# Total organic carbon concentrations in clastic cave sediments from Butler Cave, Virginia, USA: implications for contaminant fate and transport

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# Abstract

Clastic cave deposits are representative of sediments throughout the karst aquifer and thus are an abundant and accessible resource through which to study the chemistry of karst aquifer. Clastic cave sediments are attributed to depositional facies based on cave location, sorting, and particle size. These facies settings may influence different chemical parameters of the sediments, like concentrations of total organic carbon (TOC). The TOC concentrations in clastic cave sediments have not been well constrained nor has the role of clastic sediments in contaminant fate and transport through karst systems been well described. In this study, particle size, TOC, and total nitrogen were measured in sediments representing different facies in Butler Cave, Virginia, USA. TOC concentrations ranged from 0.08–0.87 weight percent and C:N molar ratio ranged from 3–15, indicating a possible terrestrial source of organic carbon in these sediments. The diamicton facies was sandier and but had similar TOC concentrations compared to the channel facies. TOC concentrations measured in Butler Cave were within the same range as those observed in above water, eogenetic clastic cave sediments from two caves in Puerto Rico. Estimated retardation factors calculated based on the TOC concentrations in the Butler Cave sediments indicate the range of TOC in this cave could be responsible for 39–987% increase in retardation of selected contaminants. This study highlights the importance of measuring the ranges of TOC in clastic cave sediments across different facies and their role in contaminant fate and transport.


# Introduction

The presence, nature, and concentration of natural organic matter in aquifer systems plays a critical role in carbon processing, nutrient cycling, and contaminant storage and transport. Natural organic matter is contained within the soil and sediments of aquifer systems and is measured as total organic carbon (TOC), yet the TOC concentrations of aquifer sediments are not as thoroughly quantified or described as the TOC for other types of sediments, such as marine or lacustrine. The amount of subsurface TOC generally decreases with depth through the soil zone and is even lower in aquifer sediments (Hicks et al. 2018), however it is important to quantify and characterize the TOC of aquifer sediments to better understand how this carbon is participating in and effecting other processes, such as contaminant fate and transport. While all aquifers are susceptible to contamination, karst aquifers and their sediments are of particular interest given the well documented vulnerability of these aquifers to contamination (Ewers et al. 1991; Vesper 2008; White 2018; Williams and Farmer 2003), their connectivity to surface inputs, and their capacity to store and transport large amounts of sediment depending on hydraulic conditions (Herman et al. 2008). Further, relatively little attention has been paid to the role of sediment in contaminant fate and transport. Karst aquifer sediments with relatively high TOC may act as a reservoir for organic contaminants via adsorption of contaminants onto sediments (Schwarzenbach et al. 2003) and as a source for reintroduction of contaminants to the surface if hydraulic conditions initiate sediment transport (Herman et al. 2008; Vesper et al. 2003). To understand the role of aquifer sediments in contaminant fate and transport, a more comprehensive data set is necessary.

Sediments deposited in caves are relatively accessible and approximately analogous to sediments stored throughout the karst aquifer. Cave sediments include material generated chemically (precipitates) or physically (clastic). Precipitates include speleothems which are primarily inorganic in composition and

contain minor amounts of TOC (Dreybrodt 1999). Clastic sediments consist of breakdown and surface derived material (White 1988) originating from collapse structures like sinkholes, injection during storms or floods, or incoming recharge (Hart and Schurger 2005). Caves are considered an oligotrophic environment with typically < 2 mg/L TOC (Barton and Jurado 2007) yet the diverse microbial communities in caves (Banks et al. 2010; Barton et al. 2004; Barton and Northup 2007; Kosznik-Kwasnicka et al. 2022; Suarez-Moo et al. 2022) may be responsible for critical generation and transformation of organic carbon in the system (Kosznik-Kwasnicka et al. 2022; Suarez-Moo et al. 2022).

In clastic cave sediments and karst systems, the spatial and temporal distribution of TOC, the range of concentrations, and the chemical and biological pathways by which this carbon is transformed are poorly constrained (Husic et al. 2017; Simon et al. 2010; Simon et al. 2007). Recent efforts have been made to characterize and measure the flux of dissolved organic matter and TOC in subsurface fluvial karst systems (Husic et al. 2017; Simon et al. 2010; Simon et al. 2007). These studies focus on sediment flux along with the dissolved and particulate organic carbon content in cave streams. In cases where the TOC concentration of clastic cave sediments has been reported, ranges of TOC vary widely depending on the climatic conditions and surface connectivity of the cave system. Tropical caves have more microbial biomass and are more microbially active (de Paula et al. 2016) and, as a result, are assumed to have higher concentrations of sediment TOC; however, in the limited data reported for clastic cave sediments, this is not the case. The amount of TOC in clastic cave sediments appears to depend on their age, connectivity of the system to the surface, and geologic and geomorphologic history of the system (Bottrell 1996; de Paula et al. 2020; de Paula et al. 2016; Downey 2020; Panno et al. 2004).

The TOC concentration of any sediment or soil positively correlates to the soil adsorption coefficient of that material and its ability to act as a sorbent for organic compounds (Schwarzenbach et al. 2003). These parameters are often reported in different types of soil and sediments but rarely reported for clastic cave sediments or karst aquifer sediments. In karst systems, few connections have been made regarding the introduction of contaminants into these systems via sediment pulses or the transport of these contaminants to the surface or downstream receptors (springs, etc.) during subsequent storms. It is well documented that cave and karst systems can store and transport sediments (Bretz 1942; Ford and Williams 2007; Herman et al. 2008; Mahler et al. 2007; Mahler 1999) and any contamination associated with incoming sediments can be stored and transported as well. Contaminants can also enter the aquifer independently through runoff and percolation through the soil and epikarst. This has been documented for volatile organic compounds and other emerging and legacy contaminants in the northern karst aquifers of Puerto Rico (Ghasemizadeh et al. 2015; Padilla et al. 2011). However, the amount of TOC in these sediments and whether it is a controlling factor in storage and transport has not been constrained. Therefore, measuring the range of TOC in clastic sediments is important for understanding and exploring the role of cave and aquifer sediments in contaminant fate and transport. Clastic cave sediments are protected from surface erosional processes but may undergo physical or chemical transformations within the cave. Land-use, geomorphology, and climatic changes will influence the amount of sediment being injected and its potential reworking in the cave. The origin, chemistry, and chemical behavior of clastic cave sediments receives little attention or analysis compared to speleothems and cave precipitates. The role of these clastic sediments may play a pivotal role in contaminant storage and transport (Mahler 1999) and supporting the cave ecosystem (Barton and Jurado

2007; Husic et al. 2017) as well as providing clues as to the paleohydrology and paleoclimate during the deposition of these sediments.

The purpose of this investigation is to physically describe clastic cave sediment deposits and measure the range of TOC concentration, total nitrogen (TN) concentration, and particle size distribution in Butler Cave, Virginia, USA with respect to cave sediment depositional facies and distance from sediment input. TOC concentrations ranged from 0.08–0.87 weight percent and TOC:N ranged from 3–15. The diamicton facies was sandier and had a similar TOC concentration to the channel facies, although the core samples in the channel facies had more TOC than core samples in the diamicton facies. TOC concentrations measured in Butler Cave were within the same range as those observed in unsaturated, eogenetic clastic cave sediments in Puerto Rico and Brazil. Estimated retardation factors calculated based on the TOC concentrations in the Butler Cave sediments indicate the range of TOC in this cave could be responsible for 39–987% increase in retardation of selected phthalates and volatile organic compounds.

# Site Description And Methods

Butler Cave was chosen for this study because the cave sediments are abundant and have been previously studied in regard to physical characteristics and mineral content. Butler Cave, located in Bath County Virginia (VA), USA is in a karst valley known as the Burnsville Cove (Fig. 1). Structurally, the valley contains a series of southwest-northeast trending folds formed during the Alleghenian Orogeny (325–270 million years ago) which resulted in layers of limestone being folded and faulted, resulting in units thick enough to support major cave development (Swezey et al. 2017). The Chestnut Ridge Anticline is the main fold axis in the valley, and it is flanked by the White Oak Syncline to the southeast and Sinking Creek Syncline to the northwest. The main trunk of Butler Cave formed along the Sinking Creek Syncline with secondary passages forming along dip on the western side of the syncline (Swezey et al. 2017). The Tonoloway Formation, a Devonian limestone with interbedded sandstones, is the rock unit which forms the cave (Fig. 1).

The sediments in Butler Cave consist of speleothems and clastic deposits. The clastic deposits, the focus of this investigation, were likely washed into the cave during various flooding events and range in size from clays to boulders (White 2015). Some of the sediments of Butler Cave have been reworked and transported by the active cave stream. The sediments were described and placed into a facies classification by Bosch and White (2004) and later White (2015). The classification system consists of five different facies based on particle size, particle sorting, and potential fluvial deposition conditions of the deposit. The framework for the facies names and descriptions are based on depositional studies of sediments in other caves and in other settings, such as glacial (Gillieson 1986; Pickle 1985; Springer and Kite 1997; Valen et al. 1997). The facies described for Butler Cave by Bosch and White (2004) include 1) backswamp facies – fine grained, poorly sorted muds and silts that show minimal stratification and are not deposited or reworked by active cave streams; 2) thalweg facies – large grained, well sorted boulders, gravels, and cobbles from which fine grained material has been winnowed away; 3) slackwater facies – fine grained, well sorted clays and silts often with layering, deposited by settling out of turbid flood waters; 4) channel facies- moderately size, moderately sorted interbedded silts and sands that often show stratification and are deposited by active cave streams; and, 5) diamicton facies – a poorly sorted, chaotic dump of cobble to silt size particles resultant from large

debris flows into the cave, also described by Gillieson (1986). Channel and diamicton facies are well represented and described in Butler Cave and represent two extremes of clastic sediment working in caves – large pulses from outside events like floods (diamicton) and sediment transport and reworking within caves (channel). The mineralogy of the Butler Cave sediments is dominated by quartz, with iron oxides, zircons, rutile, and other trace minerals (Chess et al. 2010). Paleomagnetic analysis of channel deposits in Butler Cave showed normal polarity while sediments from dip passages had reversed polarity, indicating deposition dates prior to 780,000 years before present.

For this investigation, six locations (Fig. 1) were chosen for sediment sampling. Grab samples were obtained from a sediment bank using pre-cleaned stainless-steel instruments; core samples were obtained by inserting a ~ 5 x 30.5 cm polyethylene tube into the barrel of a stainless-steel split-spoon corer and using a sliding hammer to drive the tube into the sediment bank. If the tube was filled before failure, a second tube was inserted, and sampling continued until failure. The grab samples were stored in plastic bags or amber glass jars; core samples were capped and tightly wrapped in their core sleeves. All samples were stored on ice during transportation to laboratory. Upon arrival at the laboratory, samples were refrigerated and kept out of direct light until preparation and analysis. Physical description of the sediments was completed for the sediment deposits in the field and for the grab and core samples in the laboratory. Core samples were subsampled based on observed changes in color or grain size. In total, 33 samples were collected for particle size distribution and chemical analysis (Table 1). Samples were analyzed for particle size, total carbon (TC), TN, and total inorganic carbon (TIC).

Table 1
Butler Cave data summary: sample schema, sediment type, particle size fraction, and chemical results for the ≤ 2mm fraction

| Location | Facies Represented | Sample Type | Core sample depth, cm + | Sample Number | Sediment Type | TOC wt% | N wt% | TOC:N |
|---|---|---|---|---|---|---|---|---|
| 001 | Diamicton | Core | 0–13 | 1A | very coarse silty fine sand | 0.11 | 0.02 | 5.5 |
| | | Core | 13–26 | 1B | very coarse silty fine sand | 0.08 | 0.02 | 4.0 |
| | | Grab | – | 1C | very coarse silty fine sand | 0.20 | 0.04 | 5.5 |
| | | Grab | – | 1D | fine sandy very coarse silt | 0.37 | 0.05 | 7.4 |
| | | Grab | – | 1E | fine sandy fine silt | 0.18 | 0.04 | 4.5 |
| 002 | Channel | Core | 0–4.5 | 2A | very coarse silty fine sand | 0.31 | 0.03 | 10.3 |
| | | Core | 5–9.5 | 2B | very coarse silty fine sand | 0.87 | 0.08 | 10.9 |
| | | Core | 9.5–27 | 2C | very coarse silty fine sand | 0.36 | 0.04 | 9.0 |
| | | Core | 27–42.5 | 2D | fine sandy very coarse silt | 0.27 | 0.03 | 9.0 |
| | | Grab | – | 2E | fine sandy fine silt | 0.40 | 0.04 | 10.0 |
| 003 | Channel | Core | 0–22 | 3A | poorly sorted medium sand | 0.45 | 0.03 | 15.0 |
| | | Grab | - | 3B | very coarse silty medium sand | 0.40 | 0.04 | 10.0 |
| 004 | Channel | Core | 0 | 4A | very coarse silty very fine sand | 0.26 | 0.03 | 8.7 |
| | | Core | 1–5 | 4B | very coarse silty fine sand | 0.12 | 0.02 | 6.0 |

TOC = total organic carbon; TOC:N is the molar ratio between organic carbon and nitrogen. *The facies for these locations have not been previously described in literature and was estimated based on physical description and observation. +Core sample depths are relative to the top of the sediment bank where the top = 0 cm. Ranges are given for where the respective sample was collected

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Core | 5–8 | 4C | fine silty fine sand | 0.16 | 0.03 | 5.3 |
| | | Core | 8–11 | 4D | very coarse silty fine sand | 0.12 | 0.02 | 6.0 |
| | | Core | 11–14 | 4E | very coarse silty fine sand | 0.20 | 0.03 | 6.7 |
| | | Core | 14–20 | 4F | fine silty fine sand | 0.12 | 0.02 | 6.0 |
| | | Core | 20–21 | 4G | very coarse silty fine sand | 0.21 | 0.03 | 7.0 |
| | | Core | 22–30 | 4H | muddy fine sand | 0.11 | 0.02 | 5.5 |
| | | Core | 30–45 | 4I | very coarse silty fine sand | 0.14 | 0.03 | 4.7 |
| | | Core | 45–47 | 4J | very coarse silty fine sand | 0.14 | 0.02 | 7.0 |
| | | Grab | – | 4K | very coarse silty fine sand | 0.10 | 0.02 | 5.5 |
| | | Grab | – | 4L | fine silty medium sand | 0.12 | 0.02 | 5.8 |
| | | Grab | – | 4M | fine silty medium sand | 0.10 | 0.02 | 5.2 |
| | | Grab | – | 4N | fine silty medium sand | 0.16 | 0.02 | 6.8 |
| | | Grab | – | 4O | fine silty medium sand | 0.15 | 0.02 | 7.3 |
| 005* | Channel or slackwater | Grab | – | 5A | very coarse silty fine sand | 0.29 | 0.03 | 9.8 |
| | | Grab | – | 5B | very coarse silty fine sand | 0.16 | 0.04 | 4.0 |
| 006* | Slackwater | Core | 0–3 | 6A | fine sandy very coarse silt | 0.21 | 0.03 | 7.0 |
| | | Core | 3–9 | 6B | very fine sandy very coarse silt | 0.13 | 0.03 | 4.3 |

TOC = total organic carbon; TOC:N is the molar ratio between organic carbon and nitrogen. *The facies for these locations have not been previously described in literature and was estimated based on physical description and observation. [+]Core sample depths are relative to the top of the sediment bank where the top = 0 cm. Ranges are given for where the respective sample was collected

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Core | 9–16 | 6C | very fine sandy very coarse silt | 0.14 | 0.04 | 3.5 |
| | Core | 16–23 | 6D | very fine sandy very coarse silt | 0.12 | 0.04 | 3.0 |

TOC = total organic carbon; TOC:N is the molar ratio between organic carbon and nitrogen. *The facies for these locations have not been previously described in literature and was estimated based on physical description and observation. [+]Core sample depths are relative to the top of the sediment bank where the top = 0 cm. Ranges are given for where the respective sample was collected

Sediment samples were prepared for particle size analysis by air drying in a fume hood for approximately 48 hours and then in an oven at 60 C for approximately 24 hours. The sediments were then sieved to $\leq$ 2 mm to separate the active fraction (0.2 µm – 2,000 µm) of the sediments which consists of clay (< 2 µm), silt (2–50 µm), and sand (0.05–2.0 mm). This fraction controls the physical and chemical processes of the sediment due to the high surface area relative to the coarser particles (> 2 mm). The samples were then mixed in a 1: 1.5 sediment to 5% Calgon® mass ratio solution and shaken at 70 rotations per minute on a rotary shaker for ~ 24 hours to fully disperse the particles. Particle size was measured using a Beckman Coulter single wavelength LS13-320 particle size analyzer, measuring from 0.4 µm – 2,000 µm. The particle size data are reported in volume percent; the raw data was organized in R and processed using the GRADISTAT program (Blott and Pye 2001) to determine volume percent of sand, silt, and clay.

For TC and TN analysis, samples were air-dried for 24 hours, lightly homogenized using an agate mortar and pestle, sieved to $\leq$ 2 mm, and then oven-dried at 60 C for 24 hours. TC and TN were measured on a Carlo Erba NA1500 CNHS elemental analyzer at the University of Florida Stable Isotope Mass Spectroscopy Laboratory in Gainesville, Florida. This instrument flash combusts the sample and the resultant gas is passed through a reduction column where oxygen is removed, and water is trapped. The remaining gas is passed through a 125 C chromatography column that separates the $CO_2$ and $N_2$ gases. TIC was measured by acidifying the sediment in an $N_2$ environment and quantifying the degassed $CO_2$ using an UIC 5017 $CO_2$ coulometer. TOC is determined as the difference between TC and TIC. TC, TN, and TOC are reported as a weight percent (wt %) by sample.

## Results

# Physical Description

Sample location 001 was collected from a diamicton facies (Bosch and White 2004) at the end of a passage known as Dave's Gallery (Fig. 1). One core sample was collected from the top of sediment bank with a recovery of 26 cm and three grab samples were collected from the face of the sediment bank between the bottom of the core toward the cave floor (Fig. 2a). The sediment bank consisted of a finer grained sandy cap over a thicker, gravel sized deposit (Fig. 2a). Based on field observations, the coarser sediments were poorly sorted, angular to subangular, and unsaturated. The core sample was split open in the laboratory and

appeared to be consistent in grain size and color (brownish yellow, 10 YR 6/6 on the Munsell color chart. Although no visible change in grain size or color was observed, the core was subsampled in two sections of roughly equal length for analyses (Fig. 2a). Sample location 002 was collected from the dry stream bed in a passage known as Sand Canyon. Although the stream was dry at the time of sampling, it is known to flow intermittently. Two consecutive cores with total recovery of 43 cm and one grab sample from the top of the cored area were collected. The core samples were subsampled in four sections based on visible change in grain size. The color of the core samples was dark yellowish brown (10 YR 4/5 Munsell color chart), and no distinct stratification or layering was observed. Sample location 003 was collected from the same bank deposit as 002 but slightly downstream and higher (relative to the stream bed) in the deposit stratigraphy than location 002. One core sample with 22 cm of recovery was collected and one grab sample from the bottom of the core was collected. Overall, the core sample was observed to be yellowish brown in color (10 YR 5/6 on the Munsell color chart). Sample location 004 was collected from an approximately 225 cm tall bank around the bend from Sand Canyon. Two consecutive core samples were collected from the top of the bank with total recovery of 45 cm. Five grab samples were collected from the face of the bank moving down to represent the entire bank from top to bottom, save for the last ~ 50 cm which consisted of large gravels and small boulders. The sediments appeared to be well sorted but varied in grain size from sand to large boulders (Fig. 2b). The core samples were subsampled in 10 total sections. The top 20 cm of the core had distinct layers of sand and silt sized particles that were light yellowish brown (10 YR 6/4) and dark yellowish brown (10YR 4/4), respectively. The bottom 17 cm of the core was mostly sandy with a smaller, clay-like layer between 14 – 16 cm (Table 1). The sandier bands were much thicker than the smaller particle size bands and were light yellowish brown (10 YR 6/4) while the smaller particle band was dark yellowish brown (10 YR 4/4). Sample locations 002 through 004 represent the channel facies (Bosch and White, 2004). Sample location 005 was collected from a sediment bank consisting of mostly sand sized particles capped by a smaller silt or clay-like textured sediment. One grab sample of the sand and one of the clay-like sediment were collected. This location has not been previously categorized according to the facies classification system but may represent channel or slackwater facies. Finally, sample location 006 was collected from a sediment bank further back in the cave and close to an active stream. One core sample of 23 cm recovery was collected and subsampled in four sections. While above water at the time of sampling, this core contained much more moisture when split open than other sediment cores collected in during this sampling event. This location was also not previously categorized in the facies classification scheme but may represent slackwater facies. The total list of samples and sample naming schema is listed in Table 1.

# Particle Size Analysis: Active Fraction, < 2mm

All samples were sieved  2 mm to obtain the active size fraction and these materials were analyzed for particle size. All samples at locations 001, 002, 003, 004, and 005 were classified as some type of sand (Table 1), ranging from fine to coarse, except for four samples at locations 001 and 002 that were classified as fine to coarse silts (Table 1). All the samples from location 006 were classified as course silts (Table 1). The volume percent for all the samples ranged from 16.2% – 91.4% sand, 6.1% – 83.8% silt, and 0%  – 12.7% clay. The highest sand content was at location 003 and the lowest was at location 006 (Fig. 3).

The TC concentrations ranged from 0.08 – 0.87%: the lowest concentration was at location 006 and the highest at 003. TOC also ranged from 0.08 – 0.87 % because some samples had zero measurable TIC concentrations. Location 002, in the active cave stream, had the highest average TOC while location 004 (the location with the largest grain size) had the lowest. A linear regression between TC and TOC data including all samples had slope = 0.91 ($R^2$ = 0.92), indicating that most of the carbon in all the samples was TOC. Location 001 had the largest range of TOC with slight positive skew while location 004 had a smaller range of TOC with close to normal distribution. Location 003 had the highest median TOC and location 006 had lowest median TOC (Fig. 4a).

Microbial uptake of nitrogen is a driver of organic carbon decomposition in surface leaf and root litter (Ravn, 2020); however, in caves total nitrogen is often low (and as a result the C:N ratio is low), thus slowing down the rate of organic carbon decomposition. (Ravn, 2020). Reporting TOC and N concentrations can provide information on how microbial activity may be supported in the caves and how this may contribute to carbon processing in caves. TOC:N ratios were compared to the average C:N ratios of amino acids, 3.15, (Jover et al. 2014) and C:N range of humic and fulvic acids, 6.23 - 147, (Rice and MacCarthy 1991), respectively. The C:N ratio of amino acids generally represents a microbially-based source of organic carbon (Jover et al. 2014) whereas humic and/or fulvic acids represent the heterogenous, molecular organic components of soil organic matter (Rice and MacCarthy 1991). The TOC:N molar ratio range across the six locations was 3 – 15 with the highest and lowest concentrations represented at locations 006 and 003, respectively. Location 001 and location 003 have the largest range of TOC:N but location 003 has the highest median and average of TOC:N. Location 006 has the lowest median TOC:N (Fig. 4b). Most of the TOC:N data fall above the average amino acid ratio and slightly below or well within the humic and fulvic acid range (Fig. 5). This could possibly indicate that the TOC in these samples is largely a result of soil organic matter that has been washed into the cave. Interestingly, three out of the four samples collected from the core at location 006 had a TOC:N ratio at or below 3.5 and this location also had the lowest average TC and second lowest average TOC. This could possibly indicate that the further away from source input a sample is, the less likely terrestrial OC is to be washed that deep and that microbial signatures of TOC dominate any TOC that is present even if TOC concentrations are comparatively lower.

Some of the sample locations had a positive linear relationship between the percentage of silt-sized particles and TOC but this was not true across the entire sample set. A positive linear relationship was observed in each of the diamicton facies (location 001) and channel facies (location 004) between the silt-sized fraction and TOC but not between the clay-sized fraction and TOC. For the channel facies, when the core and grab samples were compared individually, the core samples had a linear relationship in silt-sized particles and TOC, but the grab samples did not. At location 006 where silt was the dominant sized fraction, a negative linear relationship was observed between the silt-sized fraction and TOC, but a positive linear relationship was observed between the clay-sized fraction and TOC. It should be noted that small sample sizes and data clusters around high silt-size percentages and low clay-size percentages could be skewing these relationships. The data presented here show that large ranges organic carbon content can occur in clastic cave sediments across grain sizes and lithofacies.

# Comparison of channel and diamicton facies, > 2 mm fraction

The samples collected at locations 001 and 004 were selected to compare the diamicton (poorly sorted, chaotic dump of cobble to silt size particles resultant from large debris flows into the cave) and channel facies (moderately sized, moderately sorted interbedded silts and sands that often show stratification and are deposited by active cave streams). These locations were chosen based on previous mapping and descriptions (Bosch and White 2004) and each represent a potential different mechanism of clastic sediment deposition and processing in caves.

For the active fraction of the diamicton facies (location 001), the samples mostly consisted of sand-sized grains although the three grab samples had slightly more silt than the core samples (Fig. 6a). In the diamicton facies, TOC ranged from 0.08 – 0.37 % (Fig. 6b) and TOC:N ranged from 4 – 7.4 (Fig. 6b). There was an increase in TOC and TOC:N with depth from the top of the bank with the exception of location 1E (the bottom of the bank) which had a marked decrease in TOC and TOC:N (Fig. 6c, d). This could be due to the overall large grain size dominating the sample, based on field observations. Most of the TOC:N ratios fell between the average amino acid range but below the range of humic and fulvic acids (except for 1D). Given the inferred source of a diamicton facies, these samples are likely dominated by terrestrial TOC. There is a decrease in grain size with depth of sample (Fig. 6c) with sand making up 86% of the active fraction at the top of the bank and decreasing to only 45% at the bottom. The observed overall grain size at the bank (sand to boulder) was observed to increase from the top of the bank to the bottom of the bank. However, since this facies represents a large, chaotic injection of sediment, it is not advised to interpret this as a depositional feature with regard to depth in the same way one would consider it in a surface sedimentological setting.

Welch's t-test was performed to compare the means values of the sand, silt, clay, TOC, and TOC:N between the grab (n = 2) and core (n = 3) samples at location 001. The result showed a significant difference (a = 0.05) in the mean for the sand and silt size fractions (p  0.05) where the mean sand-size percentage was greater in the core samples and the mean silt-size percentage was greater in the grab samples. The remaining variables have no significant difference in means. However, because each sample size is small, these results should be interpreted with caution since Type I or Type II errors can be common in low sample size populations.

In the channel facies at location 004, the bank is capped by a sandy deposit approximately 47 cm thick and then increases in grain size down the bank from gravel to boulder. The samples are mostly sand sized with some core samples being slightly siltier than the grab samples (Fig. 7a). The core samples have alternating high percentages of sand and silt with depth in the first 20 cm which is consistent with described interbedded sands and silts that are descriptive of channel facies. The grab samples had a more consistent grain size with depth which is likely due to an overall larger grain size (cobble and boulder) dominating the deposit as observed during sample collection. The TOC ranged from 0.1 – 0.26 % and TOC:N ranged from 4.7 – 8.7 (Fig. 7b) with six samples in the humic and fulvic acid range and nine samples between the humic and fulvic acid range and the amino acid average (Fig. 7b). The TOC source in these samples is likely terrestrial. The core samples show an alternating pattern of increasing and decreasing TOC concentrations and TOC:N ratios with depth (Fig. 7c, d) which is indicative of the interbedded sands and silts characteristic of channel facies.

Results from Welch's t-test between the core and grab samples at location 004 also showed a significant difference (a = 0.05) in the means of the sand and silt size fractions (p  0.05) where the mean sand percentage was greater in the grab samples and the mean silt percentage was greater in the core samples. Differences in the core and grab samples could be due to the overall differences in grain size or exposure of the grab samples to the ambient cave environment.

A significant difference (a =0.05) was observed between the core samples at location 001 and 004 for the means of sand, silt, and TOC; the mean sand percentage was greater in the diamicton facies (001), but the mean TOC and silt percentage was greater in the channel facies (004). Since organic carbon is often associated with smaller size fractions, it is reasonable that a siltier sediment (004) will have more TOC than a less silty sediment, which is supported by these statistics. Grab samples between the diamicton and channel facies had a statistical difference (a = 0.05) only in the sand and silt size fractions where the mean sand percentage was greater at in the channel facies and mean silt was greater in the diamicton facies. It is possible error is present in this analysis due to the large difference in sample size (location 004 had three times more samples collected than location 001) and the overall low number of samples available at 001. The observed differences in the data suggest there could be a difference in the active fraction particle size and chemistry of these two sediment lithofacies. The differences in core and grab samples could be due to the sampling method, where coring is more likely to capture smaller particles than grab sampling. However, the core samples in the diamicton facies were sandier (coarser) than the grab samples.

## Discussion

# Comparison to other clastic cave sediments

Tropical caves, like those in Puerto Rico or Brazil, present an interesting comparison to temperate caves, like Butler Cave. Tropical caves in eogenetic karst settings, such as in the Caribbean, frequently receive large injections of sediments from tropical storms and hurricanes (van Hengstum et al. 2014). In 2018 and 2019, sediment samples were collected from two different caves in Puerto Rico: El Tallonal (TAL) Cave and Cueva Clara - Rio Camuy (CAM) Cave (Downey 2020). TAL cave is a privately owned cave with an active stream. Cueva Clara is part of the dry section of the Rio Camuy Cave system. It is in the Parque Nacional de las Cavernas del Rio Camuy in Quebrada, Puerto Rico and is a show and wild cave that is open for tours to the public. Rio Camuy experienced large sediment injections during Hurricane Maria in 2017 (Miller, 2018) and some of these sediments were collected as part of the study by Downey (2020). The TAL sediments in this study consisted of both saturated and unsaturated sediments found, respectively, below and above the level of the stream. Downey (2020) reported that TOC in unsaturated sediments ranged from 0.13–0.73% (Downey 2020), which is comparable to the Butler Cave samples collected in this study. Downey reported that the TOC in saturated sediments ranged from 0.11–2.36%. Most of the carbon in these TAL samples was organic in form. The TOC:N ratio for all the Puerto Rico sediments ranged from 0–34 (Downey 2020) with most samples falling in the typical range for humic and fulvic acids (6.23–147, Rice and MacCarthy 1991). Several of the CAM sediments were at or below the amino acid average (3.15, Jover et al. 2014). The CAM sediments were deposited during Hurricane Maria (they were located on the paved public tour pathways) and thus are younger than the sediments from TAL. The Butler Cave sediments described here have a similar range of

TOC:N to the unsaturated TAL sediments but much lower overall TOC concentrations than the unsaturated TAL sediments (Fig. 8). In general, microbial activity in tropical sediments and soils is likely to be much higher (de Paula et al. 2020) than in temperate sediments and soils, such as Butler Cave. This is likely why the Puerto Rico sediments have much higher TOC content overall, even though the Butler Cave sediments are also unsaturated. The similar TOC:N ratios result from overall low N concentrations in both the temperate (Butler Cave) and tropical caves (Puerto Rico), which is a common feature of oligotrophic environments. Based on Welch's t-test, a significant ($\alpha = 0.05$) difference was observed between the mean TOC concentration of Butler Cave and the mean TOC concentration of the saturated and unsaturated El Tallonal sediments, the Rio Camuy sediments, and all the Puerto Rico cave sediments as a group: Butler Cave had a significantly lower mean TOC concentration than all of the other groups.

The TOC for the Butler Cave clastic cave sediments fall within the range of TOC reported for several caves in Brazil, 0.004–1.31% (de Paula et al. 2020; de Paula et al. 2016) for various locations and through wet and dry seasons. In the Brazil caves in which N was reported, concentrations ranged from $8x10^{-7}$ – $1.95x10^{-5}$ wt % (de Paula et al. 2020), much lower than what is reported for the Butler Cave or Puerto Rico cave sediments. This may indicate possible microbial N immobilization – the conversion of inorganic N to organic N- in the Brazil sediments. Microbial biomass was isolated from the Brazil cave sediments and samples were incubated to promote reproduction. Respiration rates were estimated by quantifying $CO_2$ released from the incubated samples. Respiration rates were observed to be higher in the wetter seasons and a positive correlation was observed between microbial biomass carbon and sediment TOC in both wet and dry seasons (de Paula et al. 2016). The Butler Cave sediments have TOC concentrations within the range of both tropical settings (although overall, the Brazilian samples had much lower TOC concentrations on average than the Butler Cave or Puerto Rico cave sediments), less N than the Puerto Rico cave sediments, and more N than the Brazilian cave sediments. This indicates that multiple climatic (humidity, temperature) and geologic factors (saturation, surface connectivity) are controlling the sediment processing in caves in different regions.

Similar TOC concentrations (Table 2) have been reported for comparable temperate caves in England (Bottrell 1996) and in Illinois, USA (Panno et al. 2004). Bottrell (1996) reported an overall decrease in TOC with core depth, similar to in Butler Cave but the greater range of TOC reported by Bottrell (1996) could be due to the short length of the time of those sediments had been underground (< 7 years). However, the generally held notion that tropical caves contain more organic carbon may not be necessarily true given the comparisons between the tropical and temperate settings described here. Welch's t-test showed that mean TOC concentration at Butler Cave was significantly ($\alpha = 0.05$) higher than the TOC concentration reported by Panno et. al. (2004) in Illinois cave sediments but lower than the mean TOC concentration reported Bottrell et al. (1996) in England (Table 2b). Of the studies compared using Welch's t-test, the highest to lowest mean TOC were England (1.1 %, Bottrell 1996), TAL (0.7 %, Downey 2020), CAM (0.4 %, Downey 2020), Butler Cave (0.22, this study), and Illinois (0.12%, Panno et al. 2004). Based on these limited data, the highest TOC concentrations were observed in the most recently deposited sediments. The CAM sediment samples (highest TOC = 3.43%) were deposited within two years of collection and the England cave sediments (highest TOC = 3.37%) were deposited within seven years of collection (Bottrell 1996). Generally, between sites, higher TOC concentrations were observed in saturated or wetter sediments vs. unsaturated or drier sediments and for those sediments where ages were available, older sediments had less TOC than younger sediments (Table 2).

Although more data are needed to confirm this, it is likely that saturation and sediment age (beginning from time underground) may be more important in determining sediment TOC concentration than climate/geographic location.

Table 2
Comparison of maximum and minimum TOC values across climatic settings

| | | Highest Reported TOC wt % | | | Lowest Reported TOC wt % | | |
|---|---|---|---|---|---|---|---|
| **Climate** | **Location** | **TOC** | **In-situ wetness** | **Sediment Age** | **TOC** | **In-situ wetness** | **Sediment Age** |
| Temperate | Butler Cave | 0.87 | Ephemeral cave stream | Unknown | 0.08 | Unsaturated | ~ 70,000? |
| Temperate | England | 3.37 | Unknown | < 7 years | 0.4 | Unknown | < 7 years |
| Temperate | Illinois | 0.5 | Unknown | Modern | 0.02 | Unknown | ~ 35,000 B.P. |
| Tropical | PR TAL unsat. | 0.73 | Unsaturated | Unknown | 0.13 | Unsaturated | Unknown |
| Tropical | PR TAL sat. | 2.36 | Saturated | Unknown | 0.11 | Saturated | Unknown |
| Tropical | PR CAM | 3.43 | Unsaturated | Modern | BDL | Unsaturated | Modern |
| Tropical | Brazil 2020 | 0.12* | Dry season | Unknown | 0.004* | Dry season | Unknown |
| Tropical | Brazil 2016 | 1.31 | Higher soil moisture | Unknown | 0.49 | Lower soil moisture | Unknown |

*These data represent less TOC w.t.% than is expected based on their climate, location, and other data available (Downey, 2020; Panno et. al. 2004; Bottrell, 1996). In-situ wetness refers to various descriptions of the sediment provided by the respective study – e.g. “collected during dry season”; “collected from below water table in saturated conditions”

Table 3
Adsorption coefficients (KD) and retardation factors (RF) based on minimum (min) and maximum (max) TOC value in Butler Cave

| Chemical | Source of $K_{OC}$ values | $K_{OC}$ (measured) | Log $K_{OC}$ | $K_D$ (min) | $K_D$ (max) | $R_F$ min | $R_F$ max | % Increase $R_F$ |
|---|---|---|---|---|---|---|---|---|
| di(2-ethylhexyl)phthalate, DEPH | NCBI 2022 | 510000 | 5.71 | 408 | 4440 | 2111 | 22950 | 987 |
| diethyl phthalate, DEP | EPA Superfund Guidance | 822 | 2.91 | 0.66 | 7.15 | 4.40 | 38.0 | 763 |
| di-n-butyl phthalate, DBP | EPA Superfund Guidance | 1570 | 3.20 | 1.26 | 13.7 | 7.50 | 71.7 | 856 |
| tetrachloroethylene, PCE | EPA Superfund Guidance | 265 | 2.42 | 0.21 | 2.31 | 2.10 | 12.9 | 516 |
| trichloroethylene, TCE | EPA Superfund Guidance | 64.3 | 1.81 | 0.05 | 0.56 | 1.27 | 3.89 | 208 |
| carbon tetrachloride, CT | EPA Superfund Guidance | 152 | 2.18 | 0.12 | 1.32 | 1.63 | 7.84 | 381 |
| 1,2-dichloroethane, DCE | EPA Superfund Guidance | 38 | 1.58 | 0.03 | 0.33 | 1.16 | 2.71 | 134 |
| dichloromethane, DCM | EPA Superfund Guidance | 10 | 1.00 | 0.08 | 0.09 | 1.04 | 1.45 | 39 |

Estimated $K_D$ and $R_F$ values for chemicals frequently detected in Puerto Rico karst (Ghasemizadeh et al., 2015; Padilla et al., 2011). Organic carbon-water partition coefficients ($K_{OC}$) values were obtained from National Center for Biotechnology Information and the EPA Superfund Soil Screening Guidance Part 5: Chemical Specific Parameters. The minimum (0.08%) and maximum (0.87%) TOC concentrations measured in Butler Cave were used to calculate the minimum and maximum $K_D$ and $R_F$ values. For RF, bulk density and effective porosity were estimated from reported values for sandy sediments (Andersen et. al., 2015; Grabowski et. al., 2011; Stringer et. al., 2016; Woessner et. al., 2020)

# Data Implications For Contaminant Fate And Transport, Paleoclimate, And Microbial Activity

The ability of aquifer sediment to store or mobilize contaminants is controlled largely by the TOC of the sediments. The fraction of organic carbon ($f_{OC}$) of a sediment is positively correlated to the adsorption of an organic molecule ($K_D$) via the organic carbon sorption coefficient ($K_{OC}$) where:

$$f_{OC} = \frac{K_D}{K_{OC}}$$ Equation 1.

Simplified, an increase in organic carbon content generally results in greater adsorption of an organic chemical onto the sediment (Schwarzenbach et al. 2003). Even at very low $f_{OC}$, sorption of organic compounds onto sediments and soil is a dominant mechanism in the storage of these contaminants (Schwarzenbach et al. 2003). Common organic contaminants in karst aquifers include volatile organic compounds (VOCs), chlorinated volatile organic compounds (CVOCs), and phthalates (Ghasemizadeh et al. 2015; Padilla et al. 2011). All of these contaminants can adsorb onto sediments in the aquifer matrix which retards their movement through an aquifer. Retardation factors ($R_F$) can be calculated if the $K_D$, bulk density (ρ), and effective porosity ($n_e$) of the sediment are known. For the Butler Cave sediments, estimated $R_F$ values for various contaminants were calculated for the minimum (0.08%) and maximum (0.87%) TOC concentrations reported in Butler Cave (Table 3). Bulk density (ρ) and effective porosity ($n_e$) were averaged from values reported for sandy sediments by Aberson et al. (2011), Grabowski et al. (2011), Stringer et al. (2016), and Woessner and Poeter (2020). Retardation factors ranged from 1.04 for dichloromethane (DCM) to 22,950 for di(2-ethylhexyl)phthalate (DEHP). DEHP has a $K_{OC}$ value three to five orders of magnitude higher than the other contaminants which contributes to its high $R_F$. Excluding DEPHP, the average $R_F$ for the minimum TOC value was 2.73 and average $R_F$ for the maximum TOC value was 19.8 (Table 3). The TOC concentrations in Butler Cave were < 1%, however this is responsible for a 39–97 % increase in $R_F$ for the selected contaminants, highlighting not only the importance of low TOC concentrations in cave sediments and karst aquifers with respect to contaminant fate and transport, but also why it is necessary to know the TOC.

Contaminants adhered to sediments are considered immobile in granular aquifers given the low transmissivity of solid particles through granular systems, thereby resulting in storage and retardation of contaminants (Schwarzenbach et al. 2003). Recent research on colloidal-sized (1 nm – 0.1 μm) particles in contaminant fate and transport has shown the enhanced ability of these particles to move through aquifers (Frimmel et al. 2007; Toran and Palumbo 1992) and carry contaminants via adsorption (McCarthy and Zachara 1989). However, in karst aquifers, particles of any size can be mobilized through fractures and conduits, where the aperture threshold for turbulent flow (and thus the capacity to transport sediment) is between 0.5 and 5 cm (White 1988). These sediments may then be deposited in the aquifer or cave setting or flushed out via springs (Mahler 1999). Organic carbon content of soil and sediment is generally associated with clay and silt-sized particles, but recent studies have shown that organic carbon can be stored on the sand size fraction before the clay and silt size particles are saturated with organic carbon (Yang et al. 2016). Future research into the contaminant transport ability of cave and karst sediments should be careful to consider the organic carbon content across the active fraction, even in low concentrations.

The source of organic carbon in caves and karst aquifers is largely considered to be introduced from ex-situ as a result of pulses of soil and sediment entering the cave from the surface (Mahler 1999). However, dissolved organic carbon carried into a system via recharge water can adsorb onto in-situ sediments in the cave or aquifer. Mahler et. al. (1999) suggested that the amount of organic carbon across a karst system (from surface soil, epikarst, cave sediments, spring discharge, and sinkholes) in conjunction with the

sediment mineralogy could be useful in determining the in-situ and ex-situ components of the TOC of the system. Essentially, the highest organic carbon content is in the surface sediments and the lowest is in the cave sediments and that the relative amount of feldspar in the system is positively correlated to surface sediments. Thus, if a cave sediment has a TOC concentration similar or close to the TOC concentration of the surface sediment and a relatively higher feldspar content, it was likely washed in relatively recently compared to cave or aquifer sediments with lower TOC concentrations and feldspar content. Mahler (1999) used a threshold of 0.4% TOC or higher to consider a sediment to be recently deposited, while any value lower was associated with paleo-fill deposits. While surface samples or mineralogical characterization was not within the scope of this Butler Cave study, concentrations of TOC ranged from 0.08–0.87% and previous mineralogical studies showed that some feldspar is present in the Butler Cave sediments, but it is not the dominant mineral (Chess et al. 2010). This indicates that the source of organic carbon in Butler Cave is likely older but with some modern input related to the ephemeral cave stream since the highest TOC reported in this study were in the active stream portion at location 002. However, this feldspar-TOC relationship should be approached with caution in geological settings where feldspar containing rocks (like volcanics) are adjacent to the karst system, such as in Puerto Rico.

If most organic carbon in cave systems is introduced from the surface, and diverse microbial populations exists in caves, it is likely that these ecosystems source the organic carbon content in cave systems as a nutrient or energy source (Barton and Jurado 2007; Barton and Northup 2007; E. Northup 2001; Northup et al. 2000). de Paula et. al. (2016) isolated several genera of bacteria and fungi in clastic cave sediments and showed that ca. 90% of isolates were metabolically active - not only proving the existence of microbiota in the system but that is also actively participating in the cave ecosystem. In Butler Cave, the organic carbon content of the clastic sediments is lower than what would be expected at the surface, so it is possible that microbial activity has been re-processing the organic carbon content of the sediments. The majority of the TOC:N ratios of the Butler Cave sediments indicate a terrestrial source of organic carbon, but some samples did have TOC:N in the amino acid average range, indicating some microbial activity may be present. Because the breakdown of organic carbon by organisms results in a net release of $CO_2$ (and TOC generation from chemolithotrophs in oligotrophic environments also contributes to a net release in $CO_2$), the TOC of clastic sediments and active microbial populations of cave and karst systems should be considered when evaluating the overall carbon budget of the system.

# Conclusions

The concentrations of organic carbon in deposited cave sediments have remained largely unquantified. The data presented here show that a significant difference exists in the grain size and TOC concentrations in the active fraction of diamicton and channel facies in Butler Cave. The diamicton facies sediment was overall sandier and had less TOC in the core samples but more TOC overall compared to the channel facies sediment. Butler Cave represents a cave in a temperate climate with little modern sediment injection and most of the TOC likely resultant from paleo-filling. The Butler Cave sediments are within the same range of TOC in tropical and temperate caves. Although the amount of data is limited, the comparisons between facies and different caves suggest that higher concentrations of TOC may be associated with younger sediments and influenced by flowing water rather than climatic conditions (tropical vs. temperate). Continued sampling of

cave systems from a variety of climates with different sediment sources and should continue to determine the range of organic carbon that is stored in cave sediments and karst systems. The data presented here also show that TOC can occur across a range of grain sizes; this should be considered when evaluating the role of cave and karst sediments in contaminant fate and transport. Even small TOC concentrations, like those reported for Butler Cave, could potentially be responsible for increases in retardation of organic contaminants through the system and long-term storage of contaminants. Finally, the source and amount of organic carbon can be an indicator of paleoclimate conditions and microbial activity in oligotrophic environments.

# Declarations

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All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Jill L. Riddell and Autum R. Downey. The first draft of the manuscript was written by Jill L. Riddell and all authors commented on previous versions of the manuscript. Dorothy J. Vesper contributed to conceptualization, methodology, revision, editing, and supervision. Ingrid Y. Padilla contributed to review and editing. All authors read and approved the final manuscript.

### Data Availability

All data and code used in this manuscript as well as additional photos of the core collection are publicly available in the GitHub repository for this project: https://github.com/jlriddell12/ButlerCaveSediment

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# Figures

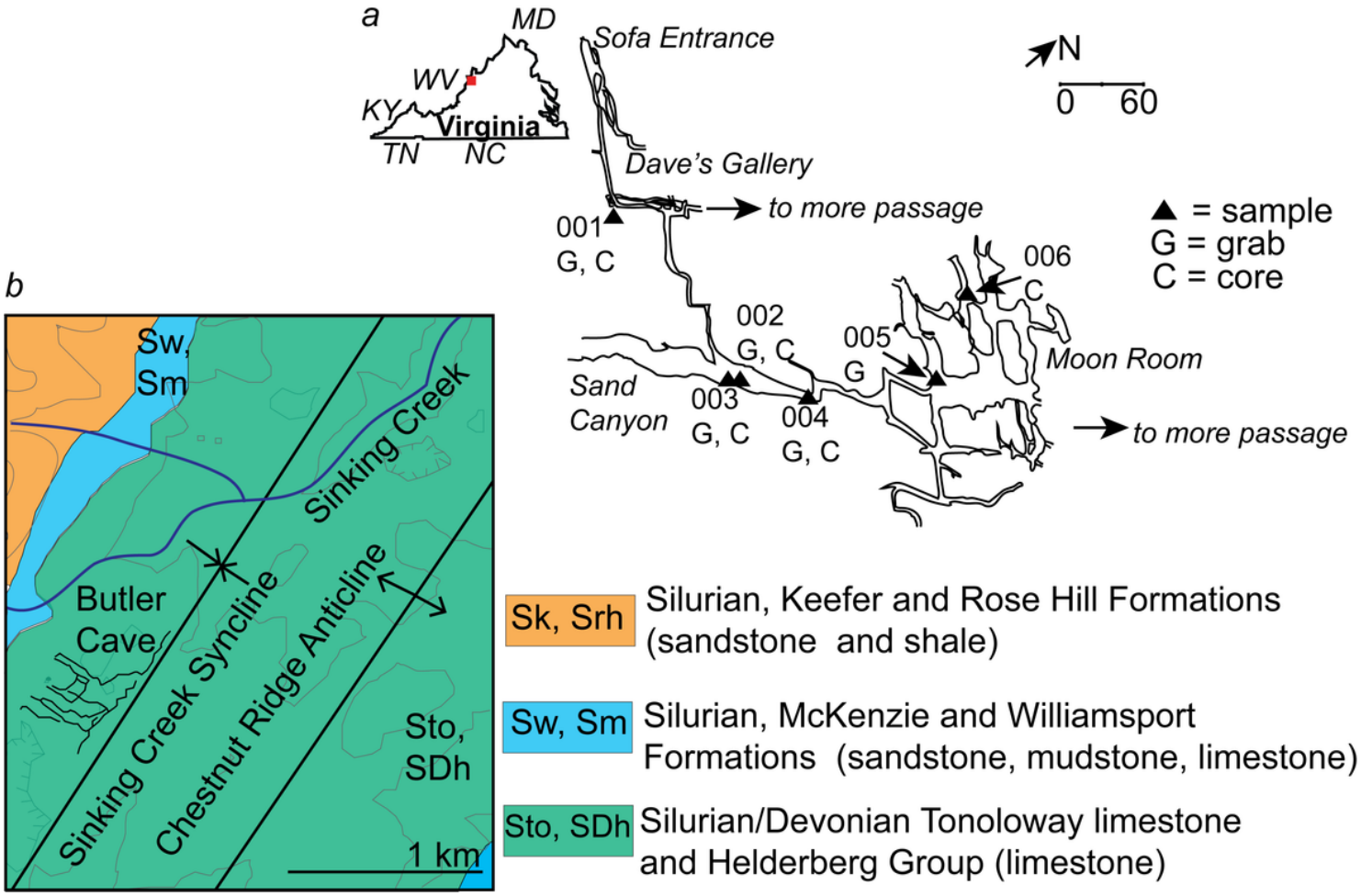
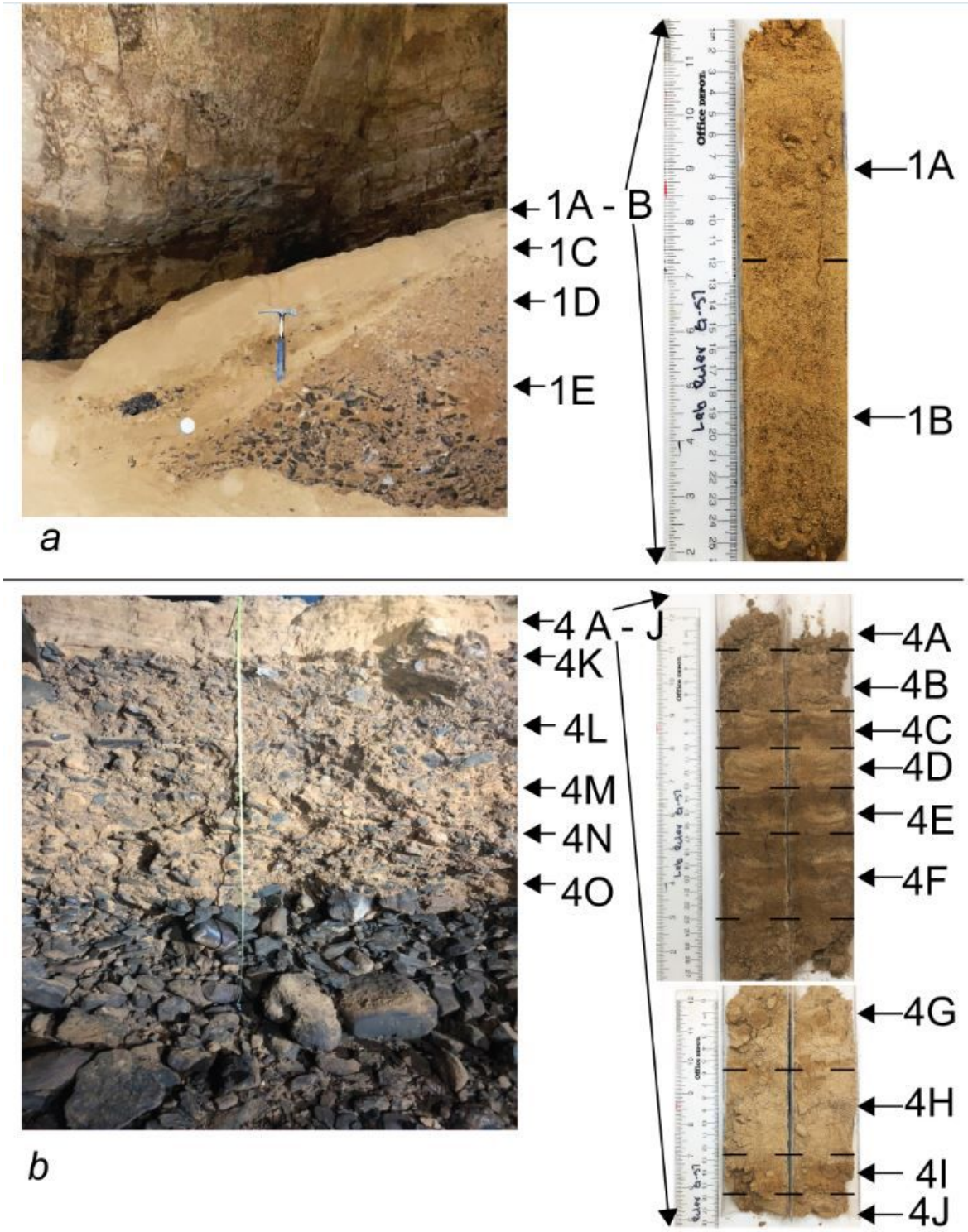



**Figure 1**

Location of Butler Cave in VA and cave map with sample locations indicated with a black triangle and location number. Grab and core samples are indicated with letter G and C, respectively (a). Geology of the Butler Cave area of Burnsville Cove. Butler Cave formed along the Sinking Creek syncline in the Tonoloway limestone and larger Helderberg Group, indicated in green (b). Modified from White (2015) and Swezey et. al. (2017)




## Figure 2

Sample locations 001 (a) and 004 (b). Location 001 shows a smaller grained cap over a relatively unsorted deposit. The core samples (1A and 1B) represent the sandy cap and the grab samples (1C – 1D) represent the unsorted deposit. The core sample was uniform in color and apparent grainsize and was subsampled in two sections(a). Location 004 shows a sorted bank from finer to coarser grains ~2 m in height. The core samples were subsampled in 10 sections (4A- 4J) and represent the upper layer, which had visible color changes and layering. The grab samples (4K – 4O) represent the lower, larger grained section of the deposit (b)

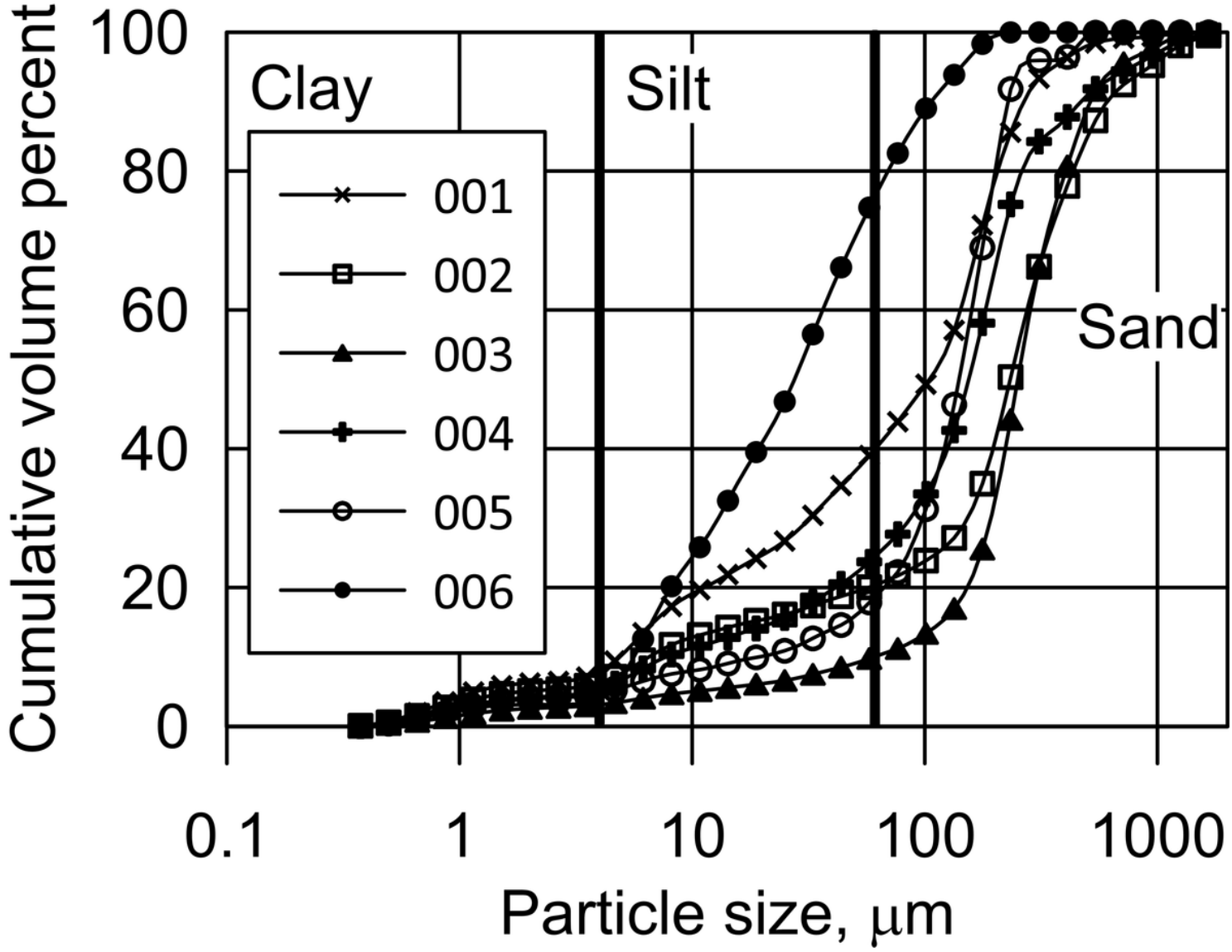



**Figure 3**

Cumulative grain size distributions averaged for all samples collected at each location. Locations 001 – 005 are mostly sandy while location 006 is siltier in comparison. Location 006 is furthest from potential sediment entrance points (relative to the other locations), suggesting that sediments are being continually processed as they are transported through the cave. This results in smaller and more uniform grain size distributions with distance from sediment input

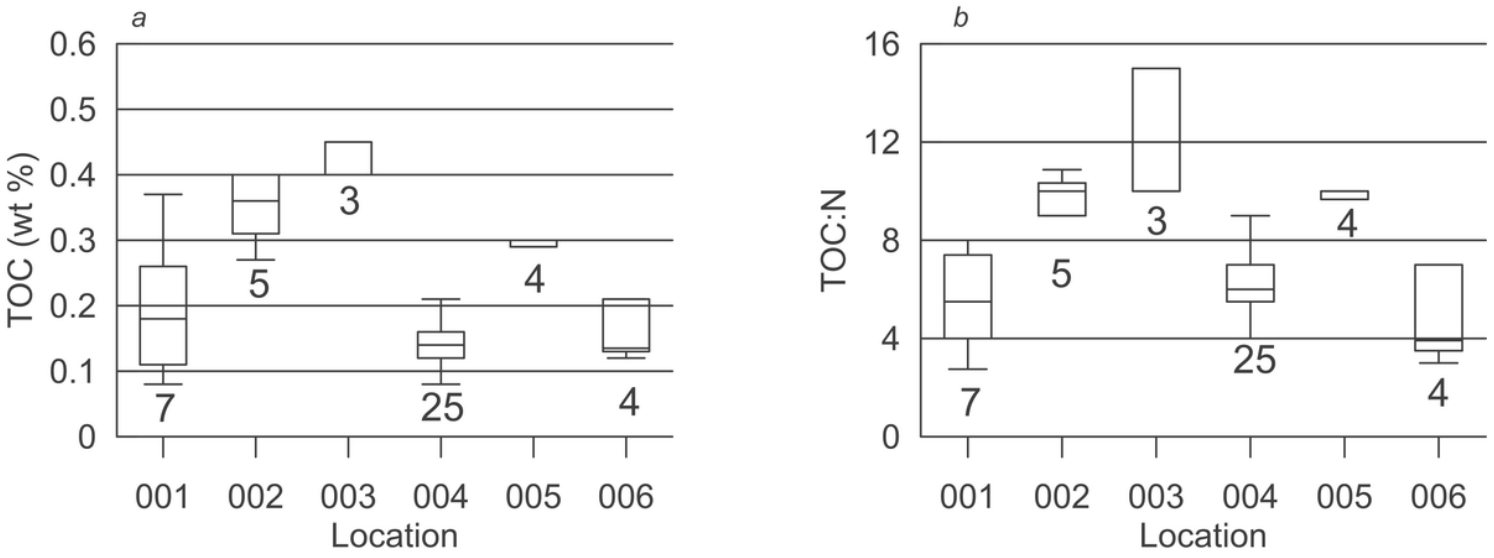



**Figure 4**

Box and whisker plot of TOC wt % showing sample size and distribution across the six locations. Locations 001, 004, and 005 include laboratory duplicates (a). Box and whisker plot of TOC:N ratios across the sampling locations with similar distribution as TOC. Location 004 has n = 23 because two samples had TN = 0. Locations 001, 004, and 005 include laboratory duplicates (b)

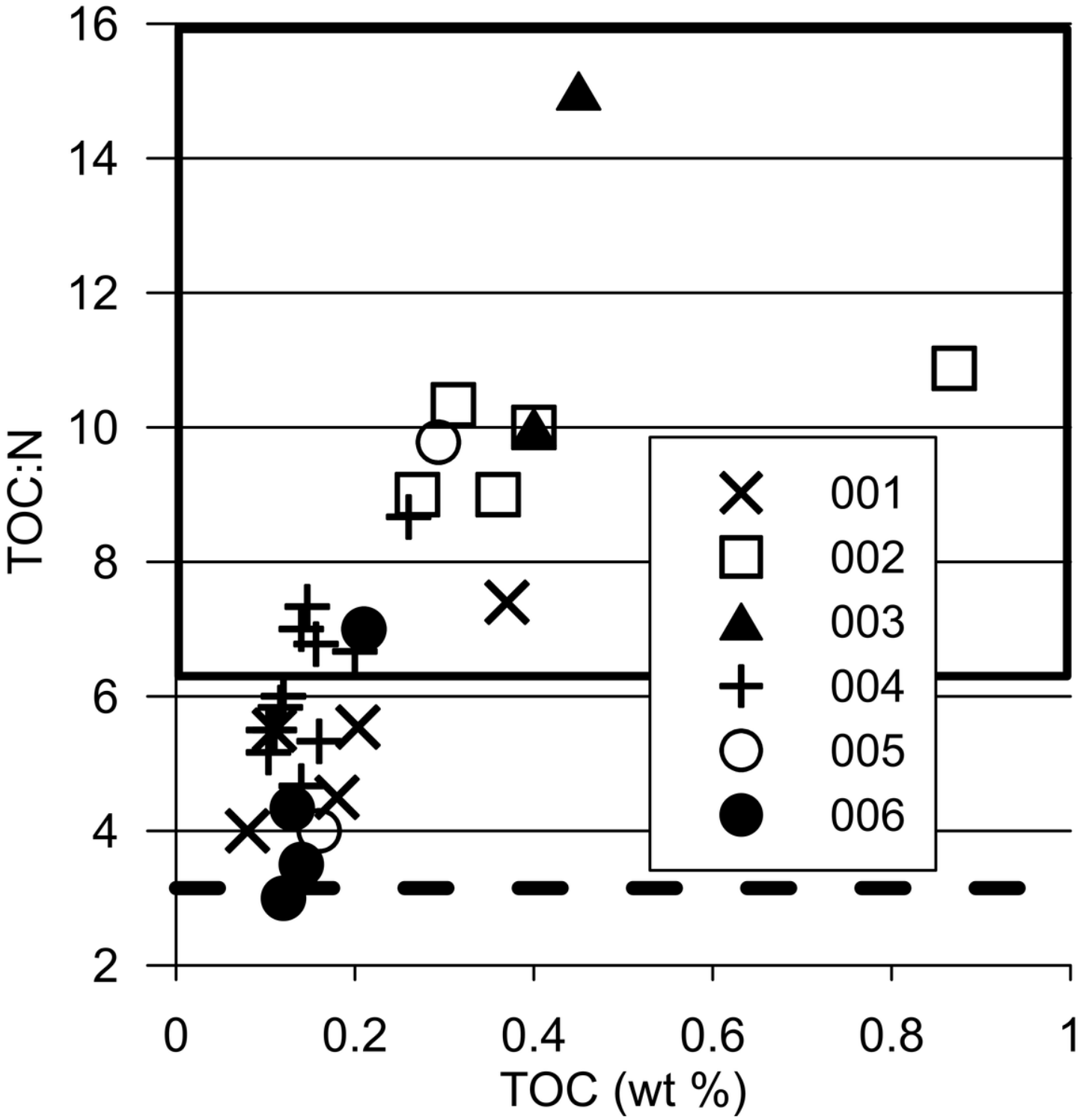
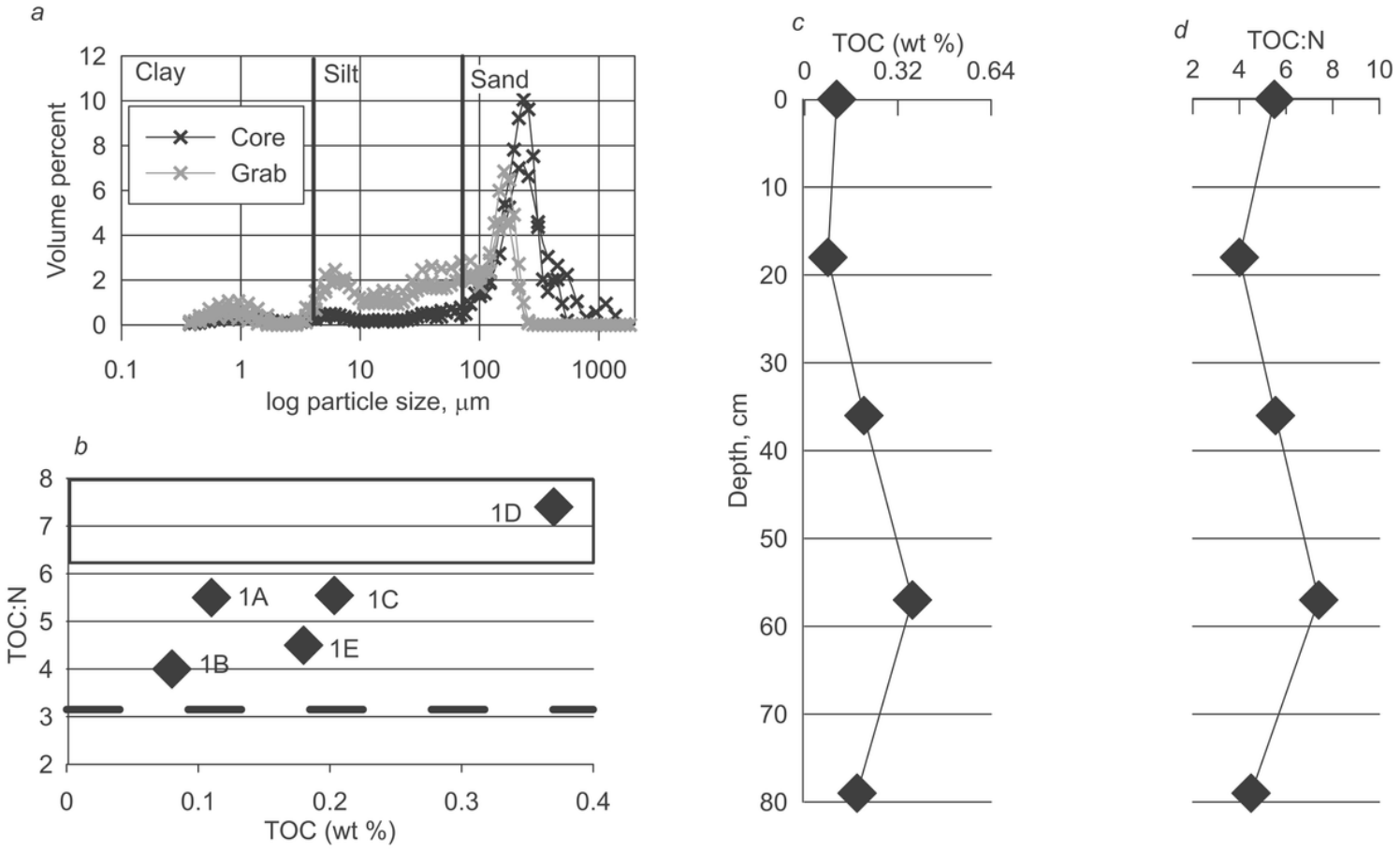


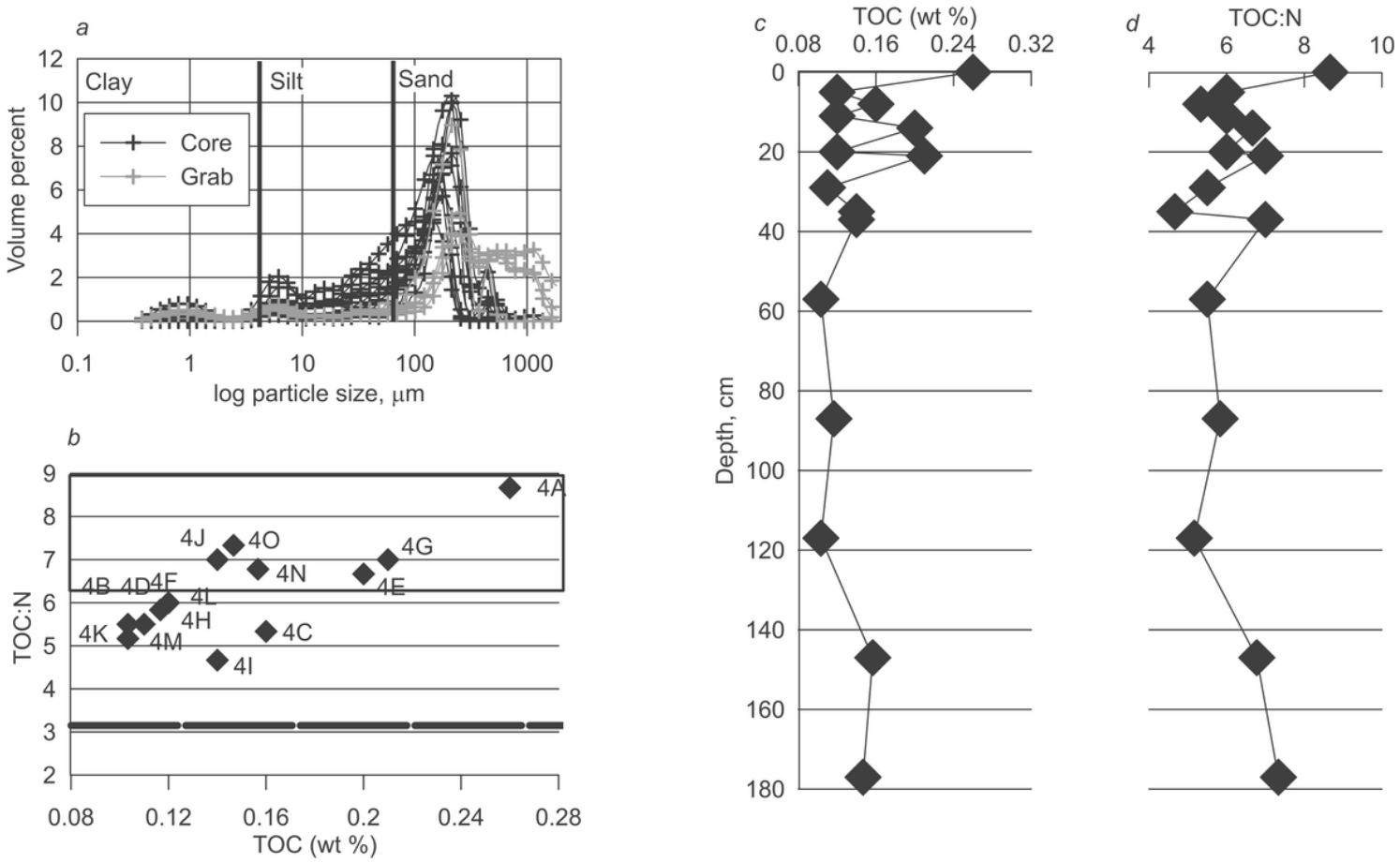

**Figure 5**

TOC:N graphed relative to TOC wt % for all analyzed samples. The boxed area from ~6.43 – 16 TOC:N represents the humic and fulvic acid TOC:N range (Rice and MacCarthy 1991) and the dashed line at 3.15 TOC:N represents the amino acid average (Jover et al. 2014). Most samples fall within the TOC:N range reported for humic and fulvic acid, which may be indicative of a terrestrial organic carbon source. Some samples at locations 001, 005, and 006 are near the amino acid average for TOC:N, which may indicate microbial processing of organic carbon at those locations



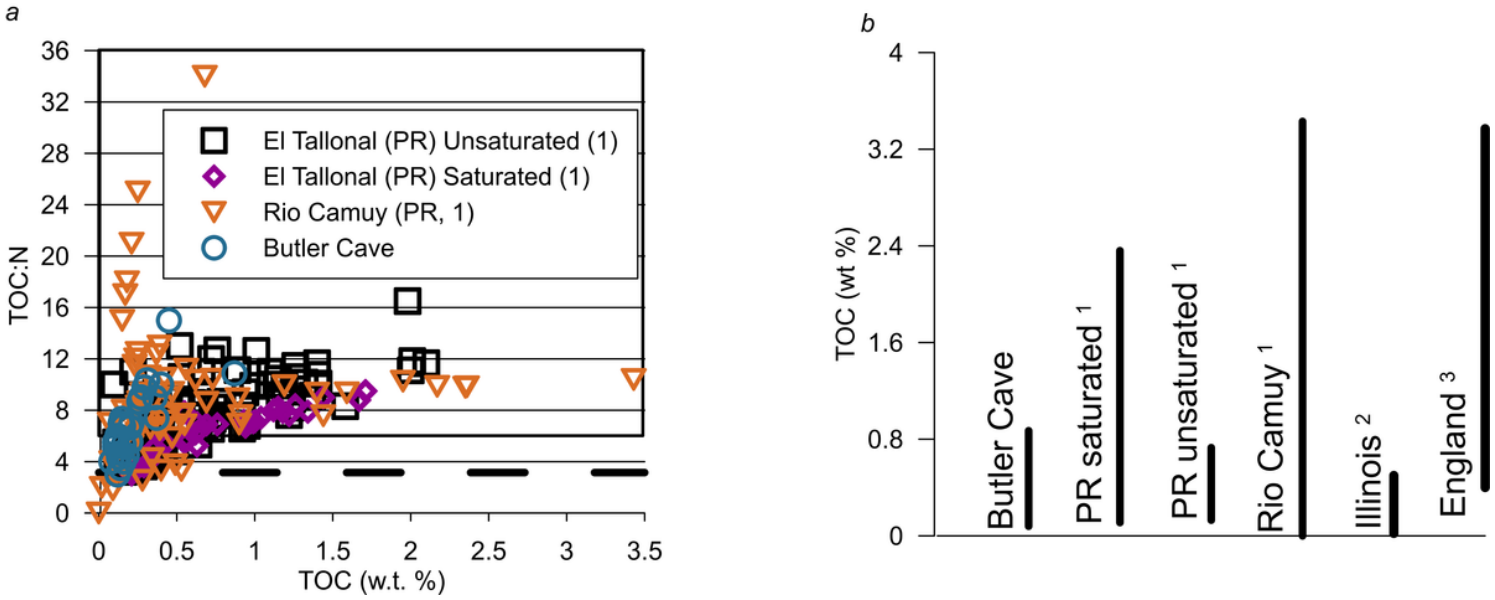

## Figure 6

Grain size percentage of the five samples analyzed at location 001 showing majority sand size grains in the samples, but with grab samples showing more silt, comparatively (a). TOC:N ratios relative to TOC wt % show four out of the five samples between the amino acid TOC:N average (Jover et al. 2014), represented by the dashed line and the humic and fulvic acid TOC:N range (Rice and MacCarthy 1991), represented by the shaded area (b). A general increase in TOC and TOC:N is observed with depth with the exception of the deepest sample, which was observed in the field to consist of very coarse gravel-sized grains (c, d)




## Figure 7

Grain size percentage of the fifteen samples analyzed at location 004 showing a majority sand size percentage in the samples (a). TOC:N ratios relative to TOC wt % show nine samples between the amino acid TOC:N average (Jover et al. 2014) represented by the dashed line and the humic and fulvic acid TOC:N range (Rice and MacCarthy 1991), represented by the boxed area and six samples within the humic and fulvic acid TOC:N range (b). In the core samples, alternating high and low concentrations of TOC wt % and TOC:N are observed which is consistent with the described interbedded silts and shales of channel facies (c, d)




## Figure 8

TOC:N ratios for Butler Cave, El Tallonal Cave, and Rio Camuy Cave. Butler cave (black circles) and unsaturated sediments from El Tallonal Cave (blue squares) show a similar range of TOC:N while Rio Camuy sediments have the largest range of TOC:N and TOC. Dashed line indicates the average amino acid TOC:N (Jover et al. 2014) and the boxed range indicates the humic and fulvic acid TOC:N range (Rice and MacCarthy 1991) (a). TOC wt % ranges for a selection of clastic sediments reported in recent literature. Butler Cave and unsaturated sediments from TAL cave show similar ranges while Rio Camuy and England cave sediments, which were sampled within two and seven years of deposition, respectively, have a similar range of TOC wt % (b). (1) Downey (2020), (2) Panno et. al. (2004), (3) Bottrell (1996)