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# African dust deposition in Puerto Rico: Analysis of a 20-year rainfall chemistry record and comparison with models

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ABSTRACT

Dust deposition represents an important flux of rock-derived nutrients such as phosphorus to ecosystems on highly weathered soils. Direct measurements of terrestrial dust deposition and its spatial variability are rare, yet they are essential for testing models of dust deposition processes and understanding the biogeochemical effects of dust. Long-term records of precipitation chemistry are available in the Luquillo Mountains of Puerto Rico, which are downwind of the world's largest dust source in Africa. We analyzed 20-year datasets of openfall, throughfall, and wet-only precipitation chemistry with weekly resolution at two different locations in the Luquillo Mountains to evaluate spatial and temporal variability of dust inputs and compare the observational records with models. Based on rainwater dissolved silica and total suspended solids content, the measured dust flux varied by a factor of 2 over a distance of 10 km despite similarities between sites in elevation and rainfall amount. In comparison with simulated dust deposition from ten models in the Aerosol Comparisons between Observations and Models (AeroCom) project, the empirical rainfall chemistry agrees well with the mean of the models on the seasonal distribution of wet dust distribution. Both the data and the models show a summer maximum in wet dust deposition that is consistent with variation in transport pathways and the dust source area emission strength based on environmental conditions in the Sahel region. The rainfall chemistry record and AeroCom models also agree in terms of attributing ~70% of the total dust deposition overall to dry deposition, although the range of uncertainty in the models is large. The results indicate value in combining long-term analysis of rainfall chemistry with data from satellites and models, and highlight the need for accurate ground-based metrics for dry deposition to improve understanding and modeling of dust deposition processes. The dataset complements earlier studies that characterize the dust plume originating from Northern Africa and its impact on ecosystems in South America and the Caribbean.

## 1. Introduction

The emission, transport, and deposition of mineral aerosol dust in the atmosphere has wide implications for Earth's climate and biogeochemical processes (Martin, 1990; Tegen et al., 1996). Dust can play an important role in fertilizing certain terrestrial ecosystems by supplying phosphorus (e.g. Aciego et al., 2017; Chadwick et al., 1999), base cations (Boy and Wilcke, 2008), nitrogen (Ping et al., 2013), or micronutrients (Reynolds et al., 2006), thereby increasing ecosystem productivity. African dust is a major supplier of limiting nutrients to the highly productive Amazon rainforest (Okin et al., 2004; Swap et al., 1992), suggesting that major terrestrial carbon sinks may be controlled by dust deposition. While dust inputs have been recognized in many terrestrial systems, dust deposition fluxes remain difficult to quantify. In order to make a link between dust and downwind terrestrial ecosystems, improved understanding of atmospheric dust removal processes is needed (Huneeus et al., 2011; Prospero et al., 2010).

Global models that simulate atmospheric dust dynamics are an essential tool for determining dust's climate and biogeochemical impact. Model utility is improved by comparison efforts, both among individual models, and between models and empirical observations. Spatial patterns of modeled dust deposition fluxes differ greatly among individual aerosol models due in part to variability in how wet and dry removal processes are represented (Kim et al., 2014). This leads to wide discrepancy between models in the predicted proportion of wet versus dry deposition (Hand et al., 2004; Jickells et al., 2005; Jickells and Spokes,

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2001), which has important implications for the spatial variability of dust deposition. Further, the parameterization of dust removal processes is limited by a lack of suitable observational data (Ginoux et al., 2001; Huneeus et al., 2011; Kim et al., 2014). Approximately 85 observational dust deposition records are available globally for use in model comparison, but these are primarily oceanic sediment trap records and many specific regions are not represented (Albani et al., 2015; Huneeus et al., 2011; Kohfeld and Harrison, 2001). While some records of atmospheric dust concentration from active aerosol samplers are available (e.g. Prospero et al., 2014), dust deposition records for the Caribbean are notably lacking, as are terrestrial dust deposition records in general. An exception is a 3-year terrestrial dust deposition record that is available from a network of 9 stations across nearby Florida (Prospero et al., 2010). The Florida study found that models correctly captured the seasonality of observed dust deposition, but performed less well in terms of simulating the magnitude of dust deposition and the spatial pattern across Florida (Prospero et al., 2010).

In addition to the overall paucity of terrestrial dust deposition records, methodological uncertainties hamper comparisons between measurements and models. In forested ecosystems, dust deposition collectors do not meaningfully measure the long-term average dust deposition, in part because they do not mimic the forest canopy structure and surface properties of leaves (Hicks et al., 1980; Lindberg and Lovett, 1985; Stoorvogel et al., 1997; White and Turner, 1970). There are no clear relationships between dry deposition and leaf area index, particularly in mountainous topography (DeLonge et al., 2008). Given the high spatial and temporal variability of dust dynamics, deposition collectors may miss significant portions of dust deposition if they are not deployed for sufficient spatial or temporal coverage (Prospero et al., 1987). Furthermore, indirect estimates of dry deposition captured by forest canopy using the difference between measured openfall and canopy throughfall can be confounded by foliar leaching or foliar uptake (Lindberg et al., 1988). Because dust inputs can be important to both terrestrial ecosystem nutrient cycling and the overall geochemical mass balance of soils, and because these observations are required to improve global aerosol models, there is a need to evaluate and improve the methods for directly observing dust deposition fluxes.

This study examines tracers of dust inputs using a 20-year record of rainfall chemistry with weekly resolution from two locations in the Luquillo Mountains of Puerto Rico. This area is downwind of the world's largest dust source in Africa, and previous work has identified the presence of African dust in Luquillo rainfall, soils, biota, and streamwater (Heartsill-Scalley et al., 2007; McClintock et al., 2015; McDowell et al., 1990; Medina et al., 2013; Pett-Ridge et al, 2009a, 2009b; Ping et al., 2013; Porder et al., 2015; Royer, 2018; Stallard, 2001, 2012). The Luquillo Mountains of Puerto Rico are ~2000 km upwind of Florida along the African dust plume trajectory, providing a point of comparison to the Florida study of Prospero et al. (2010) in contrasting mountainous topography. In addition to African dust, the ocean is a major contributor of solutes to Luquillo Mountain rainfall. While temperate northern hemisphere pollution-derived nitrogen and sulfur species are present in Luquillo Mountains rainfall, locally sourced solutes or particulates are not observed (Brown et al., 1983; Gioda et al, 2011b, 2013; McDowell et al., 1990; Ortíz-Zayas et al., 2006; Stallard, 2012). Volcanic inputs from the Lesser Antilles have also been shown to have little influence on Luquillo rainfall chemistry (Gioda et al., 2011a; Heartsill-Scalley et al., 2007). The location of the Luquillo Mountains in the northeastern corner of Puerto Rico facing the dominant east to west trade winds off the Atlantic Ocean and the lack of potential local contamination sources makes this an ideal system to investigate tracers of dust deposition (Stallard, 2012).

This study has four main objectives. First, in addition to examining dissolved non-seasalt calcium (nss-$Ca^{2+}$), a commonly used tracer of dust-derived solutes in rainfall (Rothlisberger et al., 2002; Stallard, 2012), this study adds novel consideration of dissolved silica ($dSiO_2$) and total suspended solids (TSS) in rainfall as potential tracers of dust inputs. Second, by looking at two sites that are 10 km apart with similar rainfall, elevation, and forest type, we explore the spatial variability of dust deposition fluxes that occur in the Luquillo Mountains. Third, we examine correlations between rainfall tracers of dust deposition and MODIS-based aerosol optical depth (AOD), and with dust deposition fluxes simulated by global aerosol transport models, aggregated by the Aerosol Comparisons between Observations and Models project (AeroCom) database (http://aerocom.met.no/). We examine seasonal patterns and relationships between rainfall non-seasalt $Ca^{2+}$, TSS, $dSiO_2$, satellite data, and aerosol simulation models to evaluate the rainfall metrics as dust tracers. Finally, we also estimate the proportion of total dust deposition that occurs as dry deposition as calculated by difference between different types of deposition collectors either between throughfall and openfall, or between openfall and wet-only deposition, and compare this with AeroCom model simulations of wet and dry deposition. The results presented here shed light on rainfall tracers of dust deposition, as well as the spatial and temporal variability of dust deposition in mountainous terrain.

## 2. Methods

### 2.1. Study site and rainfall chemistry

The two rain sampling locations used in this study are in the Bisley watershed (18.3138 N, −65.7443 W) and at the El Verde field station (18.336 N, −65.8165 W) in the Luquillo Experimental Forest (El Yunque National Forest) in the Luquillo Mountains of northeastern Puerto Rico (Fig. 1). These sites are part of the Luquillo Long Term Ecological Research (LTER) and Luquillo Critical Zone Observatory (CZO) programs. Both rainfall collection stations are located at approximately the same latitude; Bisley is approximately 10 km west of the northeastern coast and El Verde is approximately 24 km west of the northeastern coast. The Bisley and El Verde precipitation collectors are at approximately the same elevation (350 m) and have similar surrounding vegetation composed of a mixed forest of tabonuco, sierra palm, and colorado trees (Scatena, 1990). The two sites have very similar temperature, relative humidity, and precipitation (Gioda et al., 2013). In this paper we refer to three specific types of precipitation collection: throughfall, openfall, and wet-only precipitation. *Throughfall* is defined as rainfall that has passed through the canopy, picking up material that has been deposited on vegetation surfaces as well as chemical constituents leached out of the vegetation. *Openfall*, which is also sometimes referred to as 'bulk' deposition, is that which is collected in an open area away from vegetation using an always-open collector which catches both wet and dry deposition. *Wet-only* deposition collectors are also collected in an open area away from vegetation but have a sensor that closes a lid on the collector when it is not raining. The openfall and wet-only precipitation collectors used in this study are on the top of > 25 m walk-up towers above the forest canopy (Heartsill-Scalley et al., 2007; McDowell et al., 1990). Throughfall was measured in a 3 ha area that surrounds the location of the openfall collector at Bisley. As many as 35 throughfall collectors were operating at any one time for the duration of this study, each collector being randomly placed but located on ridges, hillslopes, gaps and stream channels (Heartsill-Scalley et al., 2007). Over the period of study, 1988 to 2009, total rainfall averaged 3.7 m $yr^{-1}$ ( ± 0.7 m $yr^{-1}$ 1 SD) at the Bisley site and 3.5 m $yr^{-1}$ ( ± 0.8 m $yr^{-1}$ 1 SD) at the El Verde Site.

The rainfall records examined here include both chemistry of the dissolved phase and the mass of particulates filtered from the weekly samples, known as total suspended solids (TSS). Both weekly precipitation flux and dissolved chemistry including $Ca^{2+}$ and $dSiO_2$ were obtained from the Luquillo Long Term Ecological Research database for the years 1988 through 2009 (https://luq.lter.network/data/luqmetadata148). Collection of TSS data began in the year 2000. All precipitation samples were collected weekly, typically on Tuesdays. Split samples were sent to the National Trends Network of the NADP

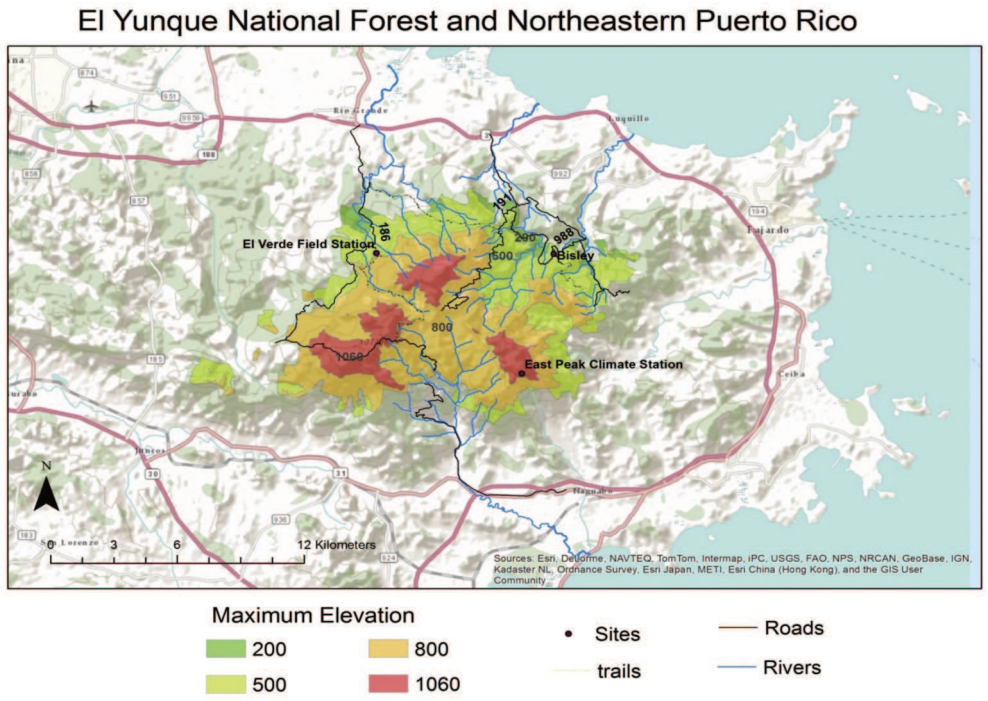


**Fig. 1.** Locations of the sites used to gather atmospheric input measurements and rain chemistry data in the Luquillo Mountains in northeastern Puerto Rico. Approximate distance between El Verde and Bisley = 10 km.

and to the UNH Water Quality Analysis Laboratory (WQAL). NADP samples were sent unfiltered to the Central Analytical Laboratory in Madison, WI where they were filtered and analyzed. Samples sent to UNH WQAL were refrigerated immediately after collection and filtered within a day at ~0.7 μm (pre-combusted Whatman GF/F glass fiber filter) and rinsed with deionized water before chemical analysis to separate total suspended solids (TSS) larger than ~0.7 μm. The filter type and pore size were chosen in accordance with standard long-term ecological research methods, not necessarily optimized for dust research. However, the silica detection limit for these samples was 0.1 mg $L^{-1}$ as $SiO_2$, which is more than double typical glass fiber filter silica blanks (de Souza et al., 2012). Due to the weekly sampling schedule, both dissolved and particulate material remained together in the collector for up to 7 days, with particulate matter potentially undergoing dissolution. This introduces variability in the degree to which dust-derived particulates in rain are either captured by the filters, or reflected in the dissolved chemistry. Calcium, Na, and Cl samples were frozen and $SiO_2$ samples were refrigerated until analysis in acid-washed (10% HCl) HDPE bottles that were rinsed three times with filtered sample before filling.

Calcium and Na were analyzed by atomic absorption spectrophotometry or ion chromatography and $Cl^-$ was measured by ion chromatography with conductivity detection, while $dSiO_2$ was measured by automated colorimetric analysis (molybdate blue; Technicon AA II, Lachat Quikchem AE, or Westco SmartChem)). Any changes in instruments or methods were tested with real samples on both instruments or methods to ensure that variability in the record were not due to those changes. (http://luq.lternet.edu/data/luqmetadata174). Values below the detection limit were recorded as half the detection limit for statistical purposes. The UNH WQAL analyzes a blank, and external quality control standard (QCS), an environmental sample that is reanalyzed over time and a replicate sample every 12 samples throughout an instrument run in addition to calibration standards that are included at the beginning and end of each instrument run. External QCS must be within 10% of the expected value and relative percent difference on replicate samples must be less than or equal to 10%. The UNH WQAL lab also participates in inter-laboratory comparisons of standard reference samples conducted by the US Geological Survey biannually to ensure high analytical performance.

We adjusted Ca concentrations using seasalt chloride mole ratios to remove seasalt contributions using the following equation (e.g. Stallard, 2001),

$$non\ seasalt\ Ca^{2+} = Ca^{2+} - Cl^- * \left(\frac{seasalt\ Ca^{2+}}{seasalt\ Cl^-}\right)$$

We also calculated non seasalt $Ca^{2+}$ using Na-based corrections, but found there was little difference in the two approaches, both when comparing the individual weekly data (Fig. S1), and when comparing the overall means. Fluxes were calculated by multiplying concentrations by the LTER rainfall flux records, which were co-located with chemical sampling. TSS in bulk rainfall was determined using the mass of total solids on pre-weighed filters used to filter samples from the Bisley and El Verde sites prior to chemical analysis. In rare instances when filtering the entire volume of sample was difficult, a representative subsample of each week's shaken openfall rain was taken. To calculate a rough estimate of dry deposition at Bisley, openfall concentrations of nss-$Ca^{2+}$ and $dSiO_2$ were subtracted from throughfall concentrations of nss-$Ca^{2+}$ and $dSiO_2$ each week. To calculate a rough estimate of dry deposition at El Verde, wet-only precipitation concentrations of nss-$Ca^{2+}$ and $dSiO_2$ were subtracted from openfall for each week.

### 2.2. Satellite aerosol optical depth (AOD) estimates and AeroCom modeled dust deposition

We compared the rainfall chemistry data with land-based MODIS aerosol optical depth (AOD) measurements at 550 nm. MODIS AOD measurements were obtained over the northeastern tip of Puerto Rico from the AeroStat website (https://giovanni.gsfc.nasa.gov/mapss/help_aerostat.html) original level 2 measurements. Detailed descriptions of the MODIS AOD algorithm are available (Chu et al., 2002; Remer et al., 2005).

The AeroCom project is an open international initiative of scientists interested in the advancement of the understanding of global aerosols

and their impact on climate (http://aerocom.met.no). Model results were aggregated in the project database from a coordinated AeroCom phase II control experiment (A2.CTRL), which aimed to provide state-of-the-art global aerosol fields (Myhre et al., 2013; Schulz et al., 2009). From 10 models monthly dry and wet dust deposition fields are available for the year 2006 (CAM5.1-MAM3-PNNL, CAM5-MAM3-PNNL, GISS-MATRIX.A2, GMI-v3, GOCART-v4Ed, HadGEM2-ES, INCA, MPI-HAM_V1_KZ, OsloCTM2, SPRINTARS-v384). Deposition values were extracted at a grid point nearest to the observation sites in Puerto Rico.

### 2.3. Statistical analyses

A small number of nss-$Ca^{2+}$, TSS, and $dSiO_2$ data points had extremely elevated values, which may reflect sample contamination as these samples did not necessarily co-occur with dusty periods based on satellite imagery. We applied a simple threshold and removed data points that were greater than three standard deviations above the mean. A nearly identical subset of outliers were identified using either the rule of thumb of semistudentized residuals absolute value $> 4$, or using a threshold of three standard deviations above the median (Neter et al., 1996). These datapoints were removed from consideration in further statistical analyses. For Bisley and El Verde $dSiO_2$, 7 out of 848 and 2 out of 818 data points were removed, respectively. For Bisley and El Verde nss-$Ca^{2+}$, 16 out of 830 and 23 out of 804 data points were removed, respectively. For Bisley and El Verde TSS, 6 out of 378 and 0 out of 371 data points were removed, respectively. The results of our analyses did not change depending on whether these outliers were removed or not.

Because of the event-based nature of dust deposition, the nss-$Ca^{2+}$, $dSiO_2$, and TSS datasets are heavily weighted toward low or minimum detectable values. This creates non-normally distributed data. Due to the non-normal nature of the overall dataset, a Kruskal-Wallis test was performed to examine medians of datasets (log transformations still produced non-normal datasets). This tested the null hypotheses that there is no relationship between site and the amount of dust deposition. Comparisons were made between openfall chemistry fluxes between sites and inter-season fluxes between and within each site. Seasonal groupings of nss-$Ca^{2+}$, $dSiO_2$, and TSS data were in thirteen-week increments, with the start of winter defined at the beginning of week 51. Interannual trends in AOD and TSS (2000–2009), and in $dSiO_2$, and nss-$Ca^{2+}$ (1988–2009) were also examined, using a seasonal Mann-Kendall trend test.

Missing data points encompass weeks where sites were inaccessible for logistic reasons, rainfall was insufficient to produce a sample large enough for chemical analysis, or when there was no $Cl^-$ measurement that week to make the seasalt correction in the Ca data. These data points are evenly distributed across the study period. These missing data points constituted between 20 and 28% of all data across all categories. For both Bisley and El Verde, weeks where the dry deposition calculation resulted in a negative value, it was assumed that dry deposition for that week equaled zero. At Bisley, there were 266 and 264 missing data points out of 1050 total in dry deposition for nss-$Ca^{2+}$ and $dSiO_2$, respectively. At El Verde, there were 302 and 318 missing data points out of 1038 total for dry deposition nss-$Ca^{2+}$ and $dSiO_2$ respectively. These missing data points do not include data points missing due to Hurricane Hugo, which caused a gap in all measurements from September 18, 1989 to December 25, 1990.

## 3. Results

The mean openfall nss-$Ca^{2+}$ fluxes to Bisley and El Verde for the duration of the study were not significantly different, with averages of 0.42 and 0.44 kg ha$^{-1}$ wk$^{-1}$, respectively (Table 1, and Fig. S2). In contrast, there was a significant difference between the two sites in the mean openfall flux of $dSiO_2$, which averaged 0.14 and 0.08 kg ha$^{-1}$ wk$^{-1}$ at Bisley and El Verde, respectively ($p < 0.05$). A similar difference was evident in the mean openfall flux of TSS, which was 1.47 and 0.65 kg ha$^{-1}$ wk$^{-1}$ at Bisley and El Verde, respectively ($p < 0.05$). In the individual weekly data, TSS was not significantly correlated with either $dSiO_2$ or nss-$Ca^{2+}$, and $dSiO_2$ and nss-$Ca^{2+}$ were not significantly correlated with each other.

The mean throughfall flux of nss-$Ca^{2+}$ at Bisley was 1.15 kg ha$^{-1}$ wk$^{-1}$ (2.7 times greater than the openfall flux), while the mean throughfall flux of $dSiO_2$ averaged 0.28 kg ha$^{-1}$ wk$^{-1}$ (2.0 times greater than the openfall flux). The mean wet-only flux of nss-$Ca^{2+}$ at El Verde was 0.19 kg ha$^{-1}$ wk$^{-1}$ (44% of the openfall flux), while wet-only $dSiO_2$ averaged a flux of 0.06 kg ha$^{-1}$ wk$^{-1}$ (80% of the openfall flux) (Table 1). The same set of statistical analyses was performed on concentration data without converting to flux values with rainfall amounts. These analyses yielded the same results in terms of when there were significant differences in comparisons between datasets.

Over the time period of this study, 1988–2009, the average annual flux of nss-$Ca^{2+}$ in openfall precipitation at Bisley is 22 kg ha$^{-1}$ yr$^{-1}$ ($\pm$ 16.5 kg ha$^{-1}$ yr$^{-1}$ 1 s.d.). Previous studies that analyzed subsets of the same Bisley dataset found similar total annual fluxes. For example, Gioda et al. (2013) calculated a nss-$Ca^{2+}$ flux of 15.6 kg ha$^{-1}$ yr$^{-1}$ ($\pm$ 16.8 kg ha$^{-1}$ yr$^{-1}$ 1 s.d.) at Bisley (1988–2007), and Heartsill-Scalley et al. (2007) calculated a flux of 16.06 kg ha$^{-1}$ yr$^{-1}$ at Bisley (1988–2002).

Both Bisley and El Verde showed similar seasonal patterns in the openfall, throughfall, and wet-only fluxes of nss-$Ca^{2+}$, $dSiO_2$, and TSS (Fig. 2 and Table 2). Generally, summer fluxes of nss-$Ca^{2+}$, $dSiO_2$, and TSS were highest, and fluxes dropped again in the fall. Seasonal variation in nss-$Ca^{2+}$, $dSiO_2$, and TSS fluxes was not simply correlated with modest seasonal variation in rainfall amount. Non-seasalt $Ca^{2+}$ fluxes were similar between Bisley and El Verde across all seasons. In contrast, during all seasons, the $dSiO_2$ and TSS fluxes were always significantly higher at Bisley than El Verde ($p < 0.05$). The same pattern in seasonal distribution with summer maxima are apparent when examining throughfall and wet-only fluxes (Fig. 2 and Table 2), and also in the concentration data. Looking across the records as a whole, there were no significant longer-term interannual trends in the $dSiO_2$ and nss-$Ca^{2+}$ data (1988–2009), or in the AOD or TSS data (2000–2009).

## 4. Discussion

### 4.1. Rainfall metrics of dust

Dust deposition estimates based on both $dSiO_2$ and TSS indicate that Bisley received approximately two times more dust in openfall as El Verde over the same time period, yet nss-$Ca^{2+}$ deposition was similar at the two sites (Table 1). Each of these rainfall-based metrics of dust deposition has some potentially confounding factors that may affect interpretation, and these factors likely explain the differences in the data between nss-$Ca^{2+}$, and $dSiO_2$ and TSS in terms of spatial variability. Overall, correlations between either nss-$Ca^{2+}$ and $dSiO_2$, TSS and $dSiO_2$, or TSS and nss-$Ca^{2+}$ are fairly weak (Figs. S3 and S4), indicating that each has independent controls.

Non-seasalt-$Ca^{2+}$ has previously been most commonly used as an indicator of a dust component in rainfall chemistry as it is unlikely to be a significant component of biomass burning or anthropogenic pollution aerosols, and because Ca is known to be a major constituent in the desert soils from which dust originates (DeAngelis et al., 1997; Hedin et al., 1994; Lequy et al., 2013; Prospero and Lamb, 2003; Rothlisberger et al., 2002; Stallard, 2001). One issue is related to the weekly resolution of the rainfall chemistry data, which means that the length of time in the sample collector can vary from hours up to 7 days. This leads to variable time for dust dissolution, and large variability in the degree of dissolution of the Ca in dust relative to dissolution of Si. Calcium in African dust is present primarily as relatively soluble calcium carbonate or calcium sulfate minerals (Reid et al., 2003), whose solubility is

**Table 1**
Average weekly fluxes based on rainfall chemistry at Bisley and El Verde.

| | Bisley | | | | El Verde | | | |
|---|---|---|---|---|---|---|---|---|
| | Openfall (kg ha$^{-1}$ wk$^{-1}$) | | | | Openfall (kg ha$^{-1}$ wk$^{-1}$) | | | |
| | n | Mean | Median | SD | n | Mean | Median | SD |
| nss-$Ca^{2+}$ | 814 | 0.42 | 0.34 | 0.32 | 804 | 0.44 | 0.37 | 0.33 |
| $dSiO_2$ | 841 | 0.14 | ***0.06*** | 0.31 | 818 | 0.08 | ***0.02*** | 0.23 |
| TSS | 390 | 1.47 | ***0.76*** | 3.40 | 367 | 0.65 | ***0.47*** | 0.71 |

| | Bisley | | | | El Verde | | | |
|---|---|---|---|---|---|---|---|---|
| | Throughfall (kg ha$^{-1}$ wk$^{-1}$) | | | | Wet Only (kg ha$^{-1}$ wk$^{-1}$) | | | |
| | n | Mean | Median | SD | n | Mean | Median | SD |
| nss-$Ca^{2+}$ | 1058 | 1.15 | 0.98 | 0.71 | 800 | 0.19 | 0.13 | 0.20 |
| $dSiO_2$ | 907 | 0.28 | 0.14 | 0.51 | 761 | 0.06 | 0.02 | 0.15 |

| | Bisley | | | | El Verde | | | |
|---|---|---|---|---|---|---|---|---|
| | Estimated dry deposition (kg ha$^{-1}$ wk$^{-1}$) | | | | Estimated dry deposition (kg ha$^{-1}$ wk$^{-1}$) | | | |
| | n | Mean | Median | SD | n | Mean | Median | SD |
| nss-$Ca^{2+}$ | 773 | 0.82 | 0.67 | 0.69 | 737 | 0.30 | 0.22 | 0.32 |
| $dSiO_2$ | 775 | 0.20 | 0.06 | 0.44 | 721 | 0.04 | 0.00 | 0.18 |

Bolded italics indicate a significant ($p < 0.05$) difference between Bisley and El Verde median openfall. Over the period of study, 1988 to 2009, total rainfall averaged 3.7 m yr-1 ( ± 0.7 m yr-1) at the Bisley site and 3.5 m yr-1 ( ± 0.8 m yr-1) at the El Verde Site

highly dependent on rainfall pH and amount. An additional factor that disproportionately affects the nss-$Ca^{2+}$ data is the large variability in the Ca content of African dust relative to that of Si. Calcium content varies more than 200-fold, with a range of 0.11–26.28 wt% CaO (Abouchami et al., 2013; Scheuvens et al., 2013).

Dissolved silica in rainwater has less frequently been used as a tracer of dust. It is not commonly measured in rainwater, and the concentrations are low due to limited solubility of silica. However, biomass burning, anthropogenic pollution, and sea salt aerosols are not expected to confound the $dSiO_2$ signal of mineral aerosols. Another advantage is that silica content varies by less than 4-fold in African dust, with a range of 20.5–79.2 wt% $SiO_2$ (Abouchami et al., 2013). Silica solubility, as either quartz or biogenic opal, is also much smaller and is largely constant between pH 2.5 and 8.5 (Cornelis et al., 2011; Dove, 1995). The solubility ranges from 36 to 250 μM for quartz, and 20–360 μM for biogenic opal (Bartoli and Wilding, 1980). In contrast, the $dSiO_2$ concentration measured in Luquillo rain ranges from 1 to 30 μM. This reduced variability in silica content of African dust along with its limited solubility suggests that it may be a more faithful tracer of dust deposition than nss-$Ca^{2+}$. In the Luquillo Mountains rainfall dataset, we find that the $dSiO_2$ fluxes are higher in summer, particularly at the Bisley site, in both openfall and throughfall (Table 2 and Fig. 2, S3 and S4).

Total suspended solids are also infrequently quantified in rainfall chemistry records. As with the other metrics, TSS could also be affected by variations in the time interval between dust deposition events and the weekly sample collection, and thus variations in degree of dissolution.

Previous measurements of median particle diameter of African dust in the Caribbean show variability between individual dust storms, with estimates ranging between 1 and 7 μm (Reid et al., 2003), although also see (Kandler et al., 2018; van der Does et al., 2016), while the filtration cut-off was 0.7 μm. Biomass burning in this region could potentially affect TSS measurements (Andreae and Merlet, 2001), however, a previous analysis of atmospheric aerosol samples collected from a nearby site in the Luquillo Mountains (Pico del Este) found that only 4% of aerosols were derived from combustion sources, with the rest sourced from sea salt and African dust (Fitzgerald et al., 2015).

### 4.2. Spatial variability of dust deposition fluxes to Bisley and El Verde

Given the more limited range in the silica content of African dust, the limited silica solubility, and the longer record of $dSiO_2$ data relative to TSS, we focus our analysis of spatial variability on the $dSiO_2$ fluxes. The ~2-fold higher $dSiO_2$ fluxes in rainfall at Bisley as compared to El Verde suggest that dust deposition is highly variable on at least a scale of 10 km, in agreement with a recent study of dust in 31 ridgetop soils across the Luquillo Mountains based on neodymium isotopes (McClintock et al., 2015). Taking into account the similarities in site characteristics between Bisley and El Verde, differences in dust deposition cannot be attributed to differences in aspect, vegetation, precipitation (3.7 ± 0 0.7 m yr$^{-1}$ at Bisley, 3.5 ± 0.8 m yr$^{-1}$ at El Verde), or elevation (361 m at Bisley, 380 m at El Verde). Instead, the most likely explanation of different dust deposition rates between these two sites is that Bisley is approximately 10 km closer to the northeast corner of Puerto Rico, which is the location where Saharan-Sahel airmasses first intersect the island during dust periods (Scholl et al., 2009), after which they travel predominantly eastward (Stallard, 2012). The sudden rise in elevation above sea level that the Puerto Rico landmass presents to Atlantic trade winds causes significant orographically-driven precipitation, comprising at least 29% of total precipitation (Daly et al., 2003; Scholl et al., 2009). This leads to enhanced dust deposition nearer the eastern coast as dust particles are scrubbed from the atmosphere. Despite the similar elevations between the two sites, a trade wind airmass travelling on a direct east-west trajectory from Bisley to El Verde would encounter complex topography with elevations up to ~900 m between the two sites, causing further orographic rainfall, turbulence, and both wet and dry removal of dust particles. The approximately 2-fold variation in dust input based on $dSiO_2$ between these two Luquillo Mountain sites is much greater than the 33% total variation in dust input (based on Fe) that is observed across 9 stations spanning more than 800 km across the state of Florida, despite larger

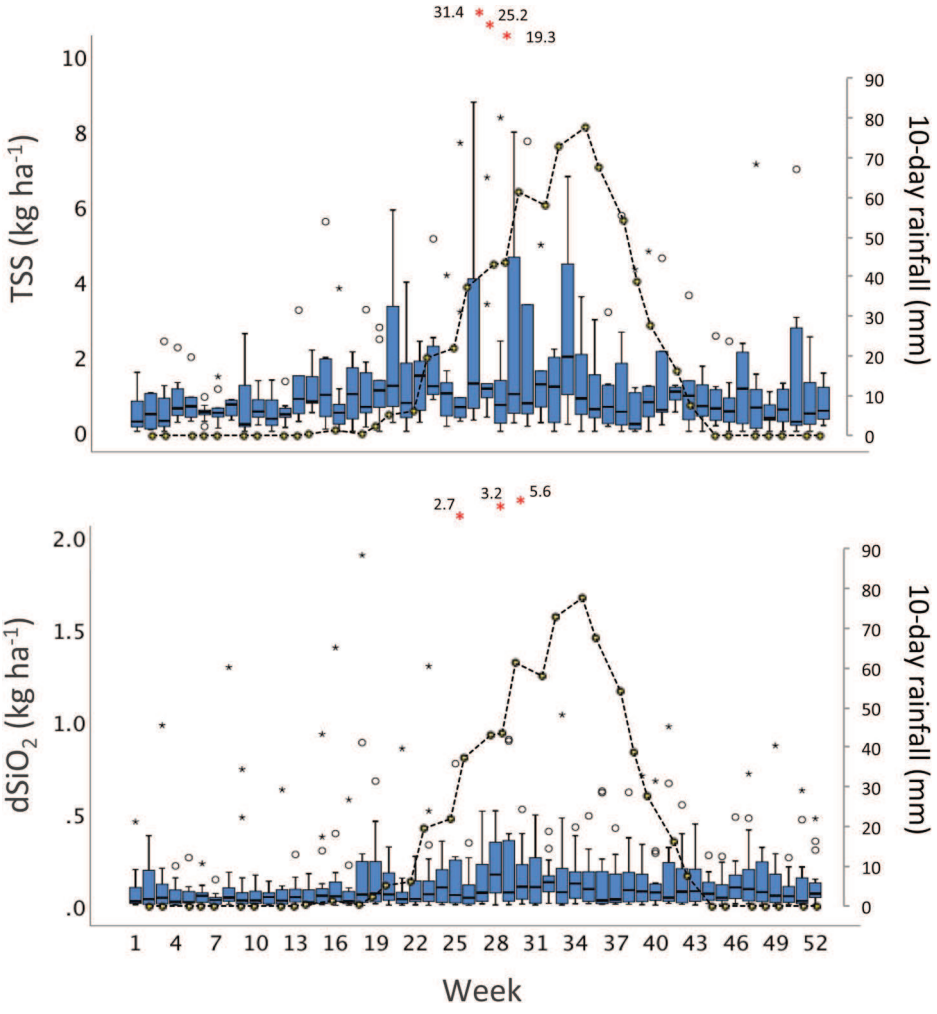


**Fig. 2.** (a) Boxplots of TSS at Bisley across each week of the year from 2000 to 2009 and (b) box plots of dSiO2 across each week of the year from 1988 to 2009. Boxes encompass the middle 50% of data, extending from the lower quartile to the upper quartile. The center line within each box shows the sample median. Whiskers encompass the 95% of the data, circles are outliers exceeding 1.5 times the range of the middle 50% range of the data and asterisks are extreme outliers with values more than three times the range of the middle 50% of the data. In each plot the y-axis excludes three extreme outliers. These are shown as asterisks with values next to the points. Also shown with the dashed line is the average amount of rainfall experienced in ten days in the Western Sahel region from 1990 to 2007 (adapted from Lebel and Ali, 2009). Peak rainfall is centered around the 33rd week of the year, however, greening of vegetation in the region persists for up to two months after precipitation has halted (Nicholson et al., 1990).

variability in rainfall amount across Florida (Prospero et al., 2010). The primary difference between this site and the Florida locations used by Prospero (2010) is the mountainous terrain with complex topography of the Luquillo Mountains. The difference in dust deposition rate between two sites 10 km apart in the Luquillo Mountains of Puerto Rico, with similar rainfall and elevation, is as large or larger than the differences in dust deposition fluxes across 100s of km found in other studies (Brahney et al., 2014; Lawrence and Neff, 2009; Prospero et al., 2010).

In addition to being spatially variable, the $dSiO_2$ fluxes at both Luquillo Mountain sites are large when compared to the limited number of other rainfall silica measurements that are available. Compilations of temperate and tropical forest $dSiO_2$ inputs show a range from 0.03 to 5.6 kg ha$^{-1}$ yr$^{-1}$ (Cornelis et al., 2011; Martin and Harr, 1988; Sommer et al., 2006), with most values $< 3.0$ kg ha$^{-1}$ yr$^{-1}$. For comparison, Bisley and El Verde have $dSiO_2$ inputs of 7.2 and 4.0 kg ha$^{-1}$ yr$^{-1}$ in openfall, respectively, similar to the $dSiO_2$ inputs measured on the island of Corsica in the Mediterranean Sea of 4.0 kg ha$^{-1}$ yr$^{-1}$, which is also subject to large African dust inputs (Treguer and De La Rocha, 2013). These large but spatially variable inputs of African dust to Luquillo Mountain ecosystems support previous work indicating potentially important implications for dust in terms of supplying the limiting nutrient phosphorus (McClintock et al., 2015; Pett-Ridge, 2009).

### 4.3. Wet versus dry deposition

The proportion of dust that comes into a landscape as dry deposition or wet deposition is usually not well known, and the current generation of dust deposition models produces diverse estimates of the proportion of deposition that is wet or dry (e.g. Textor et al., 2006). For example, the AeroCom model intercomparison project found that global aerosol models agree within a factor of 2 on atmospheric aerosol content, but vary by a factor of 10 in deposition fluxes, in part due to discrepancies between modeled wet versus dry deposition (Bergametti and Foret, 2014; Marticorena et al., 2017).

We used two independent methods to calculate an estimate of dry deposition from rainfall chemistry, based on the available data. At El Verde, we subtracted weekly wet-only precipitation fluxes from those of weekly openfall. At Bisley, we subtracted weekly openfall precipitation fluxes from those of weekly throughfall, assuming throughfall washes dry deposition dust off the forest canopy. This approach yielded an estimate of dry deposition at El Verde, based on $dSiO_2$ and nss-$Ca^{2+}$, respectively, of 53% or 67% of total deposition, an estimate that agrees with a previous estimate of 60% dry deposition in the general vicinity of El Verde (Medina et al., 2013). At Bisley our approach yielded an estimate of the percentage dry deposition based on $dSiO_2$ and nss-$Ca^{2+}$, respectively, of 72% or 71%. These methods of dry deposition estimation are rough, and each has shortcomings. Throughfall potentially oversamples dry deposition inputs because of canopy leaching of Ca derived from foliar tissue, and openfall collectors undersample dry deposition inputs because they do not reflect forest canopy surface area and structure that traps airborne particles. Previous studies comparing the two forms of deposition often find wet deposition contributes more deposition than dry deposition, but also that dry deposition is highly spatially variable (Inomata et al., 2009; Osada et al., 2014). Across Florida, a network of 9 precipitation collectors where African dust

**Table 2**
Seasonal distribution of rainfall chemistry fluxes at Bisley and El Verde.

| | | Bisley | | | | El Verde | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Openfall (kg ha$^{-1}$ wk$^{-1}$) | | | | Openfall (kg ha$^{-1}$ wk$^{-1}$) | | | |
| | | n | Mean | Median | SD | n | Mean | Median | SD |
| nss-$Ca^{2+}$ | W | 189 | 0.40 | 0.33 | 0.31 | 184 | 0.41 | 0.34 | 0.32 |
| | Sp | 201 | 0.43 | 0.33 | 0.33 | 191 | 0.47 | 0.37 | 0.36 |
| | Su | 206 | 0.53 | 0.50 | 0.34 | 217 | 0.55 | 0.47 | 0.37 |
| | F | 218 | 0.34 | 0.27 | 0.26 | 212 | 0.34 | 0.29 | 0.23 |
| $dSiO_2$ | W | 202 | 0.13 | ***0.04*** | 0.41 | 203 | 0.06 | ***0.02*** | 0.29 |
| | Sp | 208 | 0.13 | ***0.05*** | 0.28 | 196 | 0.10 | ***0.02*** | 0.33 |
| | Su | 215 | 0.17 | ***0.09*** | 0.32 | 221 | 0.08 | ***0.03*** | 0.13 |
| | F | 216 | 0.12 | ***0.07*** | 0.16 | 198 | 0.06 | ***0.03*** | 0.11 |
| TSS | W | 94 | 0.70 | ***0.52*** | 0.58 | 74 | 0.43 | ***0.30*** | 0.45 |
| | Sp | 105 | 1.29 | ***0.94*** | 1.20 | 96 | 0.68 | ***0.49*** | 0.69 |
| | Su | 111 | 1.67 | ***0.96*** | 2.00 | 112 | 0.90 | ***0.68*** | 0.91 |
| | F | 81 | 1.39 | ***0.72*** | 1.92 | 84 | 0.49 | ***0.41*** | 0.47 |

| | | Bisley | | | | El Verde | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Throughfall (kg ha$^{-1}$ wk$^{-1}$) | | | | Wet Only (kg ha$^{-1}$ wk$^{-1}$) | | | |
| | | n | Mean | Median | SD | n | Mean | Median | SD |
| nss-$Ca^{2+}$ | W | 228 | 1.29 | 1.15 | 0.73 | 192 | 0.16 | 0.10 | 0.17 |
| | Sp | 248 | 1.17 | 0.96 | 0.73 | 181 | 0.18 | 0.12 | 0.19 |
| | Su | 254 | 1.26 | 1.15 | 0.69 | 224 | 0.26 | 0.20 | 0.22 |
| | F | 242 | 1.04 | 0.91 | 0.66 | 201 | 0.16 | 0.10 | 0.17 |
| $dSiO_2$ | W | 209 | 0.24 | 0.11 | 0.48 | 183 | 0.05 | 0.01 | 0.17 |
| | Sp | 221 | 0.26 | 0.10 | 0.43 | 182 | 0.06 | 0.02 | 0.12 |
| | Su | 221 | 0.32 | 0.15 | 0.58 | 211 | 0.07 | 0.02 | 0.12 |
| | F | 223 | 0.33 | 0.20 | 0.56 | 186 | 0.06 | 0.02 | 0.17 |

Bolded italics indicate a significant ($p < 0.05$) difference between Bisley and El Verde median openfall. Over the period of study, 1988 to 2009, total rainfall averaged 3.7 m yr-1 ( ± 0.7 m yr-1) at the Bisley site and 3.5 m yr-1 ( ± 0.8 m yr-1) at the El Verde Site.

inputs were analyzed showed that dry deposition consistently represented between 20 and 30% of total deposition based on the difference between openfall and wet-only precipitation (Prospero et al., 2010). In contrast, our results based on Luquillo Mountain precipitation suggest that dry deposition at two different sites is > 50% of total dust deposition.

We further investigated the question of dry versus wet deposition using the National Weather Service weather summaries for Puerto Rico for the weeks with the highest TSS, nss-Ca and $dSiO_2$ fluxes. These summaries indicated that whenever Saharan dust was explicitly mentioned in the day's weather summary, as it was for 6 out of the 10 highest TSS flux weeks at Bisley, the weather was also described as having “dry, stable air”. Previous research has also noted that African dust events are known to be associated with dry, warm air (e.g. Prospero and Carlson, 1972), although there is substantial variability among dust events (Huang et al., 2010).

### 4.4. Comparisons of rainfall data with active aerosol collectors, satellite data, and models

The data presented here also illustrate the difference between measurements of atmospheric dust concentrations and the amount of dust falling on a landscape, which can potentially impact ecosystems and biogeochemical processes. We compared a nearby record of atmospheric Si concentration to our rainfall chemistry record (Fig. S5). Atmospheric Si concentration was determined using active air filtration on top of a tower in the Virgin Islands National Park, followed by XRF analysis or particles, as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) project, which is 80 km away from the Luquillo Mountains of Puerto Rico (IMPROVE, 2008). Only a weak relationship exists between atmospheric Si concentration in the Virgin Islands and Si deposition in Puerto Rico. This is likely due to the large distance between the two locations, and to the multiple local factors that control the deposition of dust to the ground, such as canopy trapping, rainfall amount, and meteorological conditions such as wind and turbulence. A similar issue is evident in the MODIS satellite aerosol optical depth (AOD) record for 2000 to 2009 for a coastal location on the northeastern corner of Puerto Rico. The AOD record for atmospheric dust content is not correlated with the rainfall chemistry records of either concentration or flux of nss-$Ca^{2+}$, $dSiO_2$, and TSS at El Verde and Bisley (e.g. Fig. S6). When specifically looking at the temporal record of TSS concentration next to AOD (not shown), which both reflect the sum of all particulates, only a rough coherence in the seasonal pattern is seen, and very high temporal variability is evident. The daily AOD data were binned into weeks aligning with the rainfall record by averaging the daily values over 7 day periods to allow comparison with the weekly rainfall record. Of the 506 weeks in record, 40% had zero data points available, and there were additionally many individual days missing from the remaining weeks. The combination of the high temporal variability and the large number of missing data further contributes to the lack of correlation with the rainfall dust deposition record. However, the overall seasonal pattern in the rainfall chemistry record (e.g. Fig. 2) agrees well with the monthly average AOD in the Caribbean (Velasco-Merino et al., 2018).

In order to further evaluate the rainfall chemistry and TSS records, we compared these data with results from global chemical transport models that are used to study global aerosol emissions, transport, and deposition as part of the AeroCom project. Specifically, we analyzed

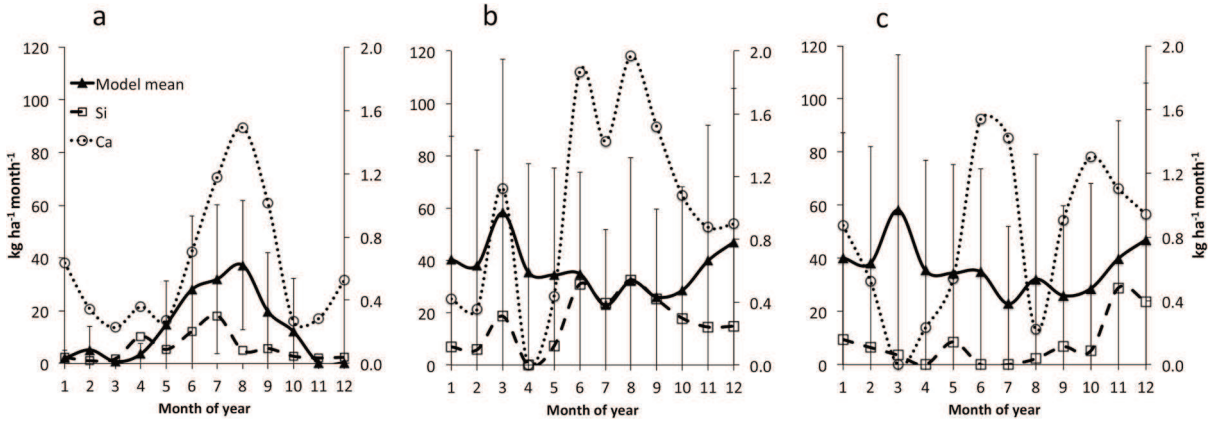


**Fig. 3.** Comparison of model outputs for dust deposition and empirical rainfall flux records for (a) wet deposition at El Verde, (b) dry deposition at El Verde, and (c) dry deposition at Bisley, for the year 2006. Solid lines with filled triangles show mean of 10 AeroCom models, along with error bars representing 1 standard deviation of the mean. Dissolved silica fluxes are shown in dashed lines with open squares, and dissolved nss-$Ca^{2+}$ fluxes are shown in dotted lines with open circles. All y axis units are kg $ha^{-1}$ $month^{-1}$. Model means are dust deposition fluxes referenced to the left y axis scales, dissolved solute fluxes are referenced to the right y axis scales.

both wet and dry deposition simulation results from 10 models using monthly data from the year 2006, for the location of the El Verde and Bisley collectors. Based on long-term climate records, 2006 was a typical rainfall year for the Luquillo Mountains (Waide, 2013). For each model, simulation results for the year 2006 were extracted for the Luquillo Mountains, however the model grid sizes vary between 5° × 4° and 2° × 2°, and cover areas much larger than the region of the Luquillo Mountains, which presumably contributes to the diversity of model output. The mean of the 10 models was calculated for both dry deposition and wet deposition, along with 1 standard deviation, for each month of the year. This is plotted along with our deposition of $dSiO_2$ and nss-$Ca^{2+}$ from empirical rainfall data in Fig. 3.

Wet-only dust deposition (Fig. 3a) has a strong seasonal pattern with a summer maximum and low inputs the rest of the year. The model and both the $dSiO_2$ and nss-$Ca^{2+}$ based metrics of dust deposition all follow the same seasonal trend of dust deposition. One difference seen in the wet deposition data is that the nss-$Ca^{2+}$ based metric of dust deposition shows somewhat elevated fluxes in winter, while both the $dSiO_2$ data and the model show very low winter inputs. Given the good agreement among models and between the models and the $dSiO_2$-based data, this implies that there is a non-dust source of nss-$Ca^{2+}$ in wet-only deposition in winter, or, alternatively, that the Ca content of dust or the Ca:sea salt ratios of the aerosols may change seasonally. In contrast to the model results for wet deposition, the model results for dry deposition simulations show very large variability illustrated by the 1 standard deviation error bars shown in Fig. 3b and c. The variability was large both in terms of seasonality and overall magnitude, and the mean of models shows no clear seasonal pattern.

Overall, the model results show that dry deposition represents 74% of total annual deposition, which agrees well with the precipitation records analyzed here and also with previous work in the Luquillo Mountains (Medina et al., 2013). Due to the summer maximum in wet deposition, dry deposition declines to ~40% of total deposition in July, but represents a much higher fraction of the total during the rest of the year. Modeled dry deposition comparisons with rainfall data reflect two different approaches to calculating dry deposition, which contributes to differences between rainfall chemistry metrics of dry dust deposition between the two sites. At El Verde, dry deposition is calculated as the difference between openfall and wet-only precipitation, and at Bisley, dry deposition is calculated as the difference between throughfall and openfall. The $dSiO_2$ and nss-$Ca^{2+}$ fluxes yield divergent seasonal patterns in dry deposition between El Verde and Bisley. The variability in modeled dry deposition was so large that a seasonal pattern could not be determined. Nevertheless, the lack of a coherent simple seasonal pattern in dry deposition from either the models or the rainfall metrics could provide an explanation for the relatively weak seasonal trends in dust inputs averaged over 20 years (Figs. 2, S3, and S4), in the general sense that dry deposition appears to be a major component of total deposition, and it occurs throughout the year.

Finally, we also assessed the Aerocom models in terms of the predicted annual dust deposition flux. The model mean annual total (dry + wet) dust deposition was 590 ± 490 (1s.d.) kg dust $ha^{-1}$ $yr^{-1}$, for the year 2006. This number roughly agrees this the Sr isotope-based watershed-scale mass balance calculation for Luquillo of 210 ± 70 kg dust $ha^{-1}$ $yr^{-1}$, which integrates over much longer timescales (Pett-Ridge et al., 2009b). The range in these values highlights the difficulties in extrapolating from rainfall chemistry in a small precipitation collector to dust deposition across a landscape. In particular, a drawback of the modeled deposition fluxes is that due to their grid size, they all include open ocean, which is expected ot have lower precipitation and differing controls on the proportions of wet and dry deposition. Our analysis also highlights the uncertainties associated with dry deposition modeling. Additional points of comparison for total dust deposition in Caribbean are lacking. For example, the DIRTMAP compilation of terrestrial and oceanic dust deposition fluxes has no records from the Caribbean region (Kohfeld and Harrison, 2001).

### 4.5. Seasonality and importance of the Sahel region

Sr and Nd isotopic tracing of dust collected on air filters in the Caribbean show that mineral aerosol particles originate primarily from the Sahel region of North Africa (Kumar et al., 2014). The temporal pattern of Luquillo Mountain rainfall chemistry likely reflects source region dynamics unique to the Sahel. The Sahel experiences a rainy season from approximately April until late October, with the most intense rainfall occurring from August through September (Fig. 2). At its peak, the western edge of the Sahel experiences on average 7.8 mm of rain per day, distributed over ~2.5 events per week, and an annual total rainfall of 300–400 mm (Lebel and Ali, 2009). While this is a relatively small amount of rainfall, it reduces dust emissions in two different ways. First, rainfall directly increases soil moisture, which reduces ejection of dust into the atmosphere (Mahowald et al., 2009). Second, rainfall spurs the growth of vegetation; enough to alter satellite-based measurements of vegetation greening of the region for two months after the rainy season has halted (Nicholson et al., 1990). These changes both hinder dust entrainment to the atmosphere.

The number of airmasses coming from the Sahara-Sahel region to the Caribbean is elevated during both the summer and fall season, as expected based on the seasonal shift in the intertropical convergence zone across the Atlantic (Perry et al., 1997; Prospero, 1999). However,

the openfall fluxes of nss-$Ca^{2+}$ and $dSiO_2$ in Luquillo Mountains rainfall decline in fall relative to summer, despite the fact that this continues to be a time of peak atmospheric transport from the dust source region to the Caribbean. Fig. 2 shows that at approximately the 33rd week of the year (mid-August) rainfall in the Western Sahel is at its peak, and the amount of dust in openfall begins to decrease despite the continued prevalence of airmasses from the Sahara-Sahel region passing over the Luquillo Mountains. While isotopic data emphasizes the role of the Sahel as a source of Caribbean dust (Abouchami et al., 2013), dust emissions also appear to decline between August and October further north in the Sahara (Engelstaedter et al., 2006). Changes in the surface conditions at the dust source therefore appear to result in the decreased dust deposition in fall. In other words, during the fall Caribbean "dust season", airmasses from the Sahara-Sahel region are counter-intuitively less likely to carry dust from Africa to the Caribbean. This finding for Puerto Rico agrees with previous observations based on dust concentrations in the atmosphere over Barbados (Prospero and Lamb, 2003), indicating a regionally coherent trend.

This observation illustrates the sensitivity of Caribbean dust deposition fluxes to land-use change or climate change affecting dust production in the Sahel region, such as agricultural plowing or vegetation loss to desertification (Mulitza et al., 2010). Before intensive agricultural practices in the Sahel region, there was a stronger correlation between drought and dust emissions (Tegen and Fung, 1994). During the 20th century, dust fluxes from the Sahara-Sahel region have doubled, although large uncertainties remain regarding the relative importance of direct human impacts and climate change (Mahowald et al., 2010). The connection between seasonal patterns in Luquillo precipitation chemistry and environmental conditions in the Sahel supports the potential cross-Atlantic sensitivity of downwind ecosystems in the Amazon and Caribbean to dust production in Africa (Swap et al., 1992).

In addition to changes in dust sources area conditions, changes in Luquillo Mountains meteorological conditions can also affect dust deposition dynamics. While rainfall is not strongly seasonal in the Luquillo Mountains, there are seasonal patterns in other rainfall characteristics, average cloud height, and the $\delta^2H$ and $\delta^{18}O$ signature of rainfall (Scholl et al., 2009; Van Beusekom et al., 2015; Van Beusekom et al., 2017). In particular, the stable isotope values of rain are consistent with lower equilibration times during fall rainstorms, indicating a difference in rainfall style such as increased droplet size (Scholl et al., 2009). Although total dust deposition is highest in summer, a fall season maximum in the proportion of dry deposition is observed based on the $dSiO_2$ dry deposition estimate (throughfall minus openfall) at Bisley (Table 2).

## 5. Conclusions

Data from two rainfall stations with records of nss-$Ca^{2+}$, $dSiO_2$, and TSS deposition over a period of twenty years at two different locations in the Luquillo Mountains suggest large spatial variability in deposition of African dust. Across a distance of 10 km, the dust deposition flux evident in openfall chemistry appears to be reduced by half as airmasses interact with the complex topography. Both Luquillo Mountain sites exhibited similar seasonal patterns with summer maxima in dust deposition. The decline in dust deposition in the fall season is coincident with the Sahel rainy season, indicating that the Caribbean dust fluxes are particularly sensitive to environmental conditions in this region of Africa. Comparisons between openfall, throughfall, and wet-only precipitation indicate that between 53 and 73% of total dust deposition in the Luquillo Mountains occurs as dry deposition.

Records of rainfall chemistry using nss-$Ca^{2+}$, $dSiO_2$, and TSS as dust tracers extend what can be inferred about the amount and spatial variability in dust deposition beyond our current understanding from airborne filtration, modeling, or satellite observations alone. We found good agreement between Luquillo Mountain rainfall chemistry and AeroCom dust models in terms of the seasonality of wet deposition, and in the proportion of annual deposition that occurs as dry deposition. On the other hand we observed very high variability and a lack of strong coherence between rainfall chemistry and either satellite or airborne filtration-based records of atmospheric dust content. These results reflect both uncertainties in the use of rainfall chemistry as dust tracers, and also the lack of equivalence between atmospheric dust content and dust deposition. Given the model and empirical data agreement in the absolute magnitude of the flux of wet dust deposition, dry deposition processes appear to represent one of the largest sources of uncertainty and current challenges to models. Given the importance of dust to both climate and biogeochemical cycles, systematic assessments of the methodology behind ground-based methods of quantifying dust are needed. The combined use of dust active sampling, precipitation sampling, meteorological and satellite data, and atmospheric aerosol models can be used improve understanding of dust deposition dynamics.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.116907.

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