, 2019; Ramos-Scharrón & Arima, 2019). This natural disaster caused enormous loss of life, health, and property (Bessette-Kirton et al., 2019; Keellings & Ayala, 2019; Chiara Lepore, Kamal, Shanahan, & Bras, 2012), but also created a natural experiment in which to directly observe the immediate impact of hurricane-induced mass wasting on fluvial sediments.

Joo et al. (2018) predict that mass wasting events supply the fluvial system with larger grains that are less weathered and derived from bedrock, regolith, or saprolite rather than soils. Additionally, they predicted that mass wasting would deliver not only larger grain sizes than systems without mass wasting events, but also a wider range of grain sizes, and less weathered grains with deep-seated landslides (Attal et al., 2015; Hubert & Filipov, 1989). However, the potential impact of transient hillslope responses to intense but short-duration precipitation events on fluvial sediments remains poorly constrained. This study aims to investigate the short-term

impact of a significant storm event - Hurricane Maria, and the resultant landslides on fluvial sediment properties as well as bridge the gap between these properties and chemical weathering indices to analyze potential impacts on climate change.

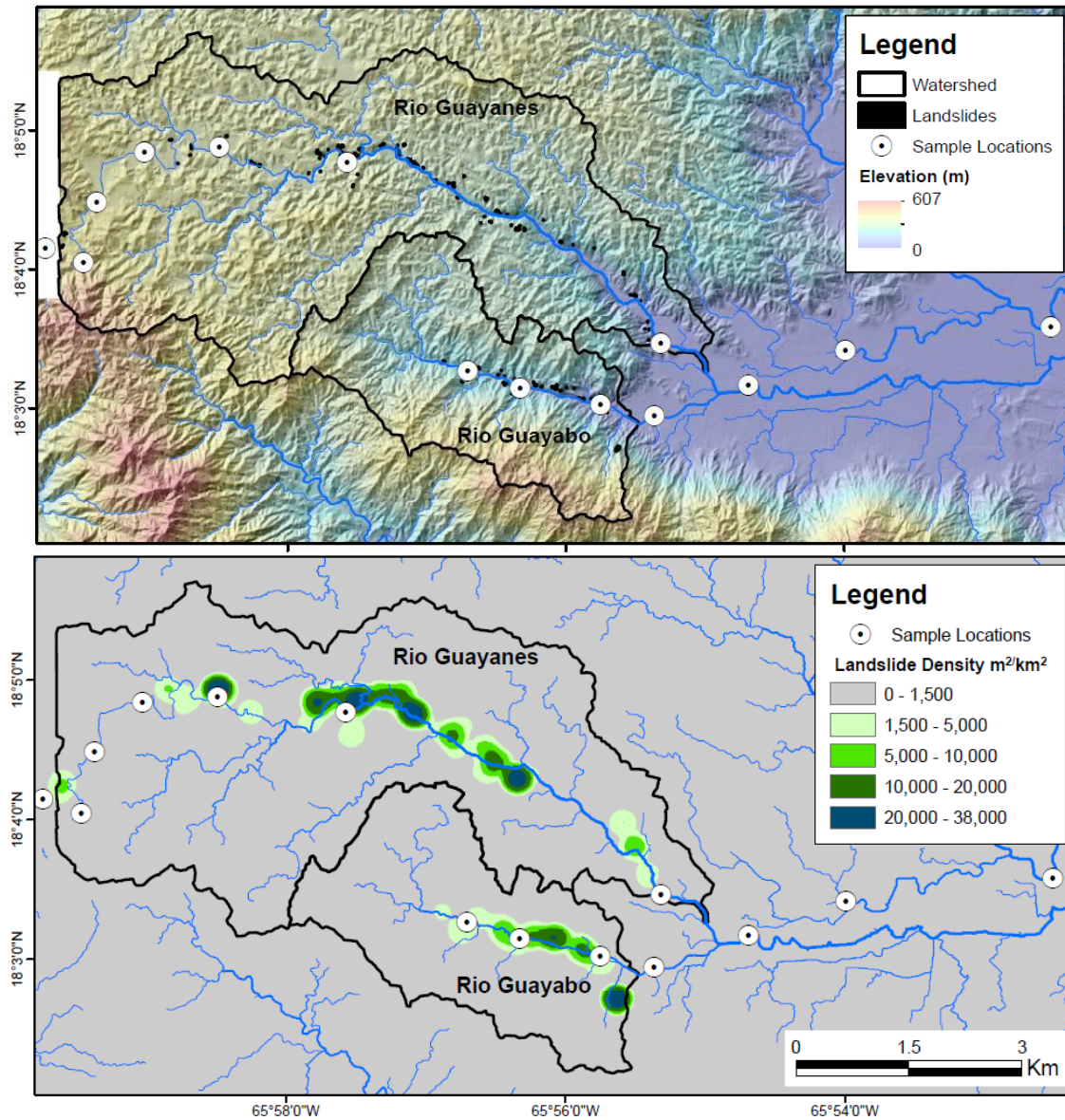


Figure 1: (A) Relief map of the Rio Guayanés located to the north and the Rio Guayabo in the south of the study region. Watersheds for the respective fluvial systems are outlined in black with sampling sites labeled as white circles and landslides indicated with black with arrows indicating landslides. (B) Inset map with study region highlighted by black box. Spatial density map for study region created using kernel density estimation of each of the mapped landslides within a $1\ km^2$ circular neighborhood.

2. Background

2.1 Geology

The regional tectonic system of Puerto Rico is characterized by left-lateral slip deformation along the Puerto Rico Trench, resulting in moderate earthquake activity (Masson & Scanlon, 1991). The specific study region is a part of the Cordillera Central Mountain range in southeastern Puerto Rico, which is characterized by Jurassic to Eocene igneous bedrock with a number of normal faults (Monroe, 1980). Major drainages in the study area include the Rio Guayabo and Rio Guayanés which also follow normal faults. The Rio Guayanés watershed is ~23 km² with a minimum elevation of 21 m and maximum elevation of 539 m above sea level. The Rio Guayabo watershed is ~8.5 km² with a minimum elevation of 23 m and maximum elevation of 497 m above sea level. Both fluvial systems are underlain by the Late Cretaceous San Lorenzo granodiorite (Rogers, Cram, Pease, & Tischler, 1977). In general, the granodiorite is overlain by ~2-8 m thick saprolite and ~0.5-1 m thick soil (Fletcher, Buss, & Brantley, 2006; Murphy, Stallard, Larsen, & Gould, 2012).

2.2 Climate and Land Usage

A tropical wet climate prevails, with an average annual temperature of ~25°C, an average annual rainfall of ~768 mm, and approximately one hurricane every two years (Larsen, 2000; Chiara Lepore et al., 2012). Subtropical wet forests and sparsely populated rural areas prevail, where agricultural land use declined by ninety-five percent from 1951 to 2000 (Birdsey & Weaver, 1982; Martinuzzi, Gould, & González, 2007). During the 16th century, European settlers began massive deforestation to support agriculture, resulting in the destruction of the majority of mature forests by the 19th century (Birdsey & Weaver, 1982). Until the 1940s, sugar cane fueled the economy, driving near-total deforestation, with regional forest returning only since the 1950s

as a result of abandonment of small farms (Birdsey & Weaver, 1982). More recent anthropogenic activity in the form of road construction increases modern deforestation and destabilizes slopes; the highest density of landslides occur within close proximity to roads (Larsen & Parks, 1997).

2.3 Mass wasting

Landslides occur in mountainous terrains of Puerto Rico and cause loss of life and property (Bessette-Kirton et al., 2019; Keellings & Ayala, 2019; Chiara Lepore et al., 2012). Lepore et al. (2012) conducted a landslide susceptibility assessment of various areas in Puerto Rico and projected varying susceptibility attributable in part to the underlying bedrock lithology (Bessette-Kirton et al., 2019). The severe deforestation along with steep slopes and frequent high precipitation observed in Puerto Rico alone or in conjunction with seismic activity results in higher rates of erosion and mass wasting than in drier, less mountainous, or more forested terrains (Birdsey & Weaver, 1982).

2.4 Chemical weathering indices

Chemical weathering tends to be most intense in densely vegetated, tropical mountainous environments where surface and sub-surface hydrologic fluxes are high (Oliva et al., 2003). The chemical index of alteration, or CIA, is an indicator of the chemical weathering of feldspars to clays (Goldberg & Humayun, 2010). The CIA values of fluvial muds have been quantified for some tropical and subtropical areas and commonly used as a proxy for paleoclimate interpretations (Nesbitt & Young, 1982). The weathering of feldspars results in the removal of mobile cations such as calcium, potassium, and sodium which leads to an increase in the proportion of Al_2O_3 in the fluvial mud (Aristizábal, Roser, & Yokota, 2005; Nesbitt & Young, 1982). High CIA values (>90) are indicative of extensively weathered soil depleted in calcium

and sodium and enriched in aluminum (Nesbitt & Young, 1982). CIA values are calculated using the following equation developed by Nesbitt and Young (1982), where CaO* is silicate-bound.

$$Eq. 1 \quad CIA = \left[\frac{Al_2O_3}{(Al_2O_3 + CaO^* + Na_2O + K_2O)} \right] \times 100$$

The CIA values observed in fluvial mud samples collected from the study area in 2014 were abnormally low (58-69) compared to expected values (>90), considering Puerto Rico exhibits very high weathering rates and a tropical-subtropical climate (Joo et al., 2018; White & Blum, 1995; White et al., 1998). Joo et al. (2018) noted that concentrations of CaO*, Na₂O, MgO, and Fe₂O₃ in the mud decreased distally, while K₂O increased distally, suggesting that the degree of chemical weathering observed in the sediments increases downstream, perhaps due to preferential transport of clays.

Ohta and Arai (2007) developed an alternative approach to determine both primary source lithology and weathering intensity (Ohta & Arai, 2007). This approach uses wt % SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, and K₂O in a multicomponent linear regression analysis to determine mafic (M) and felsic (F) portions of parent lithology and degree of weathering (W) of mafic and felsic portions, independent of the parent rock. Ternary plots of MFW have been used to display the multiple components, assuming normally distributed geochemical variability typically found in fresh mafic, fresh felsic, and weathered rock (Ohta & Arai, 2007). The combined utilization of different weathering indices based on the major elemental components of the lithology can help illustrate the extent of alteration based on the degree of elemental loss (Babechuk, Widdowson, & Kamber, 2014).

3. Methods

3.1 Landslide Mapping

We used aerial images archived in Google Earth and 1 m LiDAR topographic data (USGS National Map, 2020) to map post-Hurricane Maria landslides (24 September 2017 to 9 June 2018), and 10 m USGS National Elevation Datasets (NED) to map hillslope geometries and drainage network. Landslides were mapped only within a 350 m buffer of the Rio Guayanés and Rio Guayabo Rivers, based on our field observation that much of the sediment delivered to these streams appear to originate from landslides in adjacent hillslopes. The locations and characteristics of some of the landslides mapped from Google Earth and LiDAR shaded relief images were verified in the field. Landslide area was calculated in ArcGIS® and the volume of each landslide was modeled using an area (A) and volume (V) relationship ($V = 0.0254 * A^{1.45}$) proposed by Regmi et al. (2014) for shallow landslides of the North Fork Gunnison River catchment of western Colorado. We apply this equation because of the similarity in geomorphic and lithological environments of this study with those of the North Fork Gunnison River catchment. In addition, the equation does not differ significantly from other area-volume relationships proposed for shallow landslides in various parts of the world (equations are listed in (Regmi et al., 2014; Tron, Dani, Laio, Preti, & Ridolfi, 2014)). However, some of the landslides mapped in this study are shallower than those documented in Regmi et al. (2014), suggesting the modeled volume and depths of some of the landslides in the Puerto Rico study may be slightly overestimated. The size (area, volume, and depth), frequency, and spatial density (Guzzetti et al., 2008) of observed landslides were then evaluated to explore if any relationship exists between spatial density and measured physiochemical characteristics of fluvial sediment.

3.2 Sediment and water sampling

Saprolite, fluvial sediment, and stream water samples were collected from the Rio Guayanés and Rio Guayabo in June 2018, nine months post-Hurricane Maria, using GPS

locations to ensure similar localities compared to Joo et al. (2018). Saprolite samples were obtained from roadcut slopes (Figure 1). The top 2-5 cm of fine-grained sediment samples were collected from the slack water areas of fluvial bars using a hand trowel at intervals ranging from ~1-5 km between sampling locations, beginning at the upland source of the stream and continuing ~21 km in total distance downstream (Figure 1). Sampling locations were determined based on stream morphology and accessibility. Water samples were also collected from each of these locations. Sediment and water samples were frozen upon returning to the lab and prior to analyses.

3.3 Grain size, mineralogy, and surface area

All samples were wet sieved to obtain size fractions of gravel (>2 mm), sand ($63\text{ }\mu\text{m} - 2$ mm), and mud ($<63\text{ }\mu\text{m}$), then the mud was treated with buffered acetic acid and hydrogen peroxide to remove carbonates (rare), and organic matter (abundant), respectively. The remaining treated mud samples were freeze dried prior to specific surface area (SSA) analysis using the six-point BET (Brunauer-Emmett-Teller) nitrogen adsorption isotherm (Brunauer, Emmett, & Teller, 1938). The mud samples were passed through a 0.4 mm sieve to separate any clumps to prepare the sample for a random mounting (Harris & Norman White, 2008) on a glass slide for powder X-ray diffraction (XRD) analysis using the Rigaku Ultima IV diffractometer using Cu-K-alpha radiation at 40 kV and 44 mA. We used the Bragg-Brentano method with a range of $2-70^\circ 2\theta$ at 0.02° step size. Resulting diffraction patterns were analyzed with MDI JADE Pro software and ICDD PDF-4+ database by whole pattern fitting for bulk mineral identification.

3.4 Bulk geochemical analysis and chemical weathering indices

A split (~3-3.5 g) of the processed mud was sent to ALS Labs, where the solid samples were dissolved in strong acid and analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). In a few cases, the samples volumes were too small for analysis, so we added a known amount of corundum standard and later corrected for the added Al_2O_3 in the results.

The CIA values of the fluvial sediment mud fraction were then calculated using Equation 1, and the resulting data plotted on a ternary diagram of $\text{CaO}+\text{Na}_2\text{O}$, K_2O , and Al_2O_3 with more weathered samples plotting towards the Al_2O_3 vertex. Additionally, following Ohta and Arai (2007), an alternative chemical weathering index was also computed based on the bulk chemistry data that can be used to characterize mafic (M) and felsic (F) portion of rock source and degree of weathering (W) (Eq 1 in Supplementary Materials) and plotted on a MFW ternary diagram with more weathered samples plotting towards the W vertex.

3.5 Water chemistry

Water samples collected in the field were filtered through a $0.22\ \mu\text{m}$ filter using a Millipore vacuum system, treated with 1 M hydrochloric acid and frozen. The samples were then sent to the Oklahoma State University Soil, Water and Forage Analytical Laboratory (<http://soiltesting.okstate.edu/>) where the samples were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES). The resulting data were used to plot aqueous cation concentration versus distance downstream to analyze chemical weathering solutes released from the sediment within the fluvial system.

4. Results

4.1 Mass Wasting

Both field and aerial photographic mapping suggests that Hurricane Maria triggered mostly shallow landslides. We identified 116 shallow landslides that occurred within ~350 m from Rio Guayanés and Rio Guayabo during the nine-month period following Hurricane Maria (Figure 1). The area of these landslides ranges from ~11 m² to ~2,230 m² with an average area of ~238 m² (Table 1 and Figure 2a). Using the relationship in Regmi et al., (2014) the average volume is computed as ~110 m³, and the average depth is computed as ~0.25 m with a standard deviation of 0.14 m (Table 1 and Figure 2b).

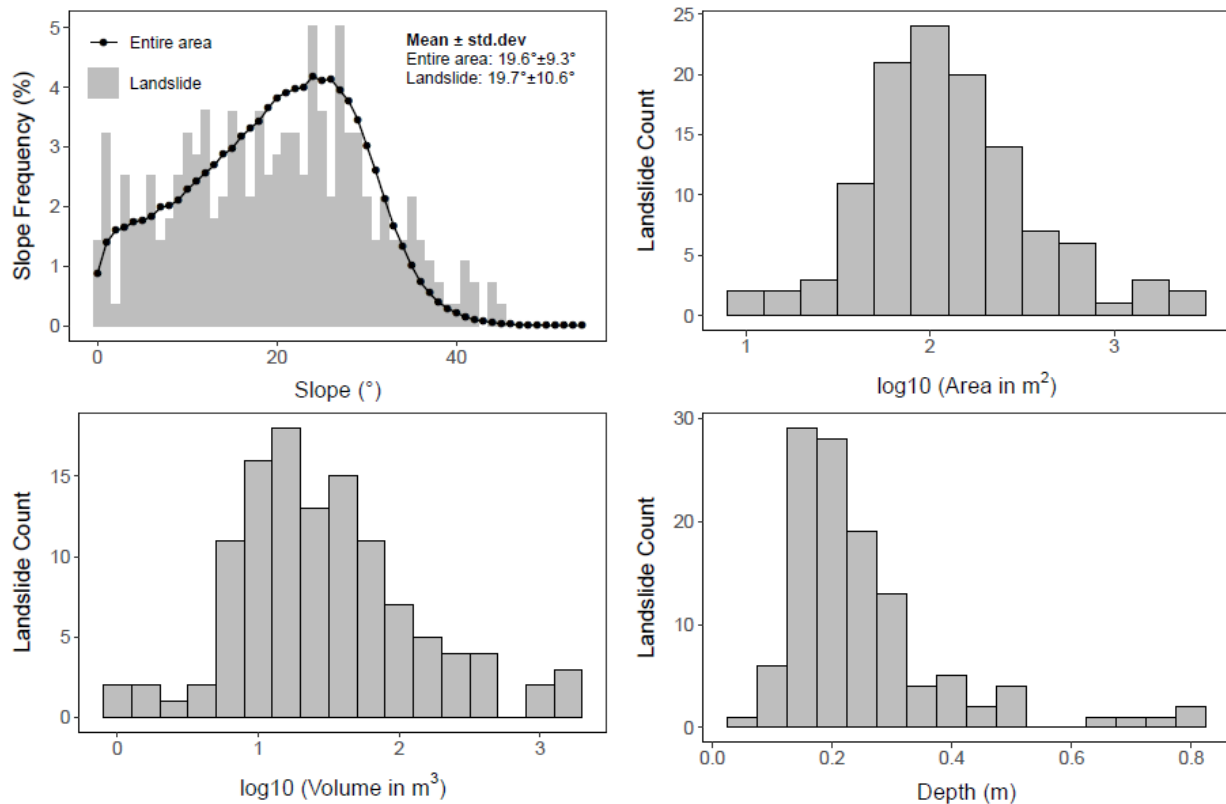
Table 1. Landslide area, volume* and depth*

Number of Landslides		116
Area (m²)	Minimum	11
	Mean (airth.)	238
	Maximum	2230
Volume (m³)	Minimum	1
	Mean (airth.)	110
	Maximum	1819
Depth (m)	Minimum	0
	Mean (airth.)	0
	Maximum	1

*Landslide volume was computed using the area-volume relationship proposed for western Colorado by (Regmi et al., 2014) and the depth was computed as a ratio of volume and area. Note: the average area (~238 m²) and volume (110 m³) may indicate that the average depth of the landslides is very shallow (~0.25 m). Full dataset in supplementary materials.

The landslide size-frequency plot (Figure 2) suggests that most of the observed landslides are relatively small. The landslides occur across a wide range of slope gradients with the largest frequency occurring at ~24-26°, which also correlates to the most prevalent slopes in the area (Figure 2d). The average slopes of the entire landscape and areas containing landslides are 19.6 °

254 $\pm 9.3^\circ$ and $19.7^\circ \pm 10.6^\circ$, respectively. Similarly, the landslide spatial density map developed
 255 using kernel density estimation and 1 km^2 circular neighborhood as a bandwidth shows the
 256 highest density of landslides between samples five and seven along Rio Guayanés and between
 257 three and four of the Rio Guayabo (Figure 1b).



258
 259 Figure 2: Observed hillslope characteristics including the distribution of slope gradients of
 260 landslides and entire hillslopes (A), landslide area (B), modeled landslide volume (C), and
 261 modeled average landslide depth (D). Note the landslide volume was computed using Landslide
 262 area – volume relationship proposed by Regmi et al., 2014, and the depth was computed as a
 263 ratio of volume and area.

264 4.2 Rio Guayanés Sediment

265 Overall, the sediment in the most proximal samples is coarser and displays more
 266 variability in grain size distributions observed between different samples in 2018 compared to
 267 2014 (samples 1-3). For samples collected in both 2014 and 2018, the weight percent of sand is
 268 much higher ($\sim 75 \text{ wt\%}$), than the weight percent of mud ($< 20 \text{ wt\%}$) (Table 2 in Supplementary

Materials). However, the proportions of the sand and mud fractions display a wider range of variability in the post-hurricane 2018 sample set. The weight percent of mud is generally higher in samples collected in 2018 from the proximal and distal portions of the stream compared to the weight percent of mud in 2014 samples from the same locations (Table 2 in Supplementary Materials). The weight percent of gravel observed in the samples collected from the mid portion of the stream (samples 4-7) was much lower in 2018 than in 2014. The most distal samples (8-10), illustrate opposite weight percent trends in gravel from 2018 and 2014, with higher gravel concentrations observed distally in 2014.

The 2018 and 2014 sample sets exhibit opposing trends in weight percent of clay-sized grains along the stream course (Table 2 in Supplementary Materials): the 2018 samples show a higher proportion of clay-sized material in more proximal samples, whereas the 2014 samples display a higher proportion of clay-sized grains in distal samples. Changes in concentration of silt-sized grains are similar for both sampling years, but slightly higher in 2018. The modal grain size within the mud fraction also show opposing trends in the two sampling years, with the mud size modes increasing with distance downstream in 2018 and decreasing with distance downstream in 2014 (Table 2 in Supplementary Materials).

The mud size fraction collected in 2018 consists of mainly albite, quartz, amphibole, clay minerals, and mica (Table 3 in Supplementary Materials). No systematic change in mineralogy was observed from proximal to distal samples within the Rio Guayanés fluvial system in the 2018 samples, while the 2014 samples exhibited a general decrease of primary minerals (quartz, plagioclase, hornblende, and K-feldspar) in the distal samples (Joo et al., 2018).

The Rio Guayanés sediment CIA values indicate a higher degree of weathering in 2018. The mean CIA values of the 2018 sediment is ~80, ranging from 66-88, while the mean value

observed in the 2014 sediment is ~65, ranging from 58-69 (Figures 3 and 5). Similar to the CIA values, the Rio Guayanés sediment MFW values also indicate the 2018 sediment is more weathered when compared to 2014 samples (Figure 3) (Joo et al., 2018). As the surface area of sediment increases, CIA values are also expected to increase. Finer grained sediment fractions have a higher surface area available for weathering and are also more likely to contain clay minerals (White et al., 1996). This relationship is only slightly observed in the 2018 Rio Guayanés sediment, while this trend is strongly observed in the 2014 Rio Guayanés sediment samples (Table 4 in Supplementary Materials).

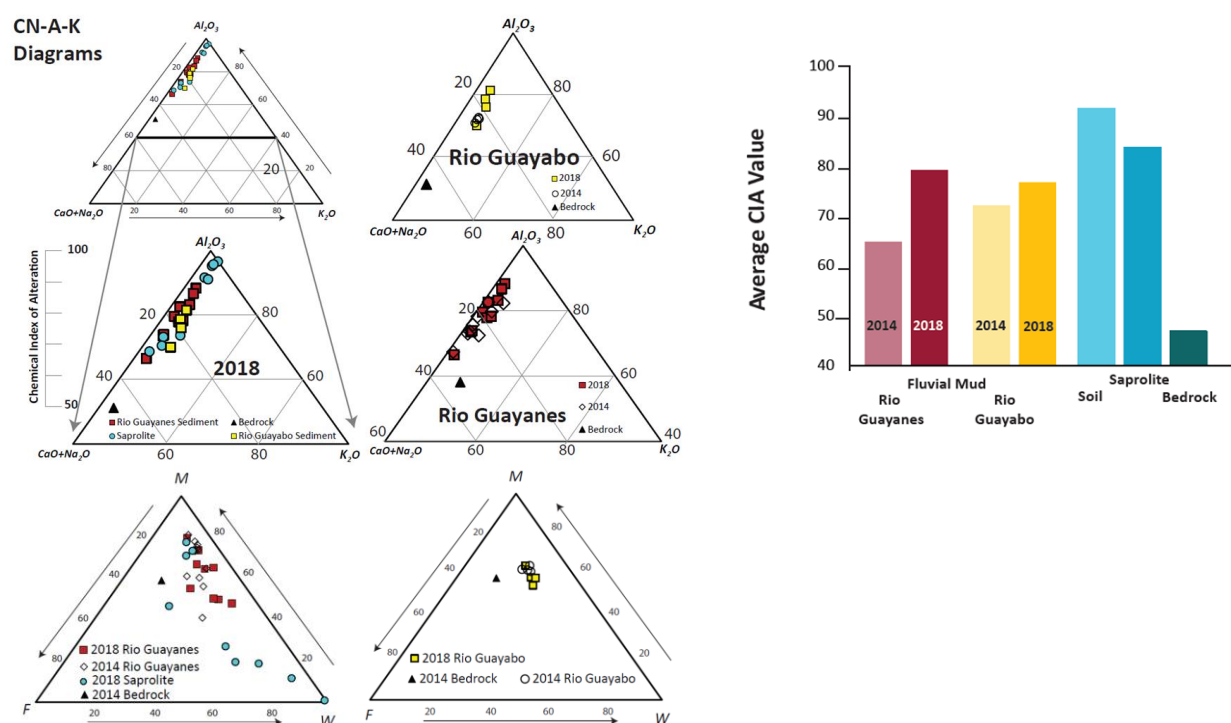


Figure 3: The chemical index of alteration for all samples. All of the samples collected in 2018 are shown on the left. Rio Guayanés sediment (red squares) and saprolite samples (blue circles), Rio Guayabo sediment (yellow squares), bedrock (black triangle). The MFW plot of sediments sampled from hillslopes and bar deposits of Rio Guayanés River (A) and Rio Guayabo River (B) in 2014 (pre-hurricane) and 2018 (post-hurricane). Note: the 2018 fluvial sediments are relatively weathered then that of the 2014 bar sediments. The average values of the chemical index of alteration for all sediment, soil, saprolite, and bedrock samples.

4.3 Rio Guayabo Sediment

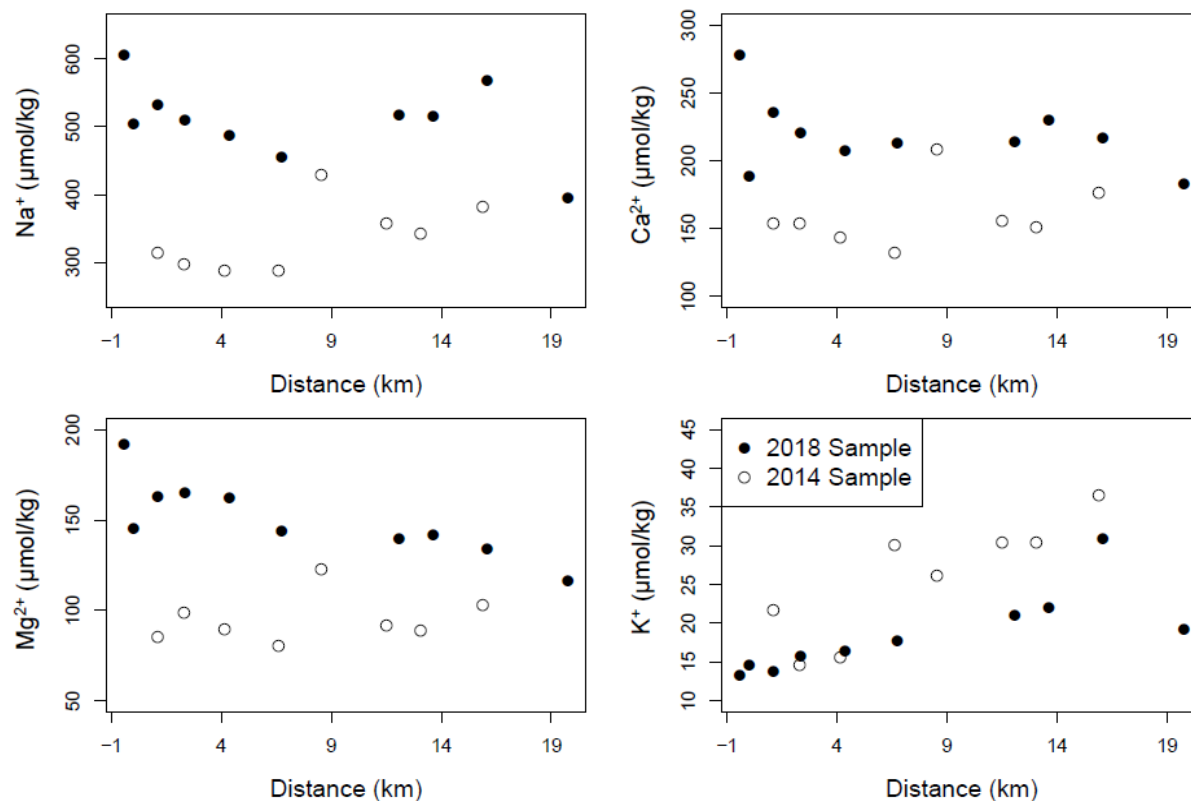
The surface area (13.74 - 15.97 m²/g) in the 2018 Rio Guayabo sediment illustrates very little variability among the four sampling locations (Table 5 in Supplementary Materials). In the 2014 samples, there is higher surface area in the proximal samples (24.64 - 32.05 m²/g) and then the surface area decreases distally (15.41 - 15.74 m²/g), reaching values similar to those observed throughout the 2018 samples (13.74 - 15.97 m²/g).

The average CIA value of the 2018 Rio Guayabo sediment is 76 (ranging from 70-81) while the 2014 sediment average is slightly lower at 73 (Figure 3). Both these values plot in the middle of the range of values observed in the Rio Guayanés sediment samples (Figure 3). The Rio Guayabo MFW plot (Figure 3, E&F) also indicates more weathered sediment in 2018 compared to 2014. Trends in specific surface area with CIA (as specific surface area increase so did CIA) were very similar for both the 2018 and 2014 samples (Table 6 in Supplementary Materials).

4.4 Saprolite

The grain size distributions and specific surface area of the mud-sized fractions observed in the saprolite samples collected within the watershed are highly variable. The mud size fraction of the saprolite samples consist mainly of clay minerals followed by plagioclase (Table 6 in Supplementary Materials). No systematic trends in mineralogy are observed within the saprolite dataset. The saprolite samples have an average CIA value of 84, ranging from 69-97 (Figure 3 and 5), greater than the average values observed in the fluvial sediment samples from both Rio Guayabo and Rio Guayanés (Figure 3). As the surface area of the saprolite sediment increases, a subsequent increase in the CIA value is also expected; this correlation is strongly observed within the saprolite samples (Table 6 in Supplementary Materials). The saprolite sediment MFW

331 plot (Figure 3, E & F) also indicates the saprolite samples are significantly more weathered than
 332 the fluvial sediments.



333
 334 Figure 4. Rio Guayanés stream water chemistry cation concentrations. Na⁺, Ca²⁺, and Mg²⁺ show
 335 a general decrease in concentration until approximately 12 km and K⁺ shows a general increase
 336 distally in 2018. Mg²⁺ and Ca²⁺ show very similar trends to one another while Na⁺ is enriched
 337 compared to Mg²⁺ and Ca²⁺ but also shows a similar trend.

338 4.5 Water Chemistry

339 The 2018 stream water samples had much higher concentrations of Na⁺, Ca²⁺, and Mg²⁺
 340 and lower overall concentration in K⁺ compared to the stream water in 2014 (Figure 4). In 2018,
 341 the Na⁺, Ca²⁺, and Mg²⁺ concentrations generally decreased from proximal to distal until
 342 approximately 12 km where an increase and then subsequent decrease occurs (Figure 4). In the
 343 2014 stream water samples Ca²⁺ and Mg²⁺ have very similar concentrations and follow similar

trends, while Na^+ was consistently enriched relative to the solutes in 2018. K^+ concentrations increased from proximal to distal across the full distance sampled in 2018 (Figure 4).

5. Discussion

As expected, a significant number of landslides occurred within the nine months following Hurricane Maria. This is significantly higher than the background rate of landslides in Puerto Rico (Larsen & Parks, 1997). The prevalence of landslides during this time likely reflects the heavy storm precipitation, in addition to continued anthropogenic forcings, such as deforestation (Larsen & Parks, 1997; Murphy et al., 2012; Silva-Tulla et al., 2020). Additionally, SSURGO soil texture data (U.S. Department of Agriculture, 2019) shows predominant hillslopes are covered by weathered bedrock (mostly granodiorite) and silty clay soil which contains organic materials. These characteristics of soil can facilitate the rapid increase in pore-water pressure during a rainstorm event (C Lepore, Arnone, Noto, Sivandran, & Bras, 2013) and predispose hillslopes to landslides. We initially hypothesized that hurricane-induced landslides would sample the deeper bedrock (Joo et al., 2018). However, despite receiving half a meter of rainfall within four days, our results indicate that the Hurricane Maria-induced landslides are dominated by shallow and small-sized landslides that moved mostly shallow slope materials, including weathered topsoil and saprolite, and only a small amount of less-weathered bedrock (Table 7 in Supplementary Materials). This model is well supported by all our results, including landslide mapping, as well as the weathering index values and MFW plots for the post-hurricane fluvial samples which were higher than those observed in pre-hurricane samples (Figure 3). However, some of the larger landslides that occurred in steeper slopes could have transported deeper soil and less-weathered bedrock, but the volume of the transported materials was likely

small compared to the total volume transported by all landslides (Figure 2). Even larger or more sustained precipitation events may be more likely to produced deeper landslides.

We also expected the fluvial sediment grain size would increase post Hurricane Maria due to the delivery of less-weathered sediments to the stream via landslides. Instead, most of the samples from Rio Guayanés show decreased weight percent of gravel and increased weight percent of sand, mud, and silt size fractions in 2018 versus in 2014 (Figure 8 in Supplementary Materials). However, the pattern is more complicated if we consider the particle size mode (Struck et al., 2015) of the mud fraction, which indicates coarser-grained mud size fraction sediments were delivered to the fluvial system upstream [sample locations 1-4], a decrease mid-stream [sample locations 5-6], followed by an increase downstream [sample locations 7-10] (Figure 1). This indicates that relatively coarser mud was delivered to the Rio Guayanés fluvial system in 2018, despite the overall finer grain size trend observed in the bulk sediment.

If landslides are the dominant source of sediment to the streams, we would not expect to see a trend in mineralogy as we moved downstream, but instead we would expect to see constant or variable mineralogy related to distance. Indeed, the mineralogy results from the x-ray diffraction data indicate no systematic trend in mineralogy within the mud-sized fraction from proximal to distal (Table 3 in Supplementary Materials). Since we observed no systematic trend downstream in both particle mode and mineralogy this indicates little sorting within the fluvial system, nor is there a significant change in the sediment source from proximal to distal stretches of the steam.

Results from the aqueous cation concentrations in the stream were similar to the results obtained by Joo et al. (2018) in that the Na^+ , Ca^{2+} , and Mg^{2+} generally decreased distally while the K^+ increased (Figure 4). However, the overall concentration of the solutes in 2018 was

greater than in 2014 for every cation with the exception of K^+ (Figure 4). This suggests that landslides impact fluvial systems by delivering both solutes and sediments to streams. Increased cation concentrations may lead to eventual carbonate precipitation downstream following a mass wasting event, resulting in a net carbon sink (Joo et al., 2018).

The anomalously low CIA values observed in the fluvial sediments collected before Hurricane Maria (Figures 3 and 5) (Joo et al., 2018) were previously interpreted as deriving from deep seated landslides that delivered partially weathered regolith to the fluvial systems. These deeper seated landslides could be a result of tectonics (Bessette-Kirton et al., 2019; Masson & Scanlon, 1991; Reid & Taber, 1920) and/or anthropogenic forcing such as the construction of roads in the hillsides (Larsen & Parks, 1997; Murphy et al., 2012). In addition, there may also be a time dependent sediment accumulation / depletion effect. For example, the fluvial sediments collected in 2014 may be the accumulated results of deposits from large landslides over a longer period of time, whereas this study reports the response of a rapid flux of sediment from very shallow landslides triggered by a short duration, but intense rainfall. The last severe weather event in Puerto Rico prior to 2014 was Hurricane Irene of 2011. It is possible that streams may have removed much of the sediments delivered by Irene-induced shallow landslides by 2014, and the 2014 observations of Joo et al. are indicating longer-term sediment properties. While the overall transport mechanism is essentially the same, variations in the initial cause of the mass wasting and the duration of sediment transport between the events likely differ. In either case, the change in weathering index values observed in the sediment record are not indicative of the rate of climate change (Figure 5) but are instead a reflection of the stochastic nature of mass wasting.

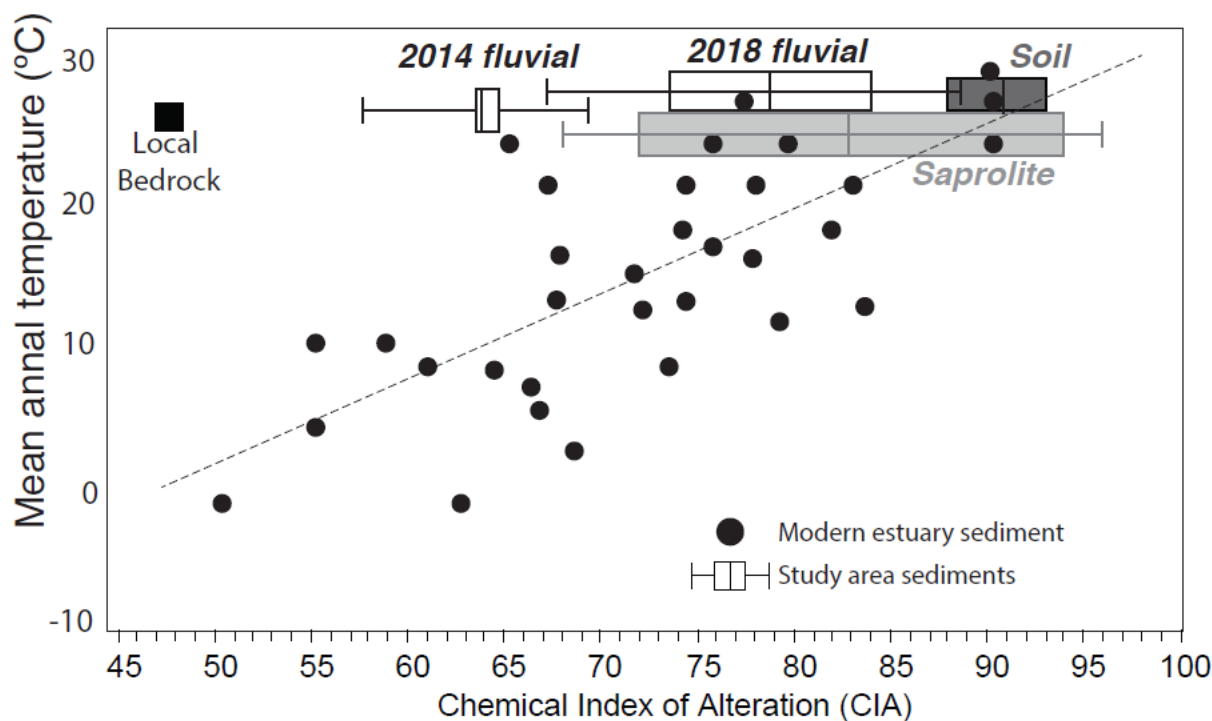


Figure 5. Plot from Joo et al. demonstrating the linear relationship between chemical index of alteration and mean annual temperatures. 2018 linear relationship of saprolite values plotted as light gray box, sediment range of values indicated with white box, and soil range indicated as dark gray box.

6. Conclusions and Implications

While the initial disturbance of mass wasting events can trigger carbon release to the atmosphere through perturbation of the short-term carbon cycle (e.g. destruction of vegetation), a longer-term result is increased silicate weathering leading to drawdown of atmospheric carbon (Fisk et al., 2013; Hall et al., 2020). The exposure of fresh bedrock through mechanical weathering due to landslides accentuates chemical weathering as water is allowed to interact with fresh bedrock (Oliva et al., 2003). Fresh surfaces lack weathered rindlets (Turner, Stallard, & Brantley, 2003), soils, or clay, enhancing susceptibility to chemical weathering (White et al., 1998). Likewise, the sediment released by landslides can be stored on hillslopes or delivered to fluvial systems (Clark et al., 2016; Hilton, Meunier, Hovius, Bellingham, & Galy, 2011).

Deposition of the material on hillslopes can result in longer-term carbon sequestration due to chemical weathering of the transported material (Clark et al., 2016; Fisk et al., 2013; Hall et al., 2020; Hilton et al., 2011; Ramos Scharrón, Castellanos, & Restrepo, 2012). Sediments entering fluvial systems tend to have a more variable and unconstrained outcome in regards to carbon sequestration amounts (Clark et al., 2016; Ramos Scharrón et al., 2012) but deposition of carbonates that consume cations released via chemical weathering results in a long-term net carbon sink. The landslide scarps sequester carbon over periods of tens to hundreds of years as forest recovery sequesters more carbon in both plants and soils compared to mature forests (Fisk et al., 2013; Hall et al., 2020; Hilton et al., 2011). Our data also demonstrate that even relatively small landslides can increase cation fluxes into stream systems, which deliver cations to the ocean where carbonate minerals likely precipitate, thus further accentuating the carbon sink. Therefore, the magnitude of a storm and associated rainfall accumulation amounts coupled with a variety of variables such as lithology, anthropogenic disturbances, and degree of hillslope can significantly affect carbon sequestration.

In addition, this study also provides high resolution data that shows how the grain size and chemistry of fluvial sediments vary over time in systems that are heavily influenced by mass wasting within the sediment transport system. Our results show hillslope dynamics closely influence fluvial sediment properties and may provide an avenue for interpreting the relative size of landslides based on trends in fluvial sediment observed in close temporal proximity of the triggering event.

Significant differences in the weathering index observed pre- and post- Hurricane Maria are not reflective of the degree of climate change over four years, but rather are indicative of numerous small landslide events that released large volumes of pre-weathered soil and

saprolite material into the fluvial system. Lower weathering index values observed before the hurricane are likely due to deep-seated landslides caused by tectonics, longer-term groundwater fluctuations, or road building that sampled deeper, less weathered materials including bedrock and regolith. Therefore, this subtle change in the transport mechanism can result in rather large differences in the weathering values recorded by the fluvial system.

These results and their implications can be translated to interpreting chemical weathering indices in different climatic and tectonic environments worldwide, and even on other planets, such as on Mars (e.g., Thorpe, Hurowitz, & Siebach, 2021), particularly when analyzing fluvial or lowland sediments within impact craters. Impact craters have a significant portion of sediment delivered to the floor via mass wasting along the crater walls. Tectonics on Mars likely results in large landslides (e.g., Lamb, Howard, Dietrich, & Perron, 2007; Lucas & Mangeney, 2007) and can be expected that subtle changes in the size of landslides can have significant impact on the weathering index values observed in landslide-derived fluvial sediments, independent of climate.

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