Dust Inputs to the Luquillo Mountains:

Impact on nutrient cycling and weathering fluxes

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_Collaborators_
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The "critical zone"

- Atmospheic inputs: including dust
- Biology
- Erosion
- Leaching
- Weathering

Soil
An understudied geochemical pathway?

Terrestrial Phosphorus Cycle
impacts of dust

Atmosphere:
- dust alters the radiation budget of the atmosphere

Oceans:
- influences marine biogeochemistry, primarily by supplying Fe to high-nutrient, low chlorophyll regions

Soils, Ecosystems:
- influences productivity via supply of limiting nutrients?
- Pathogen, pollutant, heavy metal transport?

Moore et al, Tellus 2006
why dust might be important in terrestrial systems

- Directly adds nutrients to ecosystems - P, Ca, Mg, K, micronutrients
- Adds nutrient holding capacity
- Adds buffering capacity
- Alters physical properties of surfaces it lands on
- Adds distinct isotopic and trace element signatures, which may confound the use of these proxies to study weathering
A case study: What is the importance of dust in a montane tropical forest?

1. How much dust deposition is there? Enough to matter? (negligible in actively eroding systems?)

2. Is dust an important source of nutrients?

3. Does dust affect soil chemistry and weathering fluxes?
Chinese dust storm, April 7, 2001

Terra/MODIS image, earthprobe TOMS data

Courtesy of NASA/Goddard Space Flight Center Scientific Visualization Studio
North African dust storm

over 50 million tons transported annually from Africa to the atmosphere over the Caribbean region
African dust transport

Photo taken from aircraft above Barbados of cumulus clouds poking up into Saharan Air Layer

Photo credit: Jason Dunion NOAA/HRD
Seasonal variation in total aerosols

Monthly Aerosol Optical Depth calculated from Terra/MODIS data, animation courtesy of NASA Earth Observations
spatial variation of modern atmospheric dust concentrations

IMPROVE aerosol monitoring network: 20 years of weekly sampling

Virgin Islands air sampling station consistently shows highest dust loads
Increasing drought in Sahel from ~1970 to 2000 led to increased dust concentrations in Barbados air
Puerto Rico has a modeled dust deposition flux of 5 g m\(^{-2}\) yr\(^{-1}\).

The map is based on NCAR’s CCSM model.

Deposition records lacking from the Caribbean region.
Records of dust deposition through geologic time

DIRTMAP database compiles data from marine sediment cores, marine sediment traps, loess deposits, ice cores

Kohfeld and Harrison, ESR 2001
Exogenous dust in soils- sometimes obvious

- Hawaii: quartz in soils overlying basalt

- Cameroon: zircons in soils overlying serpentinite

- Australia: “terra rosa” soil overlying limestone

www.claremontwines.com.au
Formation of limestone-hosted “terra rosa” soils:

Early theory: Soils form by accumulation of residual particles as carbonates dissolve over time

*Harrison and Anderson 1919, Vernon and Carroll 1965, Ahmad and Jones 1969*

Islands of Barbados and Guam would no longer exist given the required thickness dissolved limestone *Muhs et al 2007, Birkeland 1999*

Trace element data demonstrates major contribution of African dust to soils in Barbados, Jamaica, Bahamas, Florida Keys *Muhs et al 2007, others*
Why dust is hard to quantify

• often overlooked, an “occult” source of material inputs to a watershed

• difficult to measure the flux
  • Settling velocities don’t fully explain
  • Deposition affected by vegetation, canopy structure

• Extremely high spatial and temporal variability- how to measure in complex, vegetated terrain?

  • Puerto Rico experiences ~5 -10 dusty days/yr
How much dust is there?

Sr and Nd isotopes as dust source tracers

- Different rocks/minerals have distinct values for $^{87}\text{Sr} / ^{86}\text{Sr}$ and $\varepsilon\text{Nd}$, which are retained as unique fingerprints during mixing.

\[
\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{streamwater}} = X_{\text{Sr}} \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{bedrock}} + (1 - X_{\text{Sr}}) \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{atmospheric}}
\]

\[
\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{atmospheric}} = X_{\text{Sr}} \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{precipitation}} + (1 - X_{\text{Sr}}) \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{dust}}
\]

• end-member mixing models used to quantify local bedrock vs. Saharan dust contributions to soils:
Luquillo Mountains, Puerto Rico

Rio Icacos watershed
Rio Icacos watershed, Luquillo Mountains, Puerto Rico

- 326 ha
- 600 to 800 m elevation
- 4.6 m annual rainfall

Luquillo mountains create orographic precipitation
a natural laboratory...
role of geomorphology

• tectonics and erosion likely determine importance of atmospheric inputs

  - hypothesis: dust is most important in stable, slow-eroding environments

% foliar Sr derived from atmospheric sources

• Is dust irrelevant in a rapidly eroding environment like the Luquillo Mtns of Puerto Rico?

Porder et al, 2005
Erosion and weathering in Rio Icacos watershed

**rainfall:** 4.5 m yr⁻¹

**dust deposition rate:** ?

**erosion:**
• 34 ± 2 g m⁻² yr⁻¹ *Riebe et al 2003,¹⁰Be, basin wide average*

**weathering:**
• 56 ± 13 mg cm⁻² ka⁻¹ *Riebe et al 2003, immobile element enrichment +¹⁰Be, assumption of steady state*

• fastest reported field hornblende weathering rate
  \((6.3 \times 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1})\) *Buss et al 2008, solid-state weathering gradient*

• high solute fluxes; fastest documented granitoid weathering rate on Earth’s surface *White et al 1996, McDowell and Asbury 1994, streamwater fluxes*

**downward velocity of saprolite-bedrock interface:**
• 65 m Ma⁻¹ *Turner et al 2003, stream flux + mineralogical analyses*
is dust incorporated in Rio Icacos soil profiles?

\[ \epsilon_{\text{Nd}} \]

\[ \text{dust } \epsilon_{\text{Nd}} \]

\[ \epsilon_{\text{Nd}} \text{ (bedrock)} \]

\[ \text{depth (cm)} \]

\[ \text{La/Yb} \]

- Pett-Ridge et al, GCA 2009
how is dust incorporated?

earthworms physically mix the soil

chemical dissolution and subsequent precipitation and/or adsorption

Pett-Ridge et al, GCA 2009
Sr and Nd isotopes

<table>
<thead>
<tr>
<th></th>
<th>Saharan dust</th>
<th>local Puerto Rico quartz diorite bedrock</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$Nd</td>
<td>-12</td>
<td>7</td>
</tr>
<tr>
<td>$^{87}\text{Sr}/^{86}\text{Sr}$</td>
<td>0.71788</td>
<td>0.70412</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>% of Sr</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plagioclase</td>
<td>97.8</td>
<td>0.70410</td>
</tr>
<tr>
<td>Hornblende</td>
<td>1.6</td>
<td>0.70583</td>
</tr>
<tr>
<td>Biotite</td>
<td>0.6</td>
<td>0.72527</td>
</tr>
</tbody>
</table>

Pett-Ridge et al, GCA 2009
nearly congruent Sr weathering

• Soil biotite loses 90% of its original Sr in the initial stages of weathering

• No other sources radiogenic Sr apparent, no other sinks of unradiogenic Sr…
characterizing Saharan dust based ocean sediments, atmospheric sampling- averages out variability in North African source regions

average particle size in Caribbean ~2 μm, mica/illite (~60%), quartz (~10%), kaolinite, plagioclase, calcite, chlorite (~5%), trace apatite

Prospero et al 1970

Average [Sr] of dust is 195 ± 17 μm, \(^{87}\text{Sr}/^{86}\text{Sr}\) is 0.71788 ± 68 (s.e., n=23) Biscaye et al 1974, Grousset et al 1992, 1988a, 1988b, Rognon et al 1996
Isotope mass balance:

Streamwater isotopic Sr flux is not consistent with weathering reactions plus measured precipitation Sr-

... a missing source of radiogenic Sr dust

• 3 years of precipitation, streamwater samples (n = 40)
• Collected under wide range of discharge conditions
• 40 years of detailed discharge records

Photo credit: Jamie Shanley
quantifying unknown fluxes

\[ F_{\text{streamwater}}^{\text{Sr}} = F_{\text{precipitation}}^{\text{Sr}} + F_{\text{dust}}^{\text{Sr}} + F_{\text{bedrock}}^{\text{Sr}} \]

\[ \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{streamwater}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{precipitation}} F_{\text{precipitation}}^{\text{Sr}} \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{bedrock}} F_{\text{bedrock}}^{\text{Sr}} \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{dust}} F_{\text{dust}}^{\text{Sr}} \]

use known [Sr] and known density of bedrock...

\[ \therefore \text{propagation rate of chemical weathering front is } 66 \pm 10 \text{ m Ma}^{-1} \]

assume dust weathering flux = dust deposition flux, use known [Sr] of Saharan dust in Caribbean..

\[ \therefore \text{dust deposition flux is } 21 \pm 7 \text{ g m}^{-2} \text{ yr}^{-1} \text{ (210 kg ha}^{-1} \text{ yr}^{-1}) \]

Pett-Ridge et al, GCA 2009
comparison of dust and erosion fluxes

- **rainfall:** 4.5 m yr\(^{-1}\)
- **dust deposition rate:** 21 ± 7 g m\(^{-2}\) yr\(^{-1}\)
- **erosion:** 34 ± 2 g m\(^{-2}\) yr\(^{-1}\) (Riebe et al 2003, \(^{10}\)Be, basin wide average)

- Biological and chemical processes incorporate dust
- Style/timing of erosion matters, not just relative rate of erosion versus dust input
  - 90% is landslides - average recurrence interval is 10 ka (Larson et al 1987)
Calculated Luquillo Mountain flux agrees with estimates of open ocean deposition for the Caribbean if 4-fold enhancement due to orographically-enhanced precipitation is taken into account.

Luquillo Mountain dust deposition rate: $21 \pm 7 \text{ g m}^{-2} \text{ yr}^{-1}$

Caribbean open ocean dust deposition rate: $\sim 5 \text{ g m}^{-2} \text{ yr}^{-1}$
quantification of dust summary

• $^{87}\text{Sr}/^{86}\text{Sr}$ watershed scale mass balance is used to quantify dust flux (21 g m$^{-2}$ yr$^{-1}$) for Luquillo Mountains
  • spatially averaged, temporally averaged flux (watershed scale, time-period of dust dissolution: ~1 ka)
  • (lower bound on the deposition flux, based on assumption that dust weathers to completion in soil)

• $\varepsilon$Nd data demonstrate the presence of African dust at 3 m depth in regolith profiles- actively eroding systems can still be affected by dust!
  • Incorporation enhanced by bioturbation, chemical leaching
  • At local spatial scales, dust inputs likely exceed erosion at shorter timescales, but erosion dominates on longer (> 10 ka) timescales
Importance of dust in tropical ecosystems?
tropical soils (oversimplified)

- poor soil fertility - depleted over time
- dominated by Fe and Al-oxides and by 1:1 clays w/ low CEC
- P limited (while higher latitude systems tend to be more N limited)

Evolution of phosphorus in soil over time:

After Walker and Syers, 1976
putatively “rock-derived” nutrients (P, Ca, Mg, K, micronutrients) shift from being substrate derived to atmospherically derived with increasing age.

Example from Hawaiian soil chronosequence:

- rate of substrate supplied Ca declines
- % Ca derived from atmospheric sources increases

Chadwick et al, Nature 1999
tropical forests role in atmospheric CO₂

• > 1/3 of annual global terrestrial CO₂ exchange between atmosphere and biosphere

• Response of nutrient dynamics to changing land-use and climate is critical to predicting future CO₂

• Change in terrestrial C predicted 1870-2100, coupled CCSM-BGC model, NCAR ESSL lab

Thornton et al, GBC 2007
does dust feed the Amazon?

Quaternary dynamics of Amazon directly controlled by shifting vegetation, source area, emission, and transport patterns in North Africa?

*Reichholf 1986, Swap 1992*

Global model of soil P residence times, based on modeled dust inputs and soil P contents suggests that productivity (i.e. C balance) of Amazon Basin is highly dependent on dustborne P additions

(\(\tau_P = \sim 20 \text{ ka}\))

*Okin et al GBC 2004*
Ecuador rainforest response to Saharan dust?

- HYSPLIT wind trajectories

- Montane rainforest catchment in Ecuador receives Saharan dust-associated Ca, Mg, K deposition

- Increased Ca deposition associated with increased retention of excess Ca-enhanced plant growth?

Boy and Wilcke GBC 2008
Is dust-derived phosphorus (P) important in Luquillo Mountains?

P may be the limiting nutrient for Luquillo Mountain ecosystems. No primary mineral source of P (apatite) available for most of the landscape.

Data from Frizano et al., 2002, Johnson et al., 2003
dust-derived P inputs

- 21 g m\(^{-2}\) yr\(^{-1}\) dust flux (determined from Sr isotope mass balance) * 1100 mg g\(^{-1}\) [P] in Saharan dust yields 0.23 kg P ha\(^{-1}\) yr\(^{-1}\) (Mahowald et al., 2005a) , (Swap et al., 1992) (based on water-soluble PO\(_4\) in wet season only, December through May) (Kurtz et al., 2001) , (Tsukuda et al 2006) (Stoorvogel et al., 1997), (McTainsh 1980, Wilke et al 1984), (Avila et al 1998).
Luquillo Mountains soil P budget

dust deposition input of P is similar in magnitude to other P inputs, constitutes 10% annual plant uptake flux.


soil residence time is \( \sim 15 \) ka.

soil P turnover time \( (\tau_P) = \sim 1.5 \) ka.

- on par with equatorial Africa, \( \sim 10 \times \) faster than Amazon Okin et al 2004.

Hawaii dust-derived P flux

role of landslides- geomorphology controls importance of dust-P

landslide recurrence interval = 10 ka, average depth is 2 m \(\text{Larsen 1997}\)

- Shallow slips
  - Depletion of labile pool
- Deep landslides
  - Exposure of primary minerals
dust contributes to ecosystem resiliency?

chronosequence of shallow landslides in Luquillo Mountains

immediately post-landslide, soil is depleted of P

P accumulates over ~100 years of landslide recovery

missing 1/3 of accumulated P may derived from unmeasured dust inputs

solubility of P in dust is not well known, but most P in Saharan dust is believed to be in apatite


Frizano et al, Biotropica 2002
dust-derived P in the Rio Icacos watershed

• soil P pool turns over multiple times during the residence time of the soil

• dust contributes approximately half the total P inputs—

  *suggests that dust-derived P may be an integral part of this ecosystem*

• dust-derived P may be especially important post-disturbance
variation between Luquillo watersheds

Bisley (volcaniclastic substrate) has lower rainfall, likely less dust input (1/3 lower?)

Bisley may have longer soil residence times (fewer landslides, higher soil cohesive strength), might lead to greater impact of atmospheric inputs

Simon et al 1990, Guariguata 1990
Analysis of Ca and Sr sources in Rio Icacos

- $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are used to identify sources of Sr in vegetation (calculated with isotope mixing equations)

- Ca/Sr ratios are used to extrapolate to Ca

$$X_{\text{Ca}} = \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{foliar}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{precipitation}}} {\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{foliar}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{precipitation}}} \times \left(\frac{\text{Sr}}{\text{Ca}}\right)_{\text{precipitation}} + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{bedrock}} - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{foliar}} \times \left(\frac{\text{Sr}}{\text{Ca}}\right)_{\text{bedrock}}$$

- Simple steady-state box modeling is used to quantify fluxes between reservoirs

- Ca uptake flux is compared to Sr uptake flux

- 3 sites compared: ridgetop, moderate hillslope, and a steep hillslope (~50%)
  - only 10 meters apart
Calculating plant Sr sources

Simple end-member mixing:

\[
\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{foliar}} = X_{Sr} \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{bedrock}} + (1 - X_{Sr}) \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{atmospheric}}
\]

• Watershed average soil Ca content, based on 32 soil pits, showed no evidence of any primary sources of Ca. (Riebe et al., 2003)

• Typical soil and vegetation sampling regimes are likely to miss these nutrient “hotspots”

• Isotopic tracers indicate their presence
modeling Ca and Sr cycling

Ca/Sr uptake fractionation = 1.3

Ca/Sr uptake

biomass 17 years

foliar leaching

atmospheric deposition

uptake

litterfall

exchangeable cations 32 years

Exchange efficiency=50%

weathering

soil minerals

porewater 19 days

leaching, precipitation

• dust contributes 20-40% of actively cycled Ca in Luquillo biomass

• a larger than expected proportion of bedrock-derived Ca is biologically cycled in Luquillo Mountain vegetation

• isotopic tracing reveals large variability in nutrient cycling on a small spatial scale

• nutrient availability is not only tied to uplift and erosion rates, but to specific mechanisms of physical weathering- in this case spheroidal weathering of bedrock leading to corestone survival.
impact of dust on weathering in the Rio Icacos watershed

- Dust-derived Sr constitutes about ~7% of the total dissolved streamwater Sr flux
  - likely the same for Ca
  - not significant given uncertainties on this flux

- Dust-derived Si constitutes ~20% total dissolved stream Si?
  - Assumes all Si dissolves in soil before erosion export (unlikely)

- More important impact of dust in this watershed is its effect on soil chemistry- namely trace element and isotopic budgets
  - these tracers are used to characterize weathering processes and rates
  - dust therefore indirectly affects our understanding of the weathering fluxes
conclusions

• Luquillo Mountains receive significant African dust deposition flux
  • \(~2100 \pm 700\, \text{mg cm}^{-2} \text{ka}^{-1} (21\, \text{g m}^{-2} \text{yr}^{-1})\) in Rio Icacos watershed

• Dust-derived P inputs are similar to saprolite-derived inputs, likely an important component of biogeochemically cycled P, importance depends on landslide history at local scales

• Dust also contributes to biologically-cycled Ca (\(~10\text{-}30\%)\), highly variable on small spatial scales

• dust inputs will have a significant impact on the budgets of many trace elements