



Short communication

Carbonate dissolution cones require more than stemflow funneling from plants

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ABSTRACT

Over geologic timescales, forests have intercepted precipitation and thereby modified the intensity, duration, and spatial patterns of water fluxes to forest soils. Across a range of environmental conditions, persistent focused water flows can dissolve carbonate substrates, and form conical dissolution features—termed “dissolution cones.” These cones generally fill with soils, becoming localized soil (and water) reservoirs occupied by vegetation. A myriad of mechanisms are hypothesized to have formed dissolution cones. Prior work has sought to explain co-located palm trees and modern dissolution cones in tropical unconsolidated carbonates as the result of the chemical action of weakly acidic stemflow funneled by palm canopies down their stems, and into the substrate. Using a geochemical modeling program, PHREEQC, we find that for a range of environmental conditions and favorable assumptions, stemflow is unable to dissolve a benchmark volume of carbonate substrate that typifies tropical dissolution cones. Therefore, dissolution cone formation by abiotic dissolution from stemflow funneling is unlikely to be the chief geomorphic process. Further hypotheses to be tested are discussed.

For the past 400 million years, forests have played key regulatory roles in the Earth's climate system (Bonan, 2008). Understanding spatiotemporal patterns of forest cover over deep time is, therefore, valuable to the reconstruction of past climates and biogeochemical cycles, and may improve our understanding of long-term climate change effects (Petit et al., 2008; Delong et al., 2021). One role that forests play in the Earth system includes regulating the exchange of water between the atmosphere and soil. Thus, forest-water-soil interactions over an ecosystem's (or individual tree's) lifetime can leave chemical and physical evidence of ancient forests in the sedimentary rock record.

To reach the forest soil, precipitation (and condensation) must pass through the plant canopy—one of these “hydrologic highways” through the canopy is drainage down plant stems, or stemflow (Van Stan et al., 2021). Stemflow from trees can result in spatially concentrated water fluxes at the stem base, where 0.01 to 25% of rainfall over the canopy area can be input over 10^{-2} to 10^1 m² of soil surface area per tree (Sadeghi et al., 2020; Van Stan and Allen, 2020). Over a tree's lifetime, which without significant disturbance may be hundreds to thousands of years (Tomlinson and Huggert, 2012), cumulative stemflow can persistently focus water flows to soils at the base of the plant. As persistent, focused waterflows can dissolve unconsolidated carbonate substrates,

forming “dissolution cones” or “dissolution pipes” (Fig. 1), it has been hypothesized that a tree's lifetime stemflow production can generate these features, beginning with Herwitz (1993), whose objective was “to consider the hypothesis that the soil-filled pipes of Bermuda are the product of large volumes of acidic stemflow drainage from long-lived indigenous trees”. Of these long-lived woody plants, tropical palms were of particular interest due to their stemflow being “the most chemically altered” (i.e., having high ion concentrations), “the most acidic” (pH = 4.3–4.9) (per Herwitz, 1993), and generally being a higher fraction of rainfall across their canopies than other kinds of large woody plants (Van Stan and Gordon, 2018; Sadeghi et al., 2020). Therefore, dissolution cones in the sedimentary record could be interpreted as trace evidence for the former presence of an ancient forest. This study and its titular finding, that “stemflow influences the formation of solution pipes,” has been incorporated throughout research on this topic, including comprehensive reviews (Grimes, 2009; De Waele et al., 2011; Lipar et al., 2021).

Dissolution cones have been hypothesized to have their genesis in several other mechanisms (Ford and Williams, 2007), besides stemflow alone. The concentration of water flows through soils may form without stemflow. For example, as wetting fronts from other hydrologic fluxes

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Fig. 1. Image of (A) multiple woody plants occupying a conical surface depression. Vegetation (B) with vertical roots occupying dissolution features. Basal (C) and top (D) exposure of dissolution closely spaced dissolution cones. These images were collected on Eleuthera Island and are courtesy of David Mohrig (UT Austin).

infiltrate through karst substrates, they can produce systematic flow instabilities akin to “finger flows” that may result in localized dissolution (Lipar et al., 2015; Szymczak et al., 2015). The soil-bedrock interface will also likely play a role in spatially concentrating draining soil waters to low points, or drain holes, along this interface (i.e., growing dissolution cones). These, and other karst features, may have their origin during the very formation of the karst substrate itself, being dissolved from the soft, poorly-cemented sediments that eventually hardened to form the karst (Grimes, 2006). “Syngenetic” karst features are especially prevalent in limestones formed from dune calcarenites (Grimes, 2006). Theoretically, it is most probable that a number of these processes contribute together, in various degrees, to the genesis and development of dissolution cones. Indeed, landforms are typically shaped from a variety of competing mechanisms operating at various intensities and timescales.

In this study, to test the feasibility of abiotic cone dissolution by stemflow-sourced near-stem infiltration (Herwitz, 1993), we expand on a previous minimalistic model of cone formation (Lipar et al., 2021) to simulate hypothetical amounts of water required to equilibrate with atmospheric CO_2 and porous calcium carbonates (e.g., unconsolidated deposits or a weakly cemented calcarenite) to dissolve a cone of a fixed volume. However, soil formation is likely to entail the release of root and

microbial exudates, which can increase soil porewater acidity. In such cases, total acidity can exceed free atmosphere equilibrium due to soil respiration by up to 300 times (e.g., Ford and Williams, 2007; Hashimoto et al., 2004). Although soil formation would likely release many weak organic acids, we choose to vastly simplify and conceptualize this system of weak acids as a hypothetical range of partial pressures of CO_2 (P_{CO_2}). Thus, in our simulations, we expand the scope of the original stemflow-dissolution cone hypothesis to include a range of P_{CO_2} beyond reasonable atmospheric values. Furthermore, stemflow along low lying carbonate platforms could represent a wide range of chemical concentrations: (i) relatively free of dissolved solids, (ii) possibly enriched with solutes from sea spray, or (iii) during vigorous storm activity, effectively seawater. Thus, we include two end member initial solutions: i) pure water and ii) an approximation of average seawater.

Previously, Lipar et al. (2021) assumed that subglacial meltwaters would form carbonic acid from open communication with atmospheric CO_2 to achieve calcite saturation at a temperature of 0°C (60 mg L^{-1} , Plummer and Busenberg (1982)). This dissolved mass of CaCO_3 can then be converted into a dissolved volume by knowing the density of calcite (ρ_{CaCO_3}) and assuming a bed porosity (ϕ). Following Lipar et al. (2021), we solve for the minimum mass of weakly acidic water required to enter, equilibrate, and drain to form a dissolution cone of a reference volume of

Table 1

Concentrations of major ions typical of seawater composition are given by Riley and Chester (1971) and reported in ppm by Spencer and Hardie (1990).

Ion	Concentration (ppm)
Na ⁺	10,800
K ⁺	407
Ca ²⁺	413
Mg ²⁺	1296
Cl ⁻	19,010
SO ₄ ²⁻	2717
HCO ₃ ⁻	137

1 m³ ($v_{ref} = 1 \text{ m}^3$), as this volume characterizes dissolution cones thought to arise from stemflow near tropical latitudes, which have diameters <0.5 m and depths between <1 m and a few meters (Lipar et al., 2021). Again, following Lipar et al. (2021), the mass of water (m_{water} , g) required to infiltrate, equilibrate, and drain to remove v_{ref} is found using,

$$m_{water} = v_{ref}(1 - \phi) \left(\frac{\rho_{CaCO_3}}{m_{CaCO_3}} \right),$$

where ϕ is assumed to be 0.3, ρ_{CaCO_3} is the density of calcite ($2.71 \times 10^6 \text{ g m}^{-3}$), and m_{CaCO_3} is the mass (g) of CaCO_3 dissolved per kilogram of solvent. However, calcite solubility is a consequence of initial solution composition, and environmental factors, which include temperature and P_{CO_2} . Furthermore, ionic strength effects and speciation yield small changes in m_{CaCO_3} which cannot be ignored, as this quantity is effectively extrapolated to find a hypothetical mass of water required for cone formation (m_{water}). To account for ionic strength effects, speciation, and survey a broad range of temperature- P_{CO_2} conditions, m_{CaCO_3} is approximated using the capabilities of the computer program PHREEQC Ver. 3.7.0–15,749 using the “phreeqc.dat” database (Parkhurst and Appelo, 2013).

Because the initial ionic strength of the stemflow solution would modify activity coefficients, possibly introduce common ions, and therefore result in different amounts of calcite dissolution, two end-

member initial solution conditions are carried forward to give conceptual bounds on the total amount of equilibrated water required to generate a reasonably sized dissolution cone: pure water and seawater. For each initial condition, 10^6 equilibrium simulations are performed in PHREEQC, spanning 10^3 values of specified P_{CO_2} (10^{-4} to 1 atm) and 10^3 values of specified temperature (0° to 40°C). In each case, the simulation was allowed to equilibrate with pure calcite and the “phreeqc.dat” database was used. In batch simulation, all PHREEQC input file concentrations were entered as parts per million (ppm) concentrations. Firstly, in each speciation simulation, one kilogram of pure water (pH = 7) at specified temperature (0° to 40°C) was allowed to equilibrate with calcite at a specified P_{CO_2} (10^{-4} to 1 atm), forming carbonic acid, a weak, polyprotic acid capable of dissolving carbonate materials. Secondly, equilibrium speciation of the same chemical system is performed across the same temperature- P_{CO_2} space using an initial composition of seawater (Table 1), and an assumed initial pH of 8.22 (Nordstrom et al., 1979).

The first set of speciation simulations using initially freshwater (pH = 7, no dissolved material) yielded intuitive results. Equilibrated solutions with the warmest temperatures and lowest P_{CO_2} values have the highest pH (Fig. 2A), lowest amounts of dissolved CaCO_3 (m_{CaCO_3} , Fig. 2B), and consequently require the greatest amounts of equilibrated water (Fig. 2C) to dissolve the benchmark cone volume: 1 m³ of porous carbonate material. Oppositely, solutions with the lowest temperatures and highest P_{CO_2} values are the most acidic (Fig. 2A), have the highest dissolved carbonate mass (m_{CaCO_3} , Fig. 2B), and represent a minimum mass of equilibrated water to dissolve a benchmark cone volume (Fig. 2C). For the range of speciation simulations featured in Fig. 2A–C, P_{CO_2} exerts a visibly larger control on equilibrium pH and m_{CaCO_3} , as contoured changes in dissolved CaCO_3 plot as steeply sloped contours, that indicate only minor decreases in dissolved calcite with increasing temperature. However, in the second batch of simulations (Fig. 2D–F), the initial composition of the water was altered to approximate average seawater but included a survey of the same temperature- P_{CO_2} conditions. Because the hypothetical seawater composition is at saturation with recent concentrations of atmospheric CO_2 , only solutions with

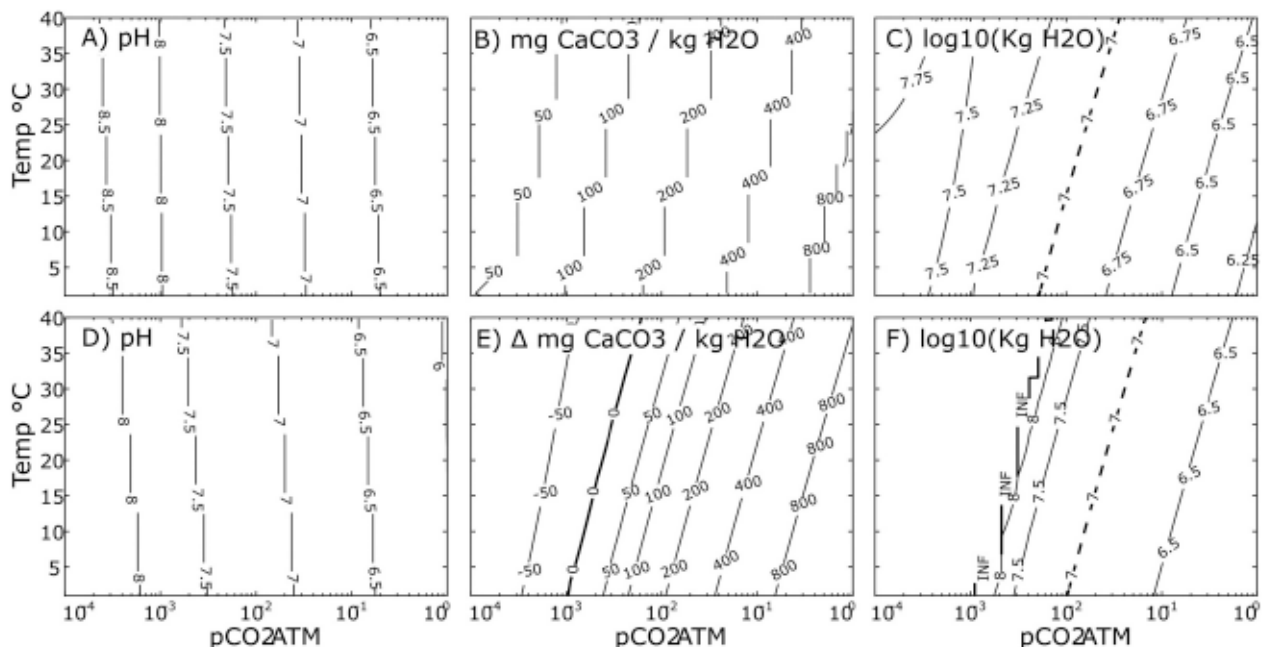


Fig. 2. Numerical speciation results for (A–C) pure water and (D–F) average seawater (for composition see Table 1) equilibrating with a constant P_{CO_2} and CaCO_3 at a given temperature ($^\circ \text{C}$). A/D) Equilibrium pH as a function of temperature and P_{CO_2} . B/E) Mass of CaCO_3 dissolved as a function of temperature and P_{CO_2} . Note that panel (E) is the change in mass of CaCO_3 dissolved in seawater (not including initial concentration). C) Kilograms of equilibrated water and F) seawater required to dissolve the benchmark cone volume ($v_{ref} = 1 \text{ m}^3$). Black dashed contour in (C) indicates the contour for $>10^7 \text{ kg H}_2\text{O}$. Negative values in (E) plot to the left of the bold infinite contour (labeled ‘INF’) in (F).

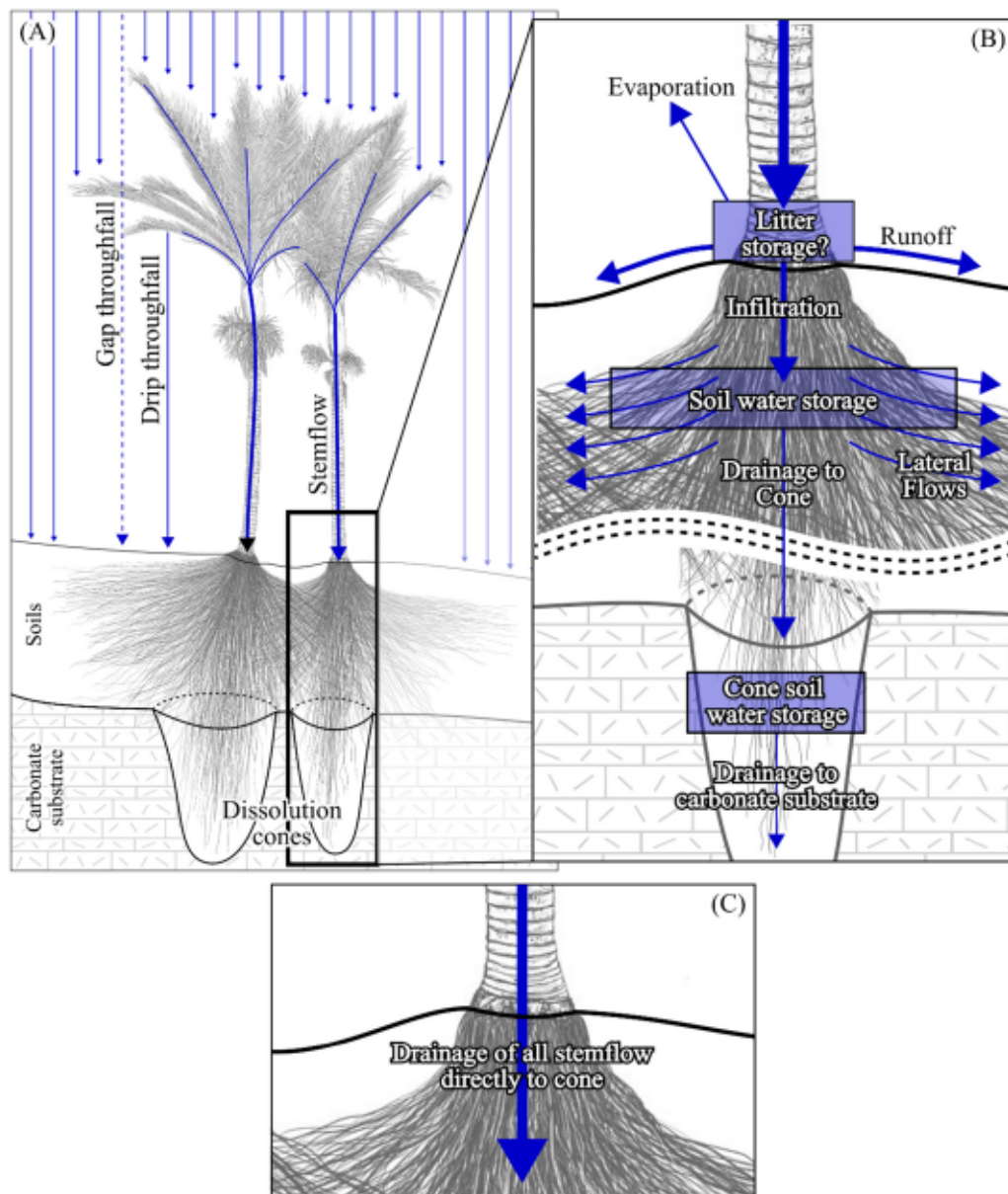


Fig. 3. Conceptual model showing (A) how precipitation reaches soils beneath palm canopies as gap throughfall, drip throughfall and stemflow. Assuming stemflow preferentially infiltrates along palm roots to reach the carbonate substrate, (B) it must first saturate litter (when present) and soils at the surface and in the dissolution cone which will reduce the stemflow available to dissolve the substrate. To provide the most favorable case for stemflow dissolution (C) our model assumes that all stemflow infiltrates, equilibrates with the carbonate substrate, and drains. Background illustration from Wikimedia Commons by Axel Aucouturier (CC BY-SA 4.0).

values of P_{CO_2} that exceed reasonable historical atmospheric concentrations are able to dissolve the carbonate substrate (Fig. 2E,F), and therefore generate a dissolution cone. Thus, results from both solution end members (freshwater and seawater) indicate that stemflow alone, over the lifetime of a tree, is insufficient to generate a dissolution cone exceeding 1 m^3 .

This conceptual model assumes that all stemflow arriving at the stem base would infiltrate, equilibrate with the carbonate substrate, and then drain (Fig. 3). Observations to date show stemflow-surface interactions can result in a broad range of hydrological outcomes, from preferential infiltration to runoff (Van Stan and Allen, 2020) (Fig. 3A–B). Direct observations of stemflow runoff versus infiltration are sparse (Carlyle-Moses et al., 2020; Allen and Van Stan, 2021); however, in the humid tropics observations have been reported that show much of the stemflow arriving at the soil surface can run off as a form of Hortonian overland flow (e.g., Herwitz, 1986). Some hypothesize that nearly all stemflow will efficiently infiltrate along root pathways (Carlyle-Moses et al., 2020); however, even the portion of stemflow that infiltrates along roots is unlikely to arrive at the soil-bedrock interface as a focused stream, with no dispersion or lateral flow (Fig. 3B). Therefore, the results of this

study represent a highly efficient system that would vastly favor dissolution cone formation via stemflow (Fig. 3C). However, despite being heavily optimistic, the amounts of water required to generate these dissolution features is 10^6 – 10^8 kg of stemflow over the lifetime of a tree. This is orders of magnitude greater than the lifetime amount of stemflow generated by individual palms in past studies where this mechanism has been hypothesized. Palms, per observations to date, tend to produce greater stemflow fractions (5 to 10% of rainfall) compared to other trees (<2%) (Van Stan and Gordon, 2018; Sadeghi et al., 2020), yet it is unlikely that individual palms would generate enough stemflow in their lifetimes. Herwitz (1993) results suggest the fraction of stemflow from *Sabal bermudiana* is 2 to 3% of gross rainfall; however, palm stemflow fractions have been reported to be 2 to 5 times higher elsewhere (~5 to 10%: Germer et al., 2012; Sadeghi et al., 2020). To be as favorable as possible, one can assume that an individual palm generates stemflow from 5 to 10% of the mean annual rainfall of Bermuda (1400 mm) across a 10 m^2 projected canopy area. Should this individual palm live 200 to 300 years, this would result in 140,000 to 420,000 L tree lifetime⁻¹. Of course, most palms likely live shorter lifespans due to various human and environmental disturbances, particularly along tropical coastlines

where they can represent the first terrestrial vegetation to attenuate tropical wind and storm surges (Frangi and Lugo, 1998; Joseph et al., 2012). This model also omits plant transpiration and stemflow interception, storage, and the possible evaporative loss of stemflow enroute to the underlying dissolution cone (Fig. 3B) (e.g., by passing through storm-lain wrack deposits (Van Stan et al., 2020)). In either case, the removal of water by evapotranspiration may drive mineral precipitation and increase the total mass of water required to form a dissolution cone. Therefore, we reject the hypothesis that formation of each dissolution feature is solely a result of augmented infiltration sourced from the stemflow of individual trees.

Several alternative hypotheses remain to be tested. (1) Dissolution cones are unlikely to be formed from infiltration of stemflow without biotic influences. Indeed, microbial communities and root exudates may help to dissolve carbonate substrate (Huang et al., 2014). In this case, in infiltrating stemflow may introduce a weak acid. Indeed, for the extremely favorable case of total acidity represented by 300 ATM of P_{CO2} at the favorable temperature of 1 °C, PHREEQC simulations demonstrate that 3.7×10^5 kg of freshwater or 2.9×10^6 kg of average seawater would be required to remove the benchmark cone volume. While these values are in the range of potential stemflow output, again, it is dubious to assume that such quantities of stemflow would infiltrate from the stem of a single plant, become highly acidified, equilibrate, and efficiently drain. (2) Cone growth may also hypothetically be aided by the mechanical breakage of carbonate substrates by root growth or stress applied by roots from gravitational or wind drag on canopies (Pawlik et al., 2016). (3) Cones may fill with soil, act as pH refugia, and therefore once initiated, occupation of dissolution cones by multiple generations of trees may be likely and could provide sufficient routing of weakly acidic water to generate a dissolution cone. Observations of closely spaced cones (e.g., Fig. 1D) weakens the refugia hypothesis (which would hypothetically create fewer, larger cones). Still, over hundreds of generations of shorter-lived palms, it is possible that these trees would benefit from using a soil filled depression and contribute many lifetimes of stemflow. (4) Pre-existing physical features may aid trees in cone formation: e.g., antecedent topographic lows or pre-existing fractures may offer nucleation sites for initial tree occupation. (5) The corollary may also occur: a tree's stemflow might be responsible only for the formation of initial, small solution voids or tubules in the underlying carbonates. After a tree begins a dissolution cone, it may become a zone of preferential infiltration, and cone growth may continue with or without tree occupation. (6) Over geologic timescales, it is also possible that environmental changes due to past climates could have substantially changed interactions along the atmosphere-plant-soil continuum. Some tropical areas experienced large Late Quaternary changes in climate (and vegetation), especially in relation to rainfall rates (Thomas, 2008), which could have altered not only infiltration rates but also soil production and tree coverage. Thus, although the lifetime stemflow production of an individual tree alone does not appear adequate for generating dissolution cones, many hypothetical research avenues (in which stemflow may play a role) remain to be tested.

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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