



Contrasting ages and dynamics of unsaturated zone carbon pools at a mid-latitude karst system

Sarah Rowan¹, Marc Luetscher², Negar Haghipour^{3,4}, Heather Stoll⁴, Laura Endres⁴, Sönke Szidat¹, Franziska A. Lechleitner^{1,5}

5 ¹Department of Chemistry, Biochemistry, and Pharmaceutical Sciences, and Oeschger Centre for Climate Change Research (OCCR), University of Bern, 3012 Bern, Switzerland

²Swiss Institute of Speleology and Karst Studies, 2300 La Chaux-de-Fonds, Switzerland

³Laboratory of Ion Beam Physics, Department of Physics, ETH Zurich, 8093 Zurich, Switzerland

⁴Department of Earth and Planetary Sciences, ETH Zurich, 8092 Zurich, Switzerland

10 ⁵Current address: Swiss Federal Institute for Forest, Snow and Landscape Research (WSL), 8903 Birmensdorf, Switzerland

Correspondence to: Franziska A. Lechleitner (franziska.lechleitner@wsl.ch)

Abstract. The sources and turnover of dissolved inorganic (DIC) and dissolved organic carbon (DOC) in the unsaturated zone of terrestrial ecosystems remain poorly understood and contribute to significant gaps in understanding terrestrial carbon export dynamics. Karst systems, and caves in particular, offer a window into the subsurface, allowing direct observation and sampling of percolating water solutions. In this study, we characterized the radiocarbon (¹⁴C) composition of DIC and DOC in subsurface drip and river water in Milandre cave, Switzerland, over a period of two years, and assessed longer-term (multidecadal) carbon cycle dynamics using secondary cave carbonate deposits (speleothems). The results reveal significant age differences between carbon pools, with DIC being consistently younger than DOC. Variations in total organic carbon (TOC) concentrations and ¹⁴C suggest carbon pools of different ages contribute to the subsurface DOC pool with significant short-term (monthly or shorter) variability. The younger DIC pool indicates a rapidly cycling carbon pool under open system carbonate dissolution conditions, i.e. with low bedrock contribution to the isotopic signature. A well-defined ¹⁴C bomb peak present in the carbonate fraction of an actively growing stalagmite confirms the trend of rapidly cycling DIC on multidecadal scales. The speleothem organic carbon fraction is several thousand years older with a muted ¹⁴C bomb peak, showing that the isotopic signature of cave water DOC is faithfully recorded in speleothems over longer time periods. These findings highlight the complexity of carbon cycling in karst environments and the importance of catchment-level assessments of carbon export signatures to better constrain the terrestrial carbon budget.

1 Introduction

The terrestrial carbon cycle plays a critical role in the regulation of global climate, as it governs the exchange of carbon between atmosphere, ecosystems, and land, and the export of carbon to the oceans (Eglinton et al., 2021; Mitchard, 2018). The plants, soils, and organisms present in terrestrial ecosystems store ~ 2,100 GtC, almost triple than present in the modern atmosphere (Friedlingstein et al., 2026). Fossil CO₂ emissions have increased rapidly since the onset of industrialization, a third of which



have been absorbed by the biosphere (Friedlingstein et al., 2026). The future ability of soils to store carbon is a particularly pressing question with respect to climate change mitigation, as the response of soils to the effects of climate change is not well understood (Terrer et al., 2021). Attempts to model the flux of carbon between atmosphere and soils under climate change scenarios have resulted in mixed conclusions ranging from little change to rapid loss of soil CO₂ to the atmosphere (Eglinton et al., 2021; van Groenigen et al., 2014; He et al., 2016; Terrer et al., 2021) due to the complex impacts of physio-chemical composition, climate, and land use on soils (Keenan and Williams, 2018).

Soils are closely linked to terrestrial aquatic systems where carbon is subject to complex processes of reworking, storage and export. However, the export of carbon from the terrestrial surface through rivers and groundwater represents a significant yet poorly constrained facet of the terrestrial carbon cycle (Tank et al., 2018). Recent research has highlighted the importance of understanding these fluxes, revealing that terrestrial landscapes may contribute up to 5.1 PgC yr⁻¹ of carbon to rivers, a figure which has been historically underestimated (Drake et al., 2018). In this respect, karst regions offer a unique setting to study the subsurface carbon cycle at high spatio-temporal scales, as well-weathered karst environments provide access to water sampling at different depths within the unsaturated zone, particularly in caves. Moreover, karst landscapes are characterized by high fluctuations in discharge due to high permeability and conduit flow, and thus, the effect of these dynamics on biogeochemical cycling and carbon export can be investigated.

Cave systems host dynamic interactions between water and various carbon sources contributing to the overall dissolved inorganic (DIC) and dissolved organic (DOC) carbon pools. DIC in belowground waters is largely derived from the dissolution of soil CO₂ from the overlying catchment, which is enriched in CO₂ by root respiration and microbial decomposition (Campeau et al., 2019). In karst systems, the acidic water dissolves the carbonate bedrock which also contributes carbon to the DIC pool (Fohlmeister et al., 2020; Yin et al., 2021). The DOC is considered to primarily originate from the incomplete decomposition of overlying soil and vegetation (Blyth et al., 2016; Liao et al., 2018; Pronk et al., 2009) and from more stable, microbially processed compounds (Kaiser and Kalbitz, 2012). Thus, both DIC and DOC are sensitive to changes in the surface ecosystem. In addition to soil carbon inputs, microbial communities actively rework DOC as water passes through the karst unsaturated zone, where organic material can also contribute to the DOC pool (Bogdan et al., 2023; Epure et al., 2014; Jones and Northup, 2021; Lechleitner et al., 2017; Shabarova et al., 2014). Furthermore, carbonate dissolution can introduce fossil petrogenic carbon into the waters (Gázquez et al., 2012). A long-term perspective on terrestrial carbon export may be gained from speleothems, secondary cave carbonate deposits that, as they are fed by percolating drip water, are thought to preserve the terrestrial DIC and DOC export signatures at the time of their formation (Xue et al., 2023; Yin et al., 2021).

Carbon isotopic analysis of cave waters can provide valuable information about the origin, reworking, transport, and age of DIC and DOC in terrestrial karstic environments. The radiocarbon content (¹⁴C) of DIC and DOC can give a temporal constraint on how long the carbon has been cycling in the environment, but also inform on the sources of carbon. The ¹⁴C of drip water DIC can be influenced by overlying ecosystem composition and respiration, soil moisture, carbonate dissolution dynamics and hydrology, as it records how open or closed the system is (Fohlmeister et al., 2010). Stable carbon isotope analysis (^δ¹³C) of DIC has been widely used to understand biogeochemical cycling and interactions between vegetation, soils



and carbonate bedrock (Knierim et al., 2015; Yin et al., 2021). DO¹⁴C analysis has, historically, focused on dating groundwater (Heine and Einsiedl, 2021; Wassenaar et al., 1991) and terrestrial surface waters (Ge et al., 2020; Jull et al., 2014; Rhyner et al., 2023). Beyond dating, constraining DO¹⁴C would provide a temporal constraint to the potential origins of the carbon. Source apportionment of cave water DOC has also been aided by various techniques such as the analysis of organic fluorescence (Baker and Genty, 1999; Endres et al., 2024; He et al., 2024), organic metal complexes in trace elements (Hartland et al., 2012), and biomarkers (Heidke et al., 2018).

Given the rarity of ¹⁴C analysis of subsurface waters, this study fills an important gap providing a temporal perspective on the carbon cycle in karst environments. We present the results from a two-year monitoring campaign from a Swiss cave whereby a suite hydrochemical analysis was implemented on drip and river water. The ¹⁴C composition of DIC and DOC, combined with trace element analysis, informs about the sources and transport pathways of carbon throughout the unsaturated zone on both spatial and temporal scales. Bulk ¹⁴C of catchment soils, and of speleothem inorganic and organic carbon fractions was also measured to contextualize these dynamics within longer term trends of terrestrial carbon export.

2 Materials and Methods

2.1 Site description

Milandre cave (47.4852 ° N, 7.0161 ° E, 373 m a.s.l.) is a 10.5 km long karst system formed within Mesozoic limestone in the Jura mountains of NW Switzerland (Fig. 1). The host rock is Upper Jurassic limestone (Middle Oxfordian St. Ursanne formation; Jeannin, 1998), which consists of marly limestones containing silicified corals at the base, followed by massive micritic reef limestones and oosparites. No organic rich lithologies are present and the limestone formation is underlain by Early to Middle Oxfordian marls (Liniger, 1970). The stratigraphy is subhorizontal (Perrin et al., 2003), thus the host rock influence across monitoring sites is expected to be relatively uniform. The cave developed in a ~ 40 to 80 m unsaturated karst and has a ~ 20 m saturated zone below (Perrin et al., 2003). A cave river drains the ~ 13 km² catchment area predominantly comprising grass meadows, arable farmland, and forest. Part of the cave is overlain by a motorway constructed in 2010, which led to the establishment of an artificial infiltration system to preserve actively growing speleothems in the underlying cave section (Jeannin et al., 2013). The decorated, actively dripping sections of Milandre cave are concentrated in a downstream section “*Galerie des Fistuleuses*” (GF) and an upstream section “*Gratte Roche*” (GR). Tritium monitoring of drip water in GF has estimated the residence time of water in the epikarst to ~ 5.5 to 6.6 years (Affolter et al., 2020). The cave air has low temperature variability between ~ 10.3 to 11 ° C. Data collected from the MeteoSwiss Fahy weather station 9.5 km SW of the cave shows an average mean annual air temperature (MAAT) of 9.4 ° C (1991 to 2020) with strong seasonality between summer and winter months (MeteoSwiss, 2024). The mean annual precipitation is 1046 mm, with mean monthly precipitation (MMP) well-distributed throughout the year according to monthly data measured at the MeteoSwiss Mormont weather station, ~ 6.5 km south of Milandre (MeteoSwiss, 2024).

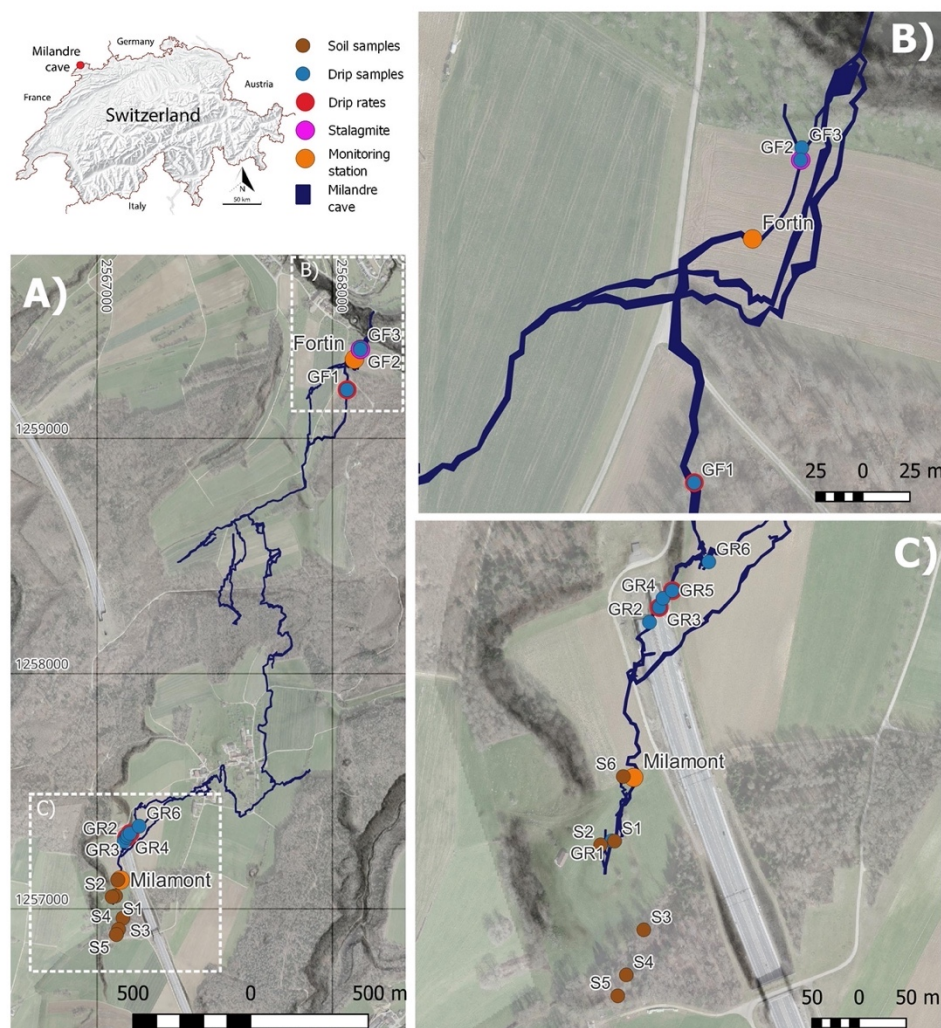


Figure 1: a) Map of the main passages of the Milandre cave network. The location of the drip water sampling (blue), drip rate monitoring (red) and soil sampling (brown) are annotated at b) the downstream section and c) the upstream section. River samples were taken from the Milandre amount (Milamont) monitoring station (orange). Cave survey modified from Gigon & Wenger (1986). Base map from ©swisstopo.

2.2 Soil sampling and analysis

Topsoil samples from six locations above the upstream entrance of the cave (Fig. 1) were collected in February 2022 by hand trowel at depths from 0 to 30 cm and transferred into plastic bags. In some locations (S3, S4, S5, and S6), the soil was too shallow to dig a depth profile, so single samples of a smaller depth range were taken. The samples were pretreated according to Hajdas et al. (2024). The soils were frozen after sampling and a subsample defrosted, softened with ultrapure water (18 MΩ·cm, total organic carbon (TOC) < 5 ppb, Purelab flex 2, ELGA LabWater, UK), and sieved to < 100 μm in a stainless-steel sieve (Retsch, Germany). The fine fraction was transferred into 50 mL falcon tubes which had been submerged for several



days in ultrapure water and dried in an oven at 60° C. The samples were left for several days for the solid fraction to decant.

110 The ultrapure water was then removed and the solid fraction dried for several days in an oven at 60° C. The dry soils were transferred into glass tubes with 5 mL 0.5 M HCl (EMSURE®, 37%, Hydrochloric acid fuming, for analysis, Supelco, Germany), and were shaken overnight. The tubes were rinsed with ultrapure water, centrifuged three times, then dried over several days at 60° C. As the TOC of soils varies, carbon concentration was determined before graphitisation. 5 to 10 mg of the samples were weighed into tin cups and analysed by an Elemental Analyser (EA, Elementar Analysensysteme, Germany).

115 The soils were then weighed accordingly to obtain ~ 1 mg of carbon. The soils were converted into graphite via an Automatic Graphitisation Equipment (AGE, Ion Plus, Switzerland) whereby the CO₂ is reduced to graphite with H₂/N₂ gas (10%) over an Fe catalyst (Wacker et al., 2010a). Oxalic acid II was used as the normalising standard (F¹⁴C = 1.3407, Standard Reference Material 4990C, National Institute of Standards and Technology, USA) and phthalic anhydride (F¹⁴C = 0, Sigma Aldrich, USA) was used for blank correction. The graphite was pressed into targets for analysis through accelerator mass spectrometry

120 (AMS) on a MIni Carbon Dating System (MICADAS) at the University of Bern, Switzerland (Synal et al., 2007; Szidat, 2020). All radiocarbon data were corrected using the BATS (4.3) software (Wacker et al., 2010b). Radiocarbon results are reported in uncalibrated radiocarbon age or F¹⁴C, where “standard” represents the internationally accepted radiocarbon dating reference value for AD 1950 (Reimer et al., 2004):

$$F^{14}C = \frac{{}^{14}C/{}^{12}C_{\text{sample}}}{{}^{14}C/{}^{12}C_{\text{standard}}} \quad (1)$$

125 2.3 Water sampling

A total of 9 actively dripping sites with variable drip rates were chosen for drip water analyses (Fig. 1). The sampling locations were focused on the GF (GF1 to GF3) and GR (GR1 to GR6) actively dripping sections of the cave. Water was also sampled from the cave river in the GR section. Washed 50 mL falcon tubes were placed underneath each drip and allowed to fill for 24 to 48 h. The vials were then collected and stored in a fridge at 4° C until further processing took place. Samples were taken

130 approximately every two months from December 2021 to January 2024. Soil pore water was taken from nearby S1 above the GR section of the cave using a suction lysimeter reaching 1m depth (Fig. 1) but collection was limited to the periods where soil moisture was high enough.

Drip water DIC ¹⁴C was collected over one year from December 2021 to December 2022. 1 mL of drip water was collected with a 5 mL syringe directly from the soda straw stalactites on the cave roof to reduce fractionation effects associated with

135 degassing. The water was injected directly into 12 mL Exetainer® vials (Round Bottom, Borosilicate, 938W, Labco Limited, UK) which had been flushed with He gas (99.999 %, Carbogas, Switzerland) to remove air, and pre-spiked with 150 µL of 85% H₃PO₄ (Suprapur®, 85%, Merck KGaA, Germany). The vials were previously acid washed in a bath of 1M H₃PO₄, rinsed with ultrapure water, and combusted in a muffle oven at 550° C for 5 h. The integrity of the vials was assessed via a “leak test” whereby the vials were filled with N₂ gas via the septum and heated at 75° C for at least 24 h. The seals of the vials were then



140 tested by piercing the septum with a needle and audibly checking that gas escaped. The vials were discarded if the piercing made no sound as they are assumed to not be leak tight.

2.4 Drip rate and river discharge monitoring

Drip rates were monitored acoustically (drops hr⁻¹) over the entire study period at three sampling locations (GF1, GR3, and GR5) using Stalagmate® Plus Mk2b drop loggers (Driptych, UK) (Collister and Matthey, 2008). The drip loggers were placed
 145 beneath active drips of different hydrological regimes, either on top of the subsequent stalagmite formation or resting on the cave floor (Fig. 1).

Discharge of the Milandre cave river was measured at 10 min intervals at “Milandre Amont”, a monitoring station maintained by the Swiss Federal Office of the Environment since 1990 (Fig. 1). The station gauges the hydrological recharge of ~ 1/3 of the Milandre catchment area. Data are averaged to daily means for the statistical analysis.

150 2.5 TOC analysis

Following sample collection, aliquots of 5 mL water were pipetted into pre-cleaned 12 mL Exetainer® vials. The samples were acidified with 50 µL of 10% HCl to conserve the organic material. TOC concentrations were then measured with a DIMATOC® 2100 (DIMATEC Analysentechnik, Germany) at the Institute of Geography, University of Bern. Standards of known TOC concentrations (i.e., 0.8, 2, and 6 ppm) and blanks of ultrapure water were measured for uncertainty quantification.

155 2.6 Trace element analysis

Aliquots of 400 µL were transferred into 2 mL Eppendorf® tubes which had previously been soaked in 10% HCl for at least 24 h, rinsed with ultrapure water, and dried overnight in an oven at 50° C. Potential prior calcite precipitation (PCP) in the vials during storage was precluded by ensuring that the transfer of the sample aliquot for trace element analysis was simultaneous with the removal of the sample for DOC analysis, and by ensuring no headspace was present in the trace element
 160 aliquots. The tubes were centrifuged at 13.2 rpm for 5 min to separate any particulate matter, and 200 µL were pipetted into gas chromatography vials. These were previously acid washed following the same protocol as the Eppendorf® tubes. The aliquots were acidified with 15 µL 65% HNO₃ so that the samples and the 2% HNO₃ standards had the same pH. In-house trace element standards were created by mixing certified mono-element standards (ISO 17034 CRM, Inorganic Ventures, USA) in a 2% HNO₃ solution. This resulted in multi-element calibration standards that cover the range of drip water chemistry.
 165 The trace element composition of the samples was measured on an 8800 QQQ-ICP-MS (Agilent, USA) at the Department of Earth and Planetary Sciences, ETH Zurich. Elements measured above the level of quantification (LOQ) where: Na, Mg, K, Ca, Fe, Zn, Si, P, S, Sr, Ba, and Al. Ca, Zn, Sr, Ba, and Al were measured with no collision gas. K, Mg, and Fe were measured in H₂ collision mode to improve stability of the measurement. P, S, and Si were measured in O₂ reaction mode to reduce the effects of O₂ and N₂. Na was measured in He reaction mode to reduce influence from ⁴⁶Ca²⁺. Linear regressions were performed



170 between $\ln(\text{Mg}/\text{Ca})$ and $\ln(\text{Sr}/\text{Ca})$, because slopes with a gradient of > 0.7 indicate that drip waters are affected by water rock interactions (WRI) and prior calcite precipitation (PCP) according to the Sinclair Test (Sinclair, 2011; Sinclair et al., 2012).

2.7 DOC ^{14}C analysis

The remaining water, typically ~ 40 mL, was acidified with 0.5 mL 10% H_3PO_4 (puriss. grade) and frozen until further processing. To ensure a high-enough concentration of carbon for a radiocarbon measurement (ideally more than $20 \mu\text{g C}$), the samples were preconcentrated to volumes of approximately 10 mL through lyophilization. Following this, the samples were defrosted, and the non-purgeable organic carbon (NPOC) fraction was oxidised through a wet chemical oxidation (WCO) procedure adapted from Lang et al. (2016) and Strähl et al. (2025). In brief, the drip waters were transferred by Eppendorf® pipette into 12 mL Exetainer® vials for the analysis. To remove the DIC fraction the samples were acidified with 0.5 mL of 8.5% H_3PO_4 (puriss. grade) and then flushed with He gas at 55 mL min^{-1} for 3 min at room temperature via needle on a Carbonate Handling System (CHS) (IonPlus, Switzerland). To avoid cross contamination during the flushing, the needle was inserted into a vial with ultrapure water for 1 min and then dried between each sample. To oxidise the sample, 0.5 mL of 10% sodium persulphate (purum p.a. $\geq 99.0\%$, Sigma Aldrich, USA) were added to each sample using a 1 mL Hamilton® syringe. The samples were reacted for 1 h at 95°C , enabling the NPOC to be oxidised to CO_2 gas. Compounds of known ^{14}C contents were used as standards (Oxa II, Oxalic acid II, $F^{14}\text{C} = 1.3407$, Standard Reference Material 4990C, National Institute of Standards and Technology, USA) and blanks (NaOAc , $F^{14}\text{C} = 0$, sodium acetate, puriss. p.a., ACS reagent, anhydrous, No. 71180, Merck KGaA, Germany) at different concentrations to assess constant contamination following the methodology by (Hanke et al., 2017). The ^{14}C concentrations were analysed through AMS (MICADAS) at ETH Zurich, Switzerland (Synal et al., 2007). Here, the CO_2 was introduced to the gas ion source through the CHS at a flow of 50 mL min^{-1} . The ^{14}C content for each sample was measured for ~ 60 cycles. As for the soil samples, the BATS software (4.3) was used for data correction and constant contamination was evaluated per Hanke et al. (2017). Due to issues during the measurement of some samples from December 2022 to June 2023, a correction with the procedural standards prepared at the same time as the samples was not possible. Instead, these samples were corrected using the highest contamination settings from the other measurements ($2.1 \mu\text{g}$ of $F^{14}\text{C} = 0$ contamination, $0.3 \mu\text{g}$ of $F^{14}\text{C} = 1.3407$ contamination). Results are shown either in uncalibrated radiocarbon age or in $F^{14}\text{C}$ (Equation 1).

195 2.8 DIC ^{14}C analysis

Because the vials for collecting DIC were flushed with He and spiked with H_3PO_4 before introducing the water, the ^{14}C content of DIC could be measured by directly sampling and analysing the headspace CO_2 on the AMS (MICADAS) at the University of Bern, Switzerland. Apart from this, the AMS measurement procedure is the same as previously described for DOC. Standard material with a carbonate matrix of similar composition to the DIC samples were used as standards; IAEA C1 ($F^{14}\text{C} = 0$) and C2 ($F^{14}\text{C} = 0.4114$), sodium bicarbonate (NaHCO_3 , Sigma Aldrich, USA) ($F^{14}\text{C} = 0$), and potassium bicarbonate (KHCO_3 ,



Sigma Aldrich, USA) ($F^{14}\text{C} = 0$). Oxa II gas ($F^{14}\text{C} = 1.3407$, Oxa II, NIST SRM 4990C, HEKAL AMS Lab, Hungary) was used as a normalising standard.

2.9 Stalagmite carbon isotope analysis

A ~ 5 cm long, actively growing stalagmite sample was collected from beneath the drip GF2 (Fig. 1). Six CaCO_3 chips weighing ~ 80 to 200 mg were sampled by wire saw along the growth axis at the Geological Institute of the University of Bern. The chips were cleaned to remove surface contamination by submerging them in ultrapure water and ultrasonicing for 15 min, repeating once. The chips were then submerged in 1:1 0.3 M HCl and ultrapure water and ultrasonicated for 2 min. Four ultrapure water rinses were done subsequently to avoid large scale dissolution of the carbonate. Before the final rinse, the solution was ultrasonicated for 3 min. The chips were then dried overnight in an oven at 70°C and transferred to pre-cleaned (acid washed and combusted) Exetainer® vials. The chips were dissolved by acidifying with 1.5 mL ultrapure water and 0.5 mL H_3PO_4 (puriss. grade). These were left covered over night at room temperature to dissolve. All the samples were then flushed for 3 min with He gas at 70 mL min^{-1} at 50°C to remove the carbonate fraction. This was repeated for a flushing time of 2 min, and then for 1 min, as tests showed that this procedure was the most efficient at removing the carbonate. To ensure that the carbonate fraction was flushed out of the vial, the evolution of vial CO_2 in each flushing round was tracked with an NDIR detector (LI-850 $\text{CO}_2/\text{H}_2\text{O}$ gas analyser, LI-COR Biosciences, USA) (Strähle et al., 2025). The needle was cleaned between each sample with the same procedure as the water samples. To oxidise the NPOC fraction, 0.25 mL of 10% sodium perchlorate (purum p.a. $\geq 99.0\%$, Sigma Aldrich, USA) was added through the septum of each vial. The vials were then reacted at 95°C for 1 h and analysed by AMS at ETH Zurich, Switzerland. The standard and blank preparation, AMS measurement, and the contamination quantification was the same as for the DOC samples previously described.

For inorganic carbonate analysis, eleven stalagmite sub-samples of ~ 8 mg CaCO_3 were either drilled with a micromill or subsampled from the larger chips intended for organic carbon ^{14}C analysis and stored in pre-cleaned 4.5 mL Exetainer® vials. Each vial was flushed for 5 min at room temperature with He gas at a flow of 60 mL min^{-1} . The samples were acidified with 0.5 mL 85% H_3PO_4 and left on a heating block overnight at 65°C . The resultant headspace CO_2 was converted into ~ 1 mg of graphite via the AGE. The graphite was pressed into targets for AMS analysis at the University of Bern, Switzerland.

Radiocarbon-dead IAEA C1 ($F^{14}\text{C} = 0$) was used for blank correction, a ^{14}C -free speleothem ($F^{14}\text{C} = 0$) (age determined by U-Th: 377'000 yr BP) was used as a procedural blank, Oxa II ($F^{14}\text{C} = 1.3407$) was the normalising standard, and IAEA C2 ($F^{14}\text{C} = 0.4114$) was used as a secondary standard.

2.10 Stalagmite confocal laser scanning microscopy

Confocal Laser Scanning Microscopy (CLSM) was performed to observe how solid phase organic fluorescence is preserved in the microfabrics and estimate the growth rate of an actively growing stalagmite beneath drip GF2. The scans were performed using an Olympus Fluoview 3000 (Olympus, USA) at the Scientific Centre for Optical and Electron Microscopy (ScopeM) at ETH Zurich, Switzerland. Raster images with a 10% overlap were made with an incident wavelength of 488 nm and a detection



window of 490 to 590 nm, as established by Sliwinski and Stoll (2021). This resulted in an optical slice thickness of $< 10 \mu\text{m}$ with a 10x objective. The images were viewed using the Fiji software (Schindelin et al., 2012)s.

235 3 Results

3.1 Bulk soil organic carbon ^{14}C

The soil composition and type above the upstream section of Milandre cave is varied (Rowan et al., 2025). Samples S1 and S2 are organic-rich histosols located in a grass meadow in a doline, whilst S3, S4 and S5 are leptosols rich in fragments of carbonate bedrock from the forested part of the upper catchment (Fig. 1). S6 was taken from a recently overturned tobacco
 240 field. Despite the differences in soil composition, the bulk soil organic matter ^{14}C signatures above the upstream section of Milandre cave are consistently modern, with an average $F^{14}\text{C}$ of ~ 1.03 (Table S1). Of the two depth profiles taken, only S1 showed a decrease in $F^{14}\text{C}$ from the 0 to 20 cm depth ~ 1.03 , to 20 to 30 cm depth ~ 0.99 . The profile at S2 comparing 0 to 10 cm depth and 10 to 20 cm depth showed a consistent $F^{14}\text{C}$ of ~ 1.07 . The soil water $F^{14}\text{C}$ DOC collected from the lysimeter at 1m depth ranged from 0.89 to 0.96.

245 3.2 Drip rates and river discharge

GF1, GR3, and GR5 have very variable drip rates over the monitored period (Fig. 2a, b, c). All drips had dry periods where no drips were recorded. GF1 was the most consistently active drip site with an average drip rate of $496 \text{ drops hr}^{-1}$ (± 537 , 1 standard deviation), and a maximum rate of $3540 \text{ drops hr}^{-1}$ in May 2022. GR3 was active with short periods of very high drip rates with a maximum rate of $2150 \text{ drops hr}^{-1}$ in May 2023 and average rate of 4 drops hr^{-1} (± 21). GR5 had a maximum of
 250 $468 \text{ drops hr}^{-1}$ and an average of 95 drops hr^{-1} (± 119). There were very few drips recorded for GR3 after July 2022, and for GR5 from the beginning of the monitoring until February 2022, and between November 2022 and May 2023. As it was possible to collect water samples during this time, the data gaps are likely a technical issue with the drip loggers. These periods were not considered in the data analysis. The drips were characterised by comparing the maximum and minimum monthly drip rates (Baldini et al., 2021) (Fig. 2f), with all drips displaying a mix between diffuse flow and fracture flow with intermittent drying
 255 (Smart and Friedrich, 1987). GF1 has most pronounced diffuse flow characteristics, whereas GR3 and GR5 are more dominated by fracture flow. The cave river discharge at Milandre Upstream varied throughout the monitoring period from 18 to 624 L s^{-1} (± 82) (Fig. 2d). A seasonal cyclicity is apparent in river discharge, with minimum values during the summer months ($\sim$ June - October) during both years, but more pronounced in 2023. These minima in discharge are not related to minima in Mean Monthly Precipitation (MMP) (Fig. 2e) measured at Mormont weather station, suggesting high
 260 evapotranspiration is the driver of this pattern, rather than a reduction in precipitation. The link between MMP and drip rate was tested by calculating the mean monthly drip rate (MMD) (Fig. 2d) and performing a Spearman's rank correlation. A significantly correlated relationship between two variables is defined by $p < 0.05$. Only the actively dripping time periods were tested to avoid bias from technical errors in the drip loggers. At most locations and time periods, no significant correlations



were observed, the exception being GF1 between December 2022 and June 2023, where MMP and MMD were significantly positively correlated ($p = 0.86$, $p = 0.014$, $n = 7$; Table S2). GF1 was also significantly positively correlated to river discharge during this period (Table S3). During periods of active dripping, the drip rates of GR3 and GR5 also showed significant positive correlations with discharge (excluding GR5 between April to June 2023 which had a significant negative correlation; Table S3).

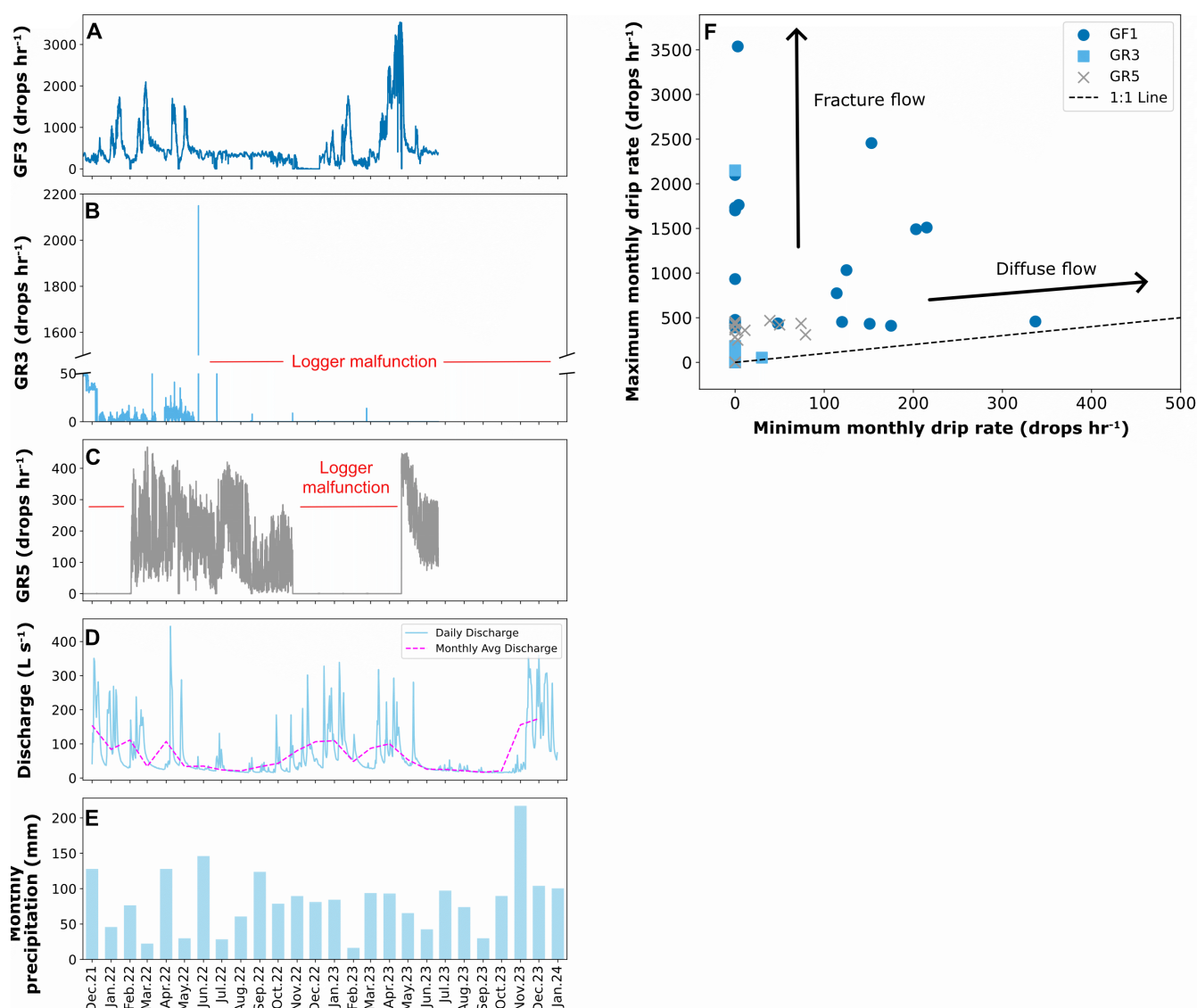


Figure 2: a) Variations in GF1, b) GR3, and c) GR5 drip rate, (drops hr⁻¹) with d) river discharge (L s⁻¹) and e) monthly precipitation (mm). f) Minimum and maximum monthly drip rate (drops hr⁻¹) of GF1 (dark blue circles), GR3 (light blue squares), and GR5 (grey crosses) (Baldini et al., 2021). Samples close to the 1:1 line are characterized as diffuse flow drips. Drips on the vertical line are characterized as more fracture flow controlled.



3.3 Drip water organic carbon characterization

275 Across all sampled locations, the drip water TOC content ranged from ~ 0 to 2.01 mg L^{-1} , with strong variability between drip sites and collection month. Drips located in the GF area of the cave had higher TOC concentrations than those in GR (Fig. 3a). GF3 had the highest average TOC (1.38 mg L^{-1}) and GR6 had the lowest (0.38 mg L^{-1} ; Fig. S1). Temporally, all drips showed higher TOC concentrations between February and April 2022, which then decreased during June and August 2022 before increasing again to similar levels as at the beginning of the year (Fig. 3a). This cyclicity was muted but still present in 2023.

280 The cave river had TOC ranging from 2.66 mg L^{-1} (August 2023) to 0.47 mg L^{-1} (October 2023), with an average of 1.26 mg L^{-1} . River TOC concentrations generally followed the concentration variability of the drip water, except for August and October 2022 when the river TOC was much higher.

There was very large variability in DOC $F^{14}\text{C}$ values (Fig. 3b) both between individual drips and over time, with a maximum of 0.97, and a minimum of 0.10. Similar to TOC concentrations, the GF drips generally had a higher $F^{14}\text{C}$ than those in GR.

285 GF3 had the highest average $F^{14}\text{C}$ (0.89), while GR5 had the lowest average $F^{14}\text{C}$ (0.45, Fig. S1). Drip water $F^{14}\text{C}$ values varied seasonally synchronously with TOC concentrations, with a large decrease from June 2022 to October 2022 across all sampled drips. The $F^{14}\text{C}$ of GF2, for example, decreased from 0.96 to 0.14 during this period, essentially spanning the entire range of ^{14}C . Similar to the TOC, the drip water $F^{14}\text{C}$ of most drips eventually recovered to the original values. In comparison with the TOC, the recovery was slower, reaching a new maximum only in February 2023. The second monitored year also

290 showed a muted but still detectable cyclicity in ^{14}C . GR5 was the exception and did not fully recover to the original values during the monitored period. The $F^{14}\text{C}$ of the river averaged at 0.84, with a minimum of 0.37 and a maximum of 0.98, and followed a similar temporal trend as the drips. The synchronous seasonal cycle in TOC concentrations and DOC $F^{14}\text{C}$ values is supported by a moderate but significant positive correlation between the two parameters over the entire period and all sites ($\rho = 0.43$, $p < 0.01$, $n = 83$, Fig. 4). This positive relationship is also observed for most months and sampling sites individually,

295 although statistical significance varies due to limited sample size (Table S4). Drip rate was not significantly correlated with either TOC concentration or DOC $F^{14}\text{C}$ (Table S5).

Spearman's rank correlations on the dataset allowed us to examine the statistical significance between variation of TOC, DOC $F^{14}\text{C}$, and MMP, MMD, and monthly averaged river discharge (Tables S6 and S7). Due to the stronger variability in TOC and $F^{14}\text{C}$ in the first year of monitoring, the data was treated separately in two yearly batches, December 2021 to December 2022

300 (year 1), and December 2022 to January 2024 (year 2). Overall, no clear trends emerged from this analysis that apply to both years, but individual drip sites showed correlations with between discharge, TOC and $F^{14}\text{C}$ at different points in time.

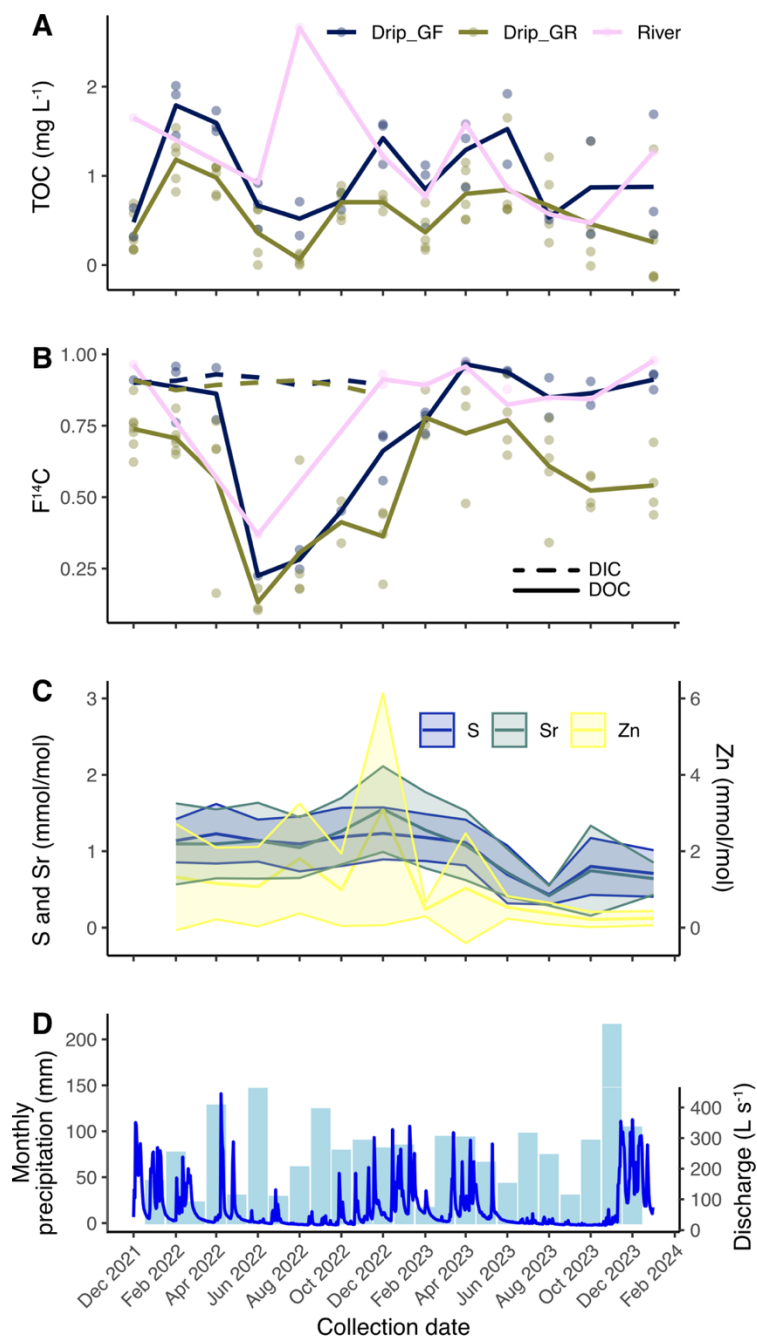


Figure 3. a) TOC (mg L⁻¹), b) F¹⁴C DOC and DIC. Lines show average monthly values by sample group, whereas dots indicate individual sampling site values. c) Normalised trace element concentration of drips for S, Sr, and Zn. Thick lines are averaged across all drip sites, shading indicates the normalised standard deviation. d) Daily cave river discharge (blue line) (L s⁻¹), mean monthly precipitation (MMP, light blue bars) (mm) collected from Mormont weather station.

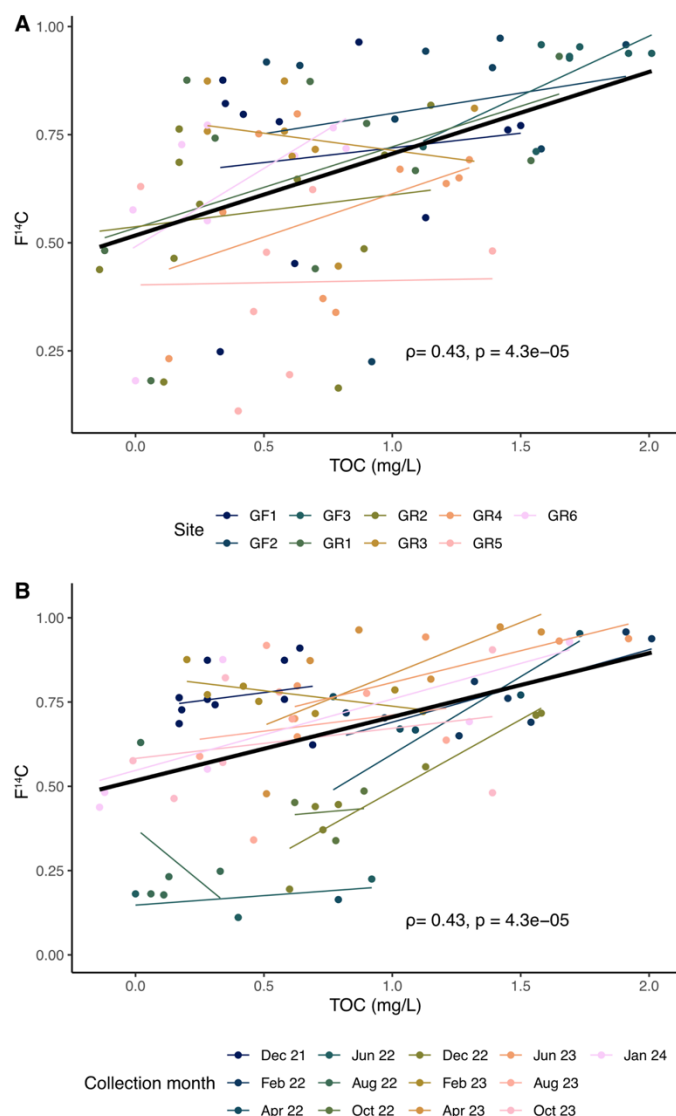


Figure 4. TOC (mg L⁻¹) and F¹⁴C of all drip and river sites grouped by a) drip / river site, and b) by month. Because of the small sample size per site and month statistical significance varies, and we only show the correlation for the entire dataset (Spearman's rho).

3.4 Drip water inorganic carbon characterization

The drip water DIC had notably higher F¹⁴C than the DOC and did not show the same temporal variability. From December 2021 to December 2022, the F¹⁴C of the drip water DIC ranged from 0.78 to 0.94, with an overall average of 0.90 (n = 53) (Fig. 3b), whereas the DOC averaged at 0.66, between 0.10 and 0.97. In contrast to TOC and DOC ¹⁴C, where values were on average higher in the GF part of the cave, no significant spatial difference appear for DIC ¹⁴C. GF3 had the highest DIC ¹⁴C (average F¹⁴C = 0.96, n = 5), whilst GF1 (average F¹⁴C = 0.86, n = 7) and GR1 (average F¹⁴C = 0.86, n = 5) consistently



had the lowest $F^{14}C$ (Fig. S1). Most of the drip sites did not show a notable temporal variation, however GR6 steadily increased in $F^{14}C$ over 2022, and decreased again in December 2022. Because of the time-consuming sampling, and given that no large seasonal variability was apparent, we refrained from collecting samples for DIC analysis during the second monitoring year.

320 3.5 Drip water trace elements

Across all 12 trace elements which were above the LOQ, Na, Mg, Ca, Si, S, and Sr have higher elemental concentrations from October 2022 to December 2022, followed by a decrease in concentrations in June 2023, which coincides with a prolonged period of reduced cave river discharge at the study site, likely resulting from enhanced surface evapotranspiration (Fig. 3c and d). While Ca is the dominant cation from bedrock dissolution, it can also be removed from dripwater by PCP. The covariation of Sr/Ca and Mg/Ca in dripwater (Sinclair test) is consistent with a common control by removal of Ca (Fig. S3), allowing us to use Sr as an indicator of dissolution intensity. Thus, it is likely that most elements exhibiting the same pattern will also be controlled by bedrock dissolution (e.g., S; Fig. 3c). Other elements, such as P, Al, Zn, and Fe appear to be less affected by hydrology and display episodic peaks (Fig. 3c, Fig. S2). These elements are typically indicative of colloidal transport (Hartland et al., 2012). Notable exceptions are Na, which is likely controlled by road salt input from the motorway, especially in winter, and K, likely dominated by fertilizer input in the fields above the cave.

3.6 Stalagmite fluorescence and ^{14}C

The CSLM imagery of the actively growing stalagmite under drip site GF2 reveals fine-scale horizontal laminations of organic fluorescence. This may signify annual or sub-annual growth cycles (Fig. 5). The stalagmite has high porosity and crystalline defects shown by sections with large voids and vertical spires which disturb the regular layering. Similar crystal morphology has been observed in previous CSLM studies on speleothem samples, indicating rapid crystallization (Endres et al., 2024; Sliwinski et al., 2023; Sliwinski and Stoll, 2021).

The inorganic carbon fraction of the stalagmite had an $F^{14}C$ ranging from ~ 1.00 to 0.85 (corresponding to an uncalibrated, i.e., apparent ^{14}C age range of ~ 0 to 1280 yrs). There is a clear bomb peak present in the sample (Fig. 5; Table S8). Taking the inflection point of the bomb peak at 39.5 mm with an $F^{14}C$ of 0.85 , and a pre-bomb Northern Hemisphere atmosphere $F^{14}C$ of 0.97 (Hua et al., 2022), the dead carbon fraction (DCF, i.e., the reservoir effect introduced by contributions of aged and fossil carbon from soil and bedrock carbonate) is estimated at $\sim 12.7\%$. Approximate layer counting of the top 2.5 mm of the sample showed a growth rate of 0.05 mm per year if one layer corresponds to one year. Assuming that the growth rate was constant throughout the formation, the year 1955 can be assigned to 34 mm depth from top. This approximately aligns with the bomb peak inflection point, supporting the notion that the layering is annual.

The organic carbon fraction of the stalagmite is significantly older than the inorganic carbon fraction over all depths, with a minimum $F^{14}C$ of 0.64 to a maximum of 0.71 (corresponding to an uncalibrated ^{14}C age range of ~ 2760 to 3640 yrs; Fig. 5). Comparing inorganic and organic carbon samples of the same depth, the average difference in $F^{14}C$ is 0.28 (corresponding to



an uncalibrated ^{14}C age difference of ~ 2750 yrs). Both fractions show an increase in $F^{14}\text{C}$ outlining the bomb peak, peaking at 21.5 mm depth, though in comparison the organic carbon bomb peak is strongly muted.

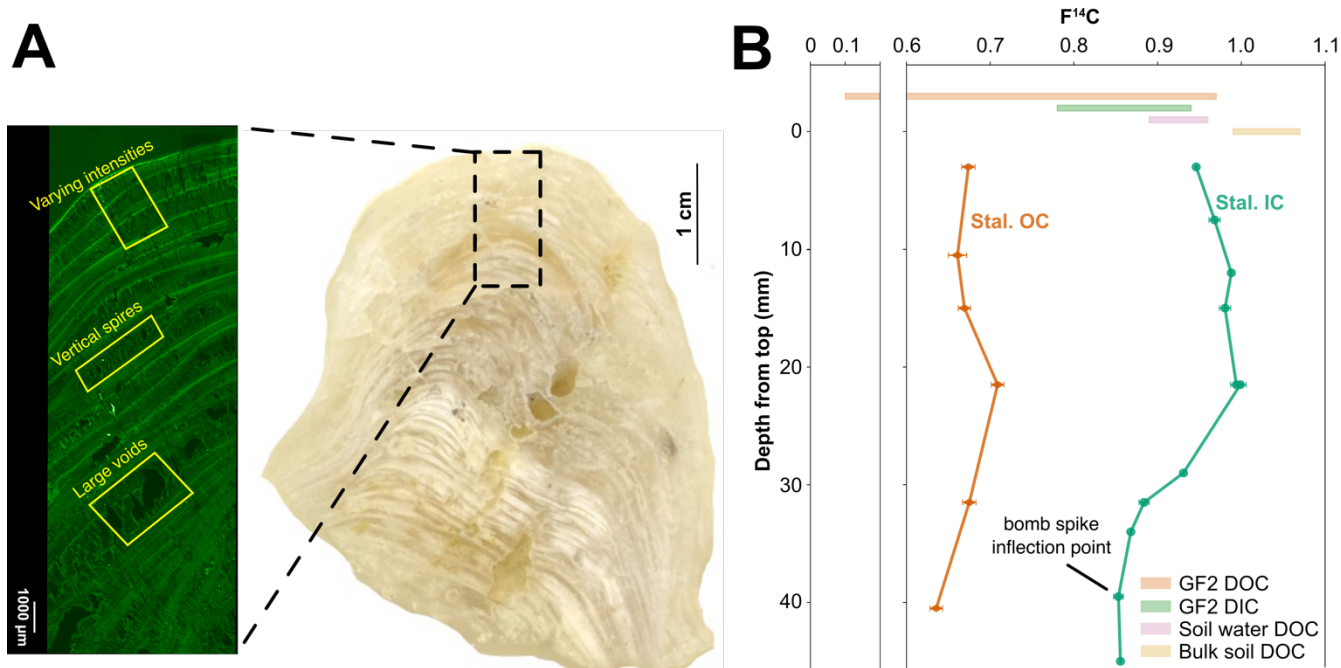


Figure 5. a) Results of the solid phase fluorescence features in the actively growing stalagmite beneath GF2, shown beside an image of the sectioned stalagmite. The approximate location of the scan is annotated by the dashed box. The image was captured by an Olympus Fluoview 3000 with an excitation of 488 nm and 490 to 590 nm detection. Fiji and Inkscape were used for processing and annotation. **b)** Comparison between inorganic (green) and organic (orange) $F^{14}\text{C}$ measured from the actively growing stalagmite in a). The $F^{14}\text{C}$ range of DOC extracted from soils (purple), and the DIC (green) and DOC (orange) of GF2 drip water are shown in the vertical bars.

4 Discussion

4.1 Sources of subsurface carbon

This study gives insight into the mechanisms driving the origins and transport of DIC and DOC from surface terrestrial ecosystems to the subsurface over spatial and temporal scales in a midlatitude karst system. The ^{14}C content of the bulk soils ($F^{14}\text{C} \sim 1.03$) and of the soil solution DOC ($F^{14}\text{C} \sim 0.92$) is modern, whereas drip water DOC shows a much larger ^{14}C range ($F^{14}\text{C}$: 0.10 to 0.97), challenging the notion that organic carbon originating directly from the overlying soil column is the primary source of DOC in cave waters at all times (Blyth et al., 2016; Hartland et al., 2012; Liao et al., 2018, 2021). The residence time of percolating water in the epikarst at our site is ~ 5.5 to 6.6 yrs (Affolter et al., 2020), a period too short for the scale of ageing observed in the drip water DOC. We need to caution that due to limited sampling capabilities, our assessment of bulk soil ages does not extend deeper than 30 cm, and soil water was sampled at 1 m depth at only one location. It is known that soil ages increase with depth in undisturbed soils (Leavitt et al., 2007; Trumbore, 2000), therefore deeper and older soil

carbon pools may not be represented in our dataset. Soil organic carbon is a heterogeneous carbon reservoir containing different proportions of modern and aged carbon on a continuum ranging from ^{14}C enriched (due to the excess release of ^{14}C into the atmosphere during nuclear weapons testing from 1950 to 1960) to $> 10^4$ yrs old (Shi et al., 2020).

Notably, the drip water DOC spans a much larger ^{14}C range than the stalagmite organic carbon fraction (Fig. 5). This is also true when comparing the drip feeding the stalagmite (GF2, DOC $F^{14}\text{C}$: 0.22 to 0.97, corresponding to an uncalibrated ^{14}C age between 11'990 and 217 yrs) and the stalagmite itself ($F^{14}\text{C}$: 0.65 to 0.72, corresponding to an uncalibrated ^{14}C age between 3430 and 2652 yrs), suggesting either that the oldest component of dripwater DOC is not well preserved in solid state, or that the speleothem sampling, which integrates several years of growth, has smoothed out the signal, due to the slower speleothem growth compared to our drip water sampling interval. The stalagmite organic carbon bomb peak is muted but visible. To assess the proportion of bomb carbon needed to create the observed stalagmite organic carbon $F^{14}\text{C}$ peak ($F^{14}\text{C}_{stal.OC} = 0.71$) the sources of carbon contributing to the organic carbon ^{14}C signature can be simplified as a mixture of ^{14}C -free organic carbon ($F^{14}\text{C}_{old} = 0$), assumed from the lower range of drip DOC values, and soil organic carbon which is enriched with bomb carbon. An equilibrium between atmosphere and soil $F^{14}\text{C}$ is presumed, thus the maximum atmospheric $F^{14}\text{C}$ value in 1963 is taken to represent the soil composition ($F^{14}\text{C}_{soil} = 1.95$) (Hua et al., 2022). A two-endmember mixing model was created to assess the proportion of modern soil (f_{soil}) and old organic carbon (f_{old}) needed to result in the $F^{14}\text{C}_{stal.OC}$ value:

$$F^{14}\text{C}_{stal.OC} = f_{soil}F^{14}\text{C}_{soil} + (1 - f_{soil})F^{14}\text{C}_{old} \quad (2)$$

$$\text{Where } f_{old} = 1 - f_{soil} \quad (3)$$

This results in a f_{soil} of 36% and f_{old} of 64%, further indicating that aged carbon is likely the dominant source of organic carbon, with a smaller contribution from modern soil. However, it should be highlighted that the end members chosen for the mass balance are extreme cases, and it is more likely that organic carbon with a range of ages contributes to the stalagmite organic carbon.

The influence of hydrological variability on the variability in TOC and DOC $F^{14}\text{C}$ observed across the catchment is complex and difficult to assess, with discharge and elemental concentrations tied to bedrock dissolution and PCP dynamics mainly reflecting the prolonged drought in summer of 2023. On the other hand, elements diagnostic for increased transport of colloidal material (e.g., Zn; Fig. 3c) peak during the time period when the TOC and DOC $F^{14}\text{C}$ are the lowest. It is possible that this reflects episodic mobilization of old carbon from deep soil pockets. In the likely absence of local glaciations during the Late and Middle Pleistocene (Buoncristiani and Campy, 2011), old soils could have easily been preserved in deep epikarst fractures at Milandre cave and thus span the entire possible range of ^{14}C .

The motorway that affects the cave above the GR sites could have an influence on DOC concentrations and age, but this seems unlikely since the seasonal pattern appears in all samples with the same magnitude irrespective of their location. Petrogenic OC, ^{14}C -free organic material stored in the carbonate bedrock and leached from the matrix, could also be a contributing source of older carbon (Gázquez et al., 2012). The Sr concentration in dripwater has been proposed as an indicator of bedrock dissolution intensity since it is not appreciably removed during PCP nor significantly depleted by biological removal, if the bedrock is homogeneous in Mg, then Mg may also be an indicator of bedrock dissolution (Kost et al., 2023). The maximum



in Sr concentrations suggests most intense bedrock dissolution between October and December 2022 (Fig. 3c, Fig. S2). The Sinclair test shows strong correlation of $\ln(\text{Mg}/\text{Ca})$ and $\ln(\text{Sr}/\text{Ca})$ with slope gradients > 0.70 (excluding GR3 and GR5; Fig. S3) suggesting that Ca concentrations are strongly influenced by PCP and therefore the Ca concentration is not a robust indicator of bedrock dissolution intensity. If periods of increased dissolution had introduced petrogenic carbon into the DOC pool, we would expect an inverse correlation between F^{14}C DOC and dripwater Sr. We observed this broadly in several drips, but the relationship is only significant in drip GR4 (Fig. S4). Drip GR4 is also the only one that does not recover to higher DOC ^{14}C values after the summer of 2022 (Fig. S1). It is possible that this drip was influenced by a significant component of DOC from petrogenic carbon. At the same time, drip GR4 also has the second highest concentration of Na, which at our site likely reflects the input of road salt from the motorway. It is thus possible that the prolonged fossil signature in this drip could also come from anthropogenic inputs (e.g., tire wear particles). Over the entire catchment, significant contributions from petrogenic carbon are unlikely, since the bedrock of Milandre cave is Upper Jurassic limestone with no association with organic rich lithologies (Liniger, 1970).

The wide range of the dripwater DOC ^{14}C signature (F^{14}C : 0.10 to 0.97) contrasts with the younger and more stable DIC ^{14}C (F^{14}C : 0.78 to 0.94; Fig. 3b) which reflects more modern carbon contributions, likely sourced from soil and root respiration, as reflected in the bulk soils ($\text{F}^{14}\text{C} \sim 1.03$) and soil DOC ($\text{F}^{14}\text{C} \sim 0.92$). As the soil sampling focused on the topmost, presumably youngest, soil layers, the slightly older DIC ^{14}C may be due to the addition of older carbon from soil pools that were not captured in our sampling. A small input of ^{14}C -free carbon from the bedrock may also have contributed to the ageing of the dripwater DIC compared to the topsoil. The inorganic carbon fraction measured in the stalagmite (most recently deposited sample: $\text{F}^{14}\text{C} = 0.95$), is at the upper end of the range in DIC in the corresponding drip (GF2, F^{14}C : 0.88 to 0.94; Fig. 5). As already mentioned for the DOC fraction, the stalagmite sample likely represents a smoothed signal over a few annual cycles, whereas the higher resolution drip water analysis detects higher frequency variations. Nevertheless, the similarity implies that the stalagmite carbonate does reflect the DIC ^{14}C content, and therefore we gain a multi-decadal perspective on DIC cycling in this cave system. The $\sim 12.7\%$ DCF suggests little contribution of bedrock dissolution (Fohlmeister et al., 2011; Markowska et al., 2019; Rudzka-Phillips et al., 2013), supporting the conclusion that most DIC at Milandre cave is introduced from soil CO_2 under open system dissolution conditions, keeping the rock-derived contribution to this pool small (Rowan et al., 2025).

4.2 Temporal trends in dripwater dissolved carbon

The temporal trends in drip water TOC and DOC F^{14}C in 2022 suggest significant seasonal changes in the source, mobilisation, and transport of unsaturated zone DOC (Fig. 3a and b). During winter 2022, the drip water DOC was more concentrated and younger, whereas in spring and summer 2022 both TOC and F^{14}C decreased drastically across all sampled drip sites. Periods of higher precipitation can cause soil OC to be mobilized, which then percolates through the epikarst causing higher TOC concentrations in drip waters (Liao et al., 2021). This has also been observed in Milandre river waters (Savoy, 2007). The TOC and F^{14}C are not significantly correlated to MMP, likely because the drip rate is not correlated to MMP, though no time-lag analysis was performed to verify possible lag effects. This suggests that MMP may not closely reflect soil saturation and



hydrological reaction of the epikarst, both of which influence how much soil organic carbon is mobilized into the dissolved phase (Chapman et al., 2024). At Milandre cave, river discharge responds to precipitation, with 64 to 78% of the total discharge volume occurring during high-precipitation events, while base flow contributes 22 to 36% (Jeannin et al., 2021). As river discharge correlates with the drip rates, this is considered a more accurate control on aquifer hydrology (Table S3). The monitored drips are primarily classified as a mixture between fracture flow and diffuse flow (Fig. 2f). The seasonal variability in drip rate that has previously been observed in Milandre in a location proximal to GF1, with lower summer and higher winter drip rates (Affolter et al., 2015) is only reproduced in our dataset during 2022 in drip GF1 (Fig. 2a). These findings suggest that the drip rates and DOC mobilization may only respond to precipitation in certain drips and time periods, likely due to the particular drip hydrological pathway and the effects of evapotranspiration strength controlling soil moisture (Affolter et al., 2015). Water can be transported through the bedrock via conduit and fracture flows, and can be stored in reservoirs for periods of time (Partin et al., 2012), resulting in a nonlinear relationship between meteoric precipitation and drip rate (Baker and Brunsdon, 2003).

It is likely that the temporal variation in TOC and $F^{14}C$ is partially due to variability in organic carbon contributions from spatial heterogeneity in the soil across the catchment and with depth that was not captured by our sampling. Though the summer months of June 2022 to August 2022 had variable MMP, higher summer temperatures would have resulted in lower soil moisture due to increased evapotranspiration, decreasing the volume of water which can be transported, and the activity of microbial communities in the soil column (Wang et al., 2014). This would decrease the concentration of labile soil organic carbon available for downwards transport. In addition, increased summer temperatures can cause accelerated consumption and oxidation of younger soil organic carbon to CO_2 , which would lead to a higher proportion of older material available to be transported downwards into the epikarst. The rewetting of dry soil by increased precipitation amounts in June 2022 could also mobilize older carbon fractions from the soil (Liao et al., 2021; Miller et al., 2005). This is also reflected in organic carbon associated trace metals, e.g. Zn (Fig. 3d, Fig. S2) (Hartland et al., 2012; Pédrot et al., 2008) which plateau in concentration from August to December 2022, possibly because of the increased mobilisation of soil organic carbon.

5 Conclusions

This research provides one of only a few datasets focused on carbon cycle dynamics within the unsaturated zone in a karst system, linking soils, unsaturated zone drip water and rivers, key areas where significant uncertainties remain about terrestrial carbon export dynamics. By demonstrating the variability in DIC and DOC composition over spatial and temporal scales, this study highlights the role of karst systems as dynamic interfaces where different carbon reservoirs interact. The stability of the DIC ^{14}C content, reflecting a dominant contribution from root and soil respiration of recently fixed carbon, contrasts with the wide and variable range in $F^{14}C$ of the DOC, which likely includes inputs from older soil and subsurface carbon reservoirs. General agreement in the range of $F^{14}C$ values measured on a recently deposited speleothem and in the drip waters provide a decadal-scale perspective on unsaturated zone carbon cycle dynamics. However, questions remain about the mechanisms



governing the transport and cycling of carbon within the unsaturated zone. This highlights the complexity of DOC sources, transport and reworking pathways in the unsaturated zone of karst systems, and underscores the importance of understanding site specific hydrological and environmental factors.

470 **Code and data availability**

The code and datasets used to generate figures 3, 4 and figures S1-4 can be found at https://github.com/flechleitner08/Rowan_Milandre_water2026.git. The drip rate, precipitation, and discharge data for figure 2 are also stored in the repository. All other datasets generated and the results of statistical analysis are available in the supplement file.

475 **Supplement link**

The link to the supplement will be included by Copernicus, if applicable.

Author contributions

Sarah Rowan: Conceptualization, Formal analysis, Data visualisation, Writing – Original draft preparation.

Marc Luetscher: Conceptualization, Formal analysis, Writing – Reviewing and Editing.

480 Negar Haghipour: Resources, Formal analysis, Writing – Reviewing and Editing

Heather Stoll: Resources, Formal analysis, Writing – Reviewing and Editing

Laura Endres: Resources, Formal analysis, Writing – Reviewing and Editing

Sönke Szidat: Writing – Reviewing and Editing

Franziska Lechleitner: Funding acquisition, Conceptualisation, Supervision, Writing – Reviewing and Editing

485 **Competing interests**

The authors declare that they have no conflict of interest.

Disclaimer

Copernicus Publications remains neutral with regard to jurisdictional claims made in the text, published maps, institutional affiliations, or any other geographical representation in this paper. While Copernicus Publications makes every effort to include
490 appropriate place names, the final responsibility lies with the authors. Views expressed in the text are those of the authors and do not necessarily reflect the views of the publisher.”



Acknowledgements

We gratefully thank the staff of the Swiss Institute of Speleology and Karst Studies for their previous and continued work in Milandre cave, and for their contribution of field assistance and expertise in karst science. We express our gratitude to the Spéléo Club Jura for the initial exploration of Milandre cave, and for their persistent work and maintenance of the area. We also appreciate Daniel Pape, for continued access to the cave entrance. Thank you also to Madalina Jaggi for her expertise in trace element analysis, Dr. Oliver Kost for assistance with CSLM, and Maarika Bischoff for the TOC measurements. Assistance in graphitisations and wet chemical oxidation by Dr. Jan Strähl, Dr. Giulia Guidobaldi, and Dr. Gang Xue is gratefully acknowledged. AMS measurements were also assisted by Michael Staub and Dr. Gary Salazar. Generative AI (ChatGPT versions 3.5, 4, and 4o) was used for code writing and troubleshooting.

Financial support

Support funds and grant agreement numbers are listed as specified upon manuscript registration and reported to FundRef upon publication.

Review statement

The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.

References

- Affolter, S., Häuselmann, A. D., Fleitmann, D., Häuselmann, P., and Leuenberger, M.: Triple isotope (δD , $\delta^{17}O$, $\delta^{18}O$) study on precipitation, drip water and speleothem fluid inclusions for a Western Central European cave (NW Switzerland), *Quaternary Science Reviews*, 127, 73–89, <https://doi.org/10.1016/j.quascirev.2015.08.030>, 2015.
- Affolter, S., Steinmann, P., Aemisegger, F., Purtschert, R., and Leuenberger, M.: Origin and percolation times of Milandre Cave drip water determined by tritium time series and beryllium-7 data from Switzerland, *Journal of Environmental Radioactivity*, 222, 106346, <https://doi.org/10.1016/j.jenvrad.2020.106346>, 2020.
- Baker, A. and Brunson, C.: Non-linearities in drip water hydrology: an example from Stump Cross Caverns, Yorkshire, *Journal of Hydrology*, 277, 151–163, [https://doi.org/10.1016/S0022-1694\(03\)00063-5](https://doi.org/10.1016/S0022-1694(03)00063-5), 2003.
- Baker, A. and Genty, D.: Fluorescence wavelength and intensity variations of cave waters, *Journal of Hydrology*, 217, 19–34, [https://doi.org/10.1016/S0022-1694\(99\)00010-4](https://doi.org/10.1016/S0022-1694(99)00010-4), 1999.
- Baldini, J. U. L., Lechleitner, F. A., Breitenbach, S. F. M., Van Hunen, J., Baldini, L. M., Wynn, P. M., Jamieson, R. A., Ridley, H. E., Baker, A. J., Walczak, I. W., and Fohlmeister, J.: Detecting and quantifying palaeoseasonality in stalagmites using geochemical and modelling approaches, *Quaternary Science Reviews*, 254, 106784, <https://doi.org/10.1016/j.quascirev.2020.106784>, 2021.



- Blyth, A. J., Hartland, A., and Baker, A.: Organic proxies in speleothems - New developments, advantages and limitations, *Quaternary Science Reviews*, 149, 1–17, <https://doi.org/10.1016/j.quascirev.2016.07.001>, 2016.
- 525 Bogdan, D. F., Baricz, A. I., Chiciudean, I., Bulzu, P.-A., Cristea, A., Năstase-Bucur, R., Levei, E. A., Cadar, O., Sitar, C., Banciu, H. L., and Moldovan, O. T.: Diversity, distribution and organic substrates preferences of microbial communities of a low anthropic activity cave in North-Western Romania, *Front. Microbiol.*, 14, <https://doi.org/10.3389/fmicb.2023.962452>, 2023.
- 530 Buonerchristiani, J.-F. and Campy, M.: Chapter 10 - Quaternary Glaciations in the French Alps and Jura, in: *Quaternary Glaciations - Extent and Chronology: A Closer Look*, vol. 15, edited by: Ehlers, J., Gibbard, P. L., and Hughes, P. D., Elsevier, Amsterdam, 117–126, <https://doi.org/10.1016/B978-0-444-53447-7.00010-6>, 2011.
- Campeau, A., Bishop, K., Amvrosiadi, N., Billett, M. F., Garnett, M. H., Laudon, H., Öquist, M. G., and Wallin, M. B.: Current forest carbon fixation fuels stream CO₂ emissions, *Nature Communications*, 10, 1876, <https://doi.org/10.1038/s41467-019-09922-3>, 2019.
- 535 Chapman, R. G., Laffan, S., McDonough, L. K., Markowska, M., and Baker, A.: Spatiotemporal variation in cave percolation waters: A functional approach, *Journal of Hydrology*, 631, 130784, <https://doi.org/10.1016/j.jhydrol.2024.130784>, 2024.
- Collister, C. and Matthey, D.: Controls on water drop volume at speleothem drip sites: An experimental study, *Journal of Hydrology*, 358, 259–267, <https://doi.org/10.1016/j.jhydrol.2008.06.008>, 2008.
- Drake, T. W., Raymond, P. A., and Spencer, R. G. M.: Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty, *Limnology and Oceanography Letters*, 3, 132–142, <https://doi.org/10.1002/lol2.10055>, 2018.
- 540 Eglinton, T. I., Galy, V. V., Hemingway, J. D., Feng, X., Bao, H., Blattmann, T. M., Dickens, A. F., Gies, H., Giosan, L., Haghipour, N., Hou, P., Lupker, M., McIntyre, C. P., Montluçon, D. B., Peucker-Ehrenbrink, B., Ponton, C., Schefuß, E., Schwab, M. S., Voss, B. M., Wacker, L., Wu, Y., and Zhao, M.: Climate control on terrestrial biospheric carbon turnover, *Proceedings of the National Academy of Sciences*, 118, e2011585118, <https://doi.org/10.1073/pnas.2011585118>, 2021.
- 545 Endres, L. S., Jacquín, C., González-Lemos, S., Rodríguez-Rodríguez, L., Sliwinski, J., Kaushal, N., Kost, O., and Stoll, H. M.: Climatic and cave settings influence on drip water fluorescent organic matter with implications for fluorescent laminations in stalagmites, *Quaternary Research*, 118, 41–61, <https://doi.org/10.1017/qua.2023.41>, 2024.
- Epure, L., Meleg, I. N., Munteanu, C.-M., Roban, R. D., and Moldovan, O. T.: Bacterial and Fungal Diversity of Quaternary Cave Sediment Deposits, *Geomicrobiology Journal*, 31, 116–127, <https://doi.org/10.1080/01490451.2013.815292>, 2014.
- 550 Fohlmeister, J., Schröder-Ritzrau, A., Spötl, C., Frisia, S., Miorandi, R., Kromer, B., and Mangini, A.: The influences of hydrology on the radiogenic and stable carbon isotope composition of cave drip water, Grotta di Ernesto (Italy), *Radiocarbon*, 52, 1529–1544, <https://doi.org/10.1017/S0033822200056289>, 2010.
- Fohlmeister, J., Scholz, D., Kromer, B., and Mangini, A.: Modelling carbon isotopes of carbonates in cave drip water, *Geochimica et Cosmochimica Acta*, 75, 5219–5228, <https://doi.org/10.1016/j.gca.2011.06.023>, 2011.
- 555 Fohlmeister, J., Voarintsoa, N. R. G., Lechleitner, F. A., Boyd, M., Brandtstätter, S., Jacobson, M. J., and Oster, J. L.: Main controls on the stable carbon isotope composition of speleothems, *Geochimica et Cosmochimica Acta*, 279, 67–87, <https://doi.org/10.1016/j.gca.2020.03.042>, 2020.
- Friedlingstein, P., O’Sullivan, M., Jones, M. W., Andrew, R. M., Bakker, D. C. E., Hauck, J., Landschützer, P., Le Quéré, C., Li, H., Luijkx, I. T., Peters, G. P., Peters, W., Pongratz, J., Schwingshackl, C., Sitch, S., Canadell, J. G., Ciais, P., Aas, K.,



- Alin, S. R., Anthoni, P., Barbero, L., Bates, N. R., Bellouin, N., Benoit-Cattin, A., Berghoff, C. F., Bernardello, R., Bopp, L.,
560 Brasika, I. B. M., Chamberlain, M. A., Chandra, N., Chevallier, F., Chini, L. P., Collier, N. O., Colligan, T. H., Cronin, M.,
Djeutchouang, L. M., Dou, X., Enright, M. P., Enyo, K., Erb, M., Evans, W., Feely, R. A., Feng, L., Ford, D. J., Foster, A.,
Fransner, F., Gasser, T., Gehlen, M., Gkritzalis, T., Goncalves De Souza, J., Grassi, G., Gregor, L., Gruber, N., Guenet, B.,
Gürses, Ö., Harrington, K., Harris, I., Heinke, J., Hurtt, G. C., Iida, Y., Ilyina, T., Ito, A., Jacobson, A. R., Jain, A. K., Jarníková,
T., Jersild, A., Jiang, F., Jones, S. D., Kato, E., Keeling, R. F., Klein Goldewijk, K., Knauer, J., Kong, Y., Korsbakken, J. I.,
565 Koven, C., Kunimitsu, T., Lan, X., Liu, J., Liu, Z., Liu, Z., Lo Monaco, C., Ma, L., Marland, G., McGuire, P. C., McKinley,
G. A., Melton, J. R., Monacci, N., Monier, E., Morgan, E. J., Munro, D. R., Müller, J. D., Nakaoka, S.-I., Nayagam, L. R.,
Niwa, Y., Nutz, T., Olsen, A., Omar, A. M., Pan, N., Pandey, S., Pierrot, D., Qin, Z., Regnier, P., Rehder, G., Resplandy, L.,
Roobaert, A., Rosan, T. M., Rödenbeck, C., Schwinger, J., Skjelvan, I., Smallman, T. L., Spada, V., Sreeush, M. G., Sun, Q.,
Sutton, A. J., Sweeney, C., Swingedouw, D., Séférian, R., Takao, S., Tatebe, H., Tian, H., Tian, X., Tilbrook, B., Tsujino, H.,
570 Tubiello, F., van Ooijen, E., van der Werf, G. R., van de Velde, S. J., Walker, A. P., Wanninkhof, R., Yang, X., Yuan, W.,
Yue, X., and Zeng, J.: Global Carbon Budget 2025, *Earth System Science Data*, 18, 3211–3288, <https://doi.org/10.5194/essd-18-3211-2026>, 2026.
- Gázquez, F., Calaforra, J. M., Rull, F., Forti, P., and García-Casco, A.: Organic matter of fossil origin in the amberine
speleothems from El Soplaio Cave (Cantabria, Northern Spain), *International Journal of Speleology*, 41, 113–123,
575 <https://doi.org/10.5038/1827-806X.41.1.12>, 2012.
- Ge, T., Xue, Y., Jiang, X., Zou, L., and Wang, X.: Sources and radiocarbon ages of organic carbon in different grain size
fractions of Yellow River-transported particles and coastal sediments, *Chemical Geology*, 534, 119452,
<https://doi.org/10.1016/j.chemgeo.2019.119452>, 2020.
- van Groenigen, K. J., Qi, X., Osenberg, C. W., Luo, Y., and Hungate, B. A.: Faster Decomposition Under Increased
580 Atmospheric CO₂ Limits Soil Carbon Storage, *Science*, 344, 508–509, <https://doi.org/10.1126/science.1249534>, 2014.
- Hajdas, I., Guidobaldi, G., Haghipour, N., and Wyss, K.: SAMPLE SELECTION, CHARACTERIZATION AND CHOICE
OF TREATMENT FOR ACCURATE RADIOCARBON ANALYSIS—INSIGHTS FROM THE ETH LABORATORY,
Radiocarbon, 66, 1152–1165, <https://doi.org/10.1017/RDC.2024.12>, 2024.
- Hanke, U. M., Wacker, L., Haghipour, N., Schmidt, M. W. I., Eglinton, T. I., and McIntyre, C. P.: Comprehensive radiocarbon
585 analysis of benzene polycarboxylic acids (BPCAs) derived from pyrogenic carbon in environmental samples, *Radiocarbon*,
59, 1103–1116, <https://doi.org/10.1017/RDC.2017.44>, 2017.
- Hartland, A., Fairchild, I. J., Lead, J. R., Borsato, A., Baker, A., Frisia, S., and Baalousha, M.: From soil to cave: transport of
trace metals by natural organic matter in karst dripwaters, *Chemical Geology*, 304–305, 68–82,
<https://doi.org/10.1016/j.chemgeo.2012.01.032>, 2012.
- 590 He, Y., Trumbore, S. E., Torn, M. S., Harden, J. W., Vaughn, L. J. S., Allison, S. D., and Randerson, J. T.: Radiocarbon
constraints imply reduced carbon uptake by soils during the 21st century, *Science*, 353, 1419–1424,
<https://doi.org/10.1126/science.aad4273>, 2016.
- He, Y., Li, J., Li, X., Liao, J., Liang, Q., Li, H., Duan, R., Wang, C., Liu, B., Xue, Y., and Li, T.: Characteristics and Influencing
Factors of Dissolved Organic Matter in Cave Drip Water—A Case Study from Furong Cave, Southwest China, *Water*, 16,
595 <https://doi.org/10.3390/w16020207>, 2024.
- Heidke, I., Scholz, D., and Hoffmann, T.: Quantification of lignin oxidation products as vegetation biomarkers in speleothems
and cave drip water, *Biogeosciences*, 15, 5831–5845, <https://doi.org/10.5194/bg-2018-253>, 2018.



- Heine, F. and Einsiedl, F.: Groundwater dating with dissolved organic radiocarbon: A promising approach in carbonate aquifers, *Applied Geochemistry*, 125, 104827, <https://doi.org/10.1016/j.apgeochem.2020.104827>, 2021.
- 600 Hua, Q., Turnbull, J. C., Santos, G. M., Rakowski, A. Z., Ancapichún, S., Pol-Holz, R. D., Hammer, S., Lehman, S. J., Levin, I., Miller, J. B., Palmer, J. G., and Turney, C. S. M.: ATMOSPHERIC RADIOCARBON FOR THE PERIOD 1950–2019, *Radiocarbon*, 64, 723–745, <https://doi.org/10.1017/RDC.2021.95>, 2022.
- Jeannin, P.-Y.: Structure et comportement hydraulique des aquifères karstiques, Doctoral dissertation, University of Neuchâtel, <https://doi.org/10.35662/unine-thesis-1431>, 1998.
- 605 Jeannin, P.-Y., Häuselmann, P., Lüscher, M., Blant, D., and Meury, P.-X.: Presentation of a water injection system to control the growth of speleothems at the Milandre test-site (JU, Switzerland), *Proceedings 16. Int. Speleological Congress, Brno, CZ*, 408–412, https://digitalcommons.usf.edu/kip_talks/13, 2013.
- Jeannin, P.-Y., Artigue, G., Butscher, C., Chang, Y., Charlier, J.-B., Duran, L., Gill, L., Hartmann, A., Johannet, A., Jourde, H., Kavousi, A., Liesch, T., Liu, Y., Lüthi, M., Malard, A., Mazzilli, N., Pardo-Igúzquiza, E., Thiéry, D., Reimann, T., Schuler, P., Wöhling, T., and Wunsch, A.: Karst modelling challenge 1: Results of hydrological modelling, *Journal of Hydrology*, 600, 126508, <https://doi.org/10.1016/j.jhydrol.2021.126508>, 2021.
- 610 Jones, D. S. and Northup, D. E.: Cave Decorating with Microbes: Geomicrobiology of Caves, *Elements*, 17, 107–112, <https://doi.org/10.2138/gselements.17.2.107>, 2021.
- Jull, A. J. T., Burr, G. S., Zhou, W., Cheng, P., Song, S. H., Leonard, A. G., Cheng, L., and An, Z. S.: ^{14}C Measurements of Dissolved Inorganic and Organic Carbon in Qinghai Lake and Inflowing Rivers (NE Tibet, Qinghai Plateau), China, *Radiocarbon*, 56, 1115–1127, <https://doi.org/10.2458/56.17776>, 2014.
- 615 Kaiser, K. and Kalbitz, K.: Cycling downwards - dissolved organic matter in soils, *Soil Biology and Biochemistry*, 52, 29–32, <https://doi.org/10.1016/j.soilbio.2012.04.002>, 2012.
- Keenan, T. F. and Williams, C. A.: The Terrestrial Carbon Sink, *Annual Review of Environment and Resources*, 43, 219–243, <https://doi.org/10.1146/annurev-environ-102017-030204>, 2018.
- 620 Knierim, K., Pollock, E., Hays, P., and Khojasteh, J.: Using Stable Isotopes of Carbon to Investigate the Seasonal Variation of Carbon Transfer in a North-western Arkansas Cave, *JCKS*, 77, 12–27, <https://doi.org/10.4311/2011ES0264>, 2015.
- Kost, O., González-Lemos, S., Rodríguez-Rodríguez, L., Sliwinski, J., Endres, L., Haghipour, N., and Stoll, H.: Relationship of seasonal variations in drip water $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, and trace elements with surface and physical cave conditions of La Vallina cave, NW Spain, *Hydrology and Earth System Sciences*, 27, 2227–2255, <https://doi.org/10.5194/hess-27-2227-2023>, 2023.
- 625 Lang, S. Q., McIntyre, C. P., Bernasconi, S. M., Früh-Green, G. L., Voss, B. M., Eglinton, T. I., and Wacker, L.: Rapid ^{14}C Analysis of Dissolved Organic Carbon in Non-Saline Waters, *Radiocarbon*, 58, 505–515, <https://doi.org/10.1017/RDC.2016.17>, 2016.
- Leavitt, S. W., Follett, R. F., Kimble, J. M., and Pruessner, E. G.: Radiocarbon and $\delta^{13}\text{C}$ depth profiles of soil organic carbon in the U.S. Great Plains: A possible spatial record of paleoenvironment and paleovegetation, *Quaternary International*, 162–163, 21–34, <https://doi.org/10.1016/j.quaint.2006.10.033>, 2007.
- 630 Lechleitner, F. A., Dittmar, T., Baldini, J. U. L., Pruffer, K. M., and Eglinton, T. I.: Molecular signatures of dissolved organic matter in a tropical karst system, *Organic Geochemistry*, 113, <https://doi.org/10.1016/j.orggeochem.2017.07.015>, 2017.



- 635 Liao, J., Hu, C., Wang, M., Li, X., Ruan, J., Zhu, Y., Fairchild, I. J., and Hartland, A.: Assessing acid rain and climate effects on the temporal variation of dissolved organic matter in the unsaturated zone of a karstic system from southern China, *Journal of Hydrology*, 556, 475–487, <https://doi.org/10.1016/j.jhydrol.2017.11.043>, 2018.
- Liao, J., Hu, C., Li, X., and Ruan, J.: Drying increases organic colloidal mobilization in the karst vadose zone: Evidence from a 15-year cave-monitoring study, *Hydrological Processes*, 35, e14163, <https://doi.org/10.1002/hyp.14163>, 2021.
- 640 Liniger, H.: *Geologischer Atlas der Schweiz*, 1:25 000. 1065 Bonfol mit Anhängsel von Blatt 1066 Rodersdorf, Kommissionsverlag: Kümmerly&Frey AG., Geographischer Verlag, Bern, <https://shop.swisstopo.admin.ch>, 1970.
- Markowska, M., Fohlmeister, J., Treble, P. C., Baker, A., Andersen, M. S., and Hua, Q.: Modelling the 14C bomb-pulse in young speleothems using a soil carbon continuum model, *Geochimica et Cosmochimica Acta*, 261, 342–367, <https://doi.org/10.1016/j.gca.2019.04.029>, 2019.
- 645 Miller, A. E., Schimel, J. P., Meixner, T., Sickman, J. O., and Melack, J. M.: Episodic rewetting enhances carbon and nitrogen release from chaparral soils, *Soil Biology and Biochemistry*, 37, 2195–2204, <https://doi.org/10.1016/j.soilbio.2005.03.021>, 2005.
- Mitchard, E. T. A.: The tropical forest carbon cycle and climate change, *Nature*, 559, 527–534, <https://doi.org/10.1038/s41586-018-0300-2>, 2018.
- 650 Partin, J. W., Jenson, J. W., Banner, J. L., Quinn, T. M., Taylor, F. W., Sinclair, D., Hardt, B., Lander, M. a., Bell, T., Miklavic, B., Jocson, J. M. U., and Taboroš, D.: Relationship between modern rainfall variability, cave dripwater, and stalagmite geochemistry in Guam, USA, *Geochemistry, Geophysics, Geosystems*, 13, 1–17, <https://doi.org/10.1029/2011GC003930>, 2012.
- Pédrot, M., Dia, A., Davranche, M., Bouhnik-Le Coz, M., Henin, O., and Gruau, G.: Insights into colloid-mediated trace element release at the soil/water interface, *Journal of Colloid and Interface Science*, 325, 187–197, <https://doi.org/10.1016/j.jcis.2008.05.019>, 2008.
- 655 Perrin, J., Jeannin, P.-Y., and Zwahlen, F.: Epikarst storage in a karst aquifer: a conceptual model based on isotopic data, Milandre test site, Switzerland, *Journal of Hydrology*, 279, 106–124, [https://doi.org/10.1016/S0022-1694\(03\)00171-9](https://doi.org/10.1016/S0022-1694(03)00171-9), 2003.
- Pronk, M., Goldscheider, N., Zopfi, J., and Zwahlen, F.: Percolation and Particle Transport in the Unsaturated Zone of a Karst Aquifer, *Groundwater*, 47, 361–369, <https://doi.org/10.1111/j.1745-6584.2008.00509.x>, 2009.
- 660 Reimer, P. J., Brown, T. A., and Reimer, R. W.: Discussion: reporting and calibration of post-bomb ¹⁴C data, *Radiocarbon*, 46, 1299–1304, <https://doi.org/10.1017/S0033822200033154>, 2004.
- Rhyner, T. M. Y., Bröder, L., White, M. E., Mittelbach, B. V. A., Brunmayr, A., Hagedorn, F., Storck, F. R., Passera, L., Haghipour, N., Zobrist, J., and Eglinton, T. I.: Radiocarbon signatures of carbon phases exported by Swiss rivers in the Anthropocene, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 381, 20220326, <https://doi.org/10.1098/rsta.2022.0326>, 2023.
- 665 Rowan, S. A., Luetscher, M., Laemmel, T., Harrison, A., Szidat, S., and Lechleitner, F. A.: Subsurface CO₂ dynamics in a temperate karst system reveal complex seasonal and spatial variations, *Biogeosciences*, 22, 6173–6203, <https://doi.org/10.5194/bg-22-6173-2025>, 2025.



- 670 Rudzka-Phillips, D., McDermott, F., Jackson, A., and Fleitmann, D.: Inverse modelling of the ^{14}C bomb pulse in stalagmites to constrain the dynamics of soil carbon cycling at selected European cave sites, *Geochimica et Cosmochimica Acta*, 112, 32–51, <https://doi.org/10.1016/j.gca.2013.02.032>, 2013.
- Savoy, L.: Use of natural and artificial reactive tracers to investigate the transfer of solutes in karst systems, Doctoral dissertation, University of Neuchâtel, Neuchâtel, <https://doi.org/10.35662/unine-thesis-1985>, 2007.
- 675 Schindelin, J., Arganda-Carreras, I., Frise, E., Kaynig, V., Longair, M., Pietzsch, T., Preibisch, S., Rueden, C., Saalfeld, S., Schmid, B., Tinevez, J.-Y., White, D. J., Hartenstein, V., Eliceiri, K., Tomancak, P., and Cardona, A.: Fiji: an open-source platform for biological-image analysis, *Nat Methods*, 9, 676–682, <https://doi.org/10.1038/nmeth.2019>, 2012.
- Shabarova, T., Villiger, J., Morenkov, O., Niggemann, J., Dittmar, T., and Pernthaler, J.: Bacterial community structure and dissolved organic matter in repeatedly flooded subsurface karst water pools, *Microbiology Ecology*, 89, 111–126, <https://doi.org/10.1111/1574-6941.12339>, 2014.
- 680 Shi, Z., Allison, S. D., He, Y., Levine, P. A., Hoyt, A. M., Beem-Miller, J., Zhu, Q., Wieder, W. R., Trumbore, S., and Randerson, J. T.: The age distribution of global soil carbon inferred from radiocarbon measurements, *Nature Geoscience*, <https://doi.org/10.1038/s41561-020-0596-z>, 2020.
- Sinclair, D. J.: Two mathematical models of Mg and Sr partitioning into solution during incongruent calcite dissolution. Implications for dripwater and speleothem studies, *Chemical Geology*, 283, 119–133, <https://doi.org/10.1016/j.chemgeo.2010.05.022>, 2011.
- 685 Sinclair, D. J., Banner, J. L., Taylor, F. W., Partin, J., Jenson, J., Mylroie, J., Goddard, E., Quinn, T., Jocson, J., and Miklavič, B.: Magnesium and strontium systematics in tropical speleothems from the Western Pacific, *Chemical Geology*, 294–295, 1–17, <https://doi.org/10.1016/j.chemgeo.2011.10.008>, 2012.
- Sliwinski, J. T. and Stoll, H. M.: Combined fluorescence imaging and LA-ICP-MS trace element mapping of stalagmites: Microfabric identification and interpretation, *Chemical Geology*, 581, 120397, <https://doi.org/10.1016/j.chemgeo.2021.120397>, 2021.
- 690 Sliwinski, J. T., Kost, O., Endres, L., Iglesias, M., Haghipour, N., González-Lemos, S., and Stoll, H. M.: Exploring soluble and colloiddally transported trace elements in stalagmites: The strontium-yttrium connection, *Geochimica et Cosmochimica Acta*, 343, 64–83, <https://doi.org/10.1016/j.gca.2022.12.023>, 2023.
- 695 Smart, P. and Friedrich, H.: Water movement and storage in the un-saturated zone of a maturely karstified carbonate aquifer, Mendip Hills, England, in: *Environmental Problems in Karst Terranes and Their Solutions*, Nat. Water well association, https://digitalcommons.usf.edu/kip_articles/5613, 1987.
- 700 Strähl, J., Lechleitner, F. A., Laemmel, T., Geissbühler, D., Salazar, G. A., Daellenbach, K. R., and Szidat, S.: An improved setup for radiocarbon analysis of water-soluble organic carbon in environmental matrices, *Radiocarbon*, 67, 220–233, <https://doi.org/10.1017/RDC.2024.113>, 2025.
- Synal, H. A., Stocker, M., and Suter, M.: MICADAS: A new compact radiocarbon AMS system, *Nuclear Instruments and Methods in Physics Research B*, 259, 7–13, <https://doi.org/10.1016/j.nimb.2007.01.138>, 2007.
- Szidat, S.: ^{14}C Research at the Laboratory for the Analysis of Radiocarbon with AMS (LARA), University of Bern, CHIMIA, 74, 1010–1010, <https://doi.org/10.2533/chimia.2020.1010>, 2020.



- 705 Tank, S. E., Fellman, J. B., Hood, E., and Kritzberg, E. S.: Beyond respiration: Controls on lateral carbon fluxes across the terrestrial-aquatic interface, *Limnology and Oceanography Letters*, 3, 76–88, <https://doi.org/10.1002/lol2.10065>, 2018.
- Terrer, C., Phillips, R. P., Hungate, B. A., Rosende, J., Pett-Ridge, J., Craig, M. E., van Groenigen, K. J., Keenan, T. F., Sulman, B. N., Stocker, B. D., Reich, P. B., Pellegrini, A. F. A., Pendall, E., Zhang, H., Evans, R. D., Carrillo, Y., Fisher, J. B., Van Sundert, K., Vicca, S., and Jackson, R. B.: A trade-off between plant and soil carbon storage under elevated CO₂,
710 *Nature*, 591, 599–603, <https://doi.org/10.1038/s41586-021-03306-8>, 2021.
- Trumbore, S.: Age of Soil Organic Matter and Soil Respiration: radiocarbon constraints on belowground dynamics, *Ecological Applications*, 10, 399–411, [https://doi.org/10.1890/1051-0761\(2000\)010\[0399:AOSOMA\]2.0.CO;2](https://doi.org/10.1890/1051-0761(2000)010[0399:AOSOMA]2.0.CO;2), 2000.
- Wacker, L., Némec, M., and Bourquin, J.: A revolutionary graphitisation system: Fully automated, compact and simple, *Nuclear Instruments and Methods in Physics Research B*, 268, 931–934, <https://doi.org/10.1016/j.nimb.2009.10.067>, 2010a.
- 715 Wacker, L., Christl, M., and Synal, H. A.: Bats: A new tool for AMS data reduction, *Nuclear Instruments and Methods in Physics Research, Section B*, 268, 976–979, <https://doi.org/10.1016/j.nimb.2009.10.078>, 2010b.
- Wang, Y., Hao, Y., Cui, X. Y., Zhao, H., Xu, C., Zhou, X., and Xu, Z.: Responses of soil respiration and its components to drought stress, *J Soils Sediments*, 14, 99–109, <https://doi.org/10.1007/s11368-013-0799-7>, 2014.
- Wassenaar, L., Aravena, R., Hendry, J., and Fritz, P.: Radiocarbon in Dissolved Organic Carbon, A Possible Groundwater Dating Method: Case Studies From Western Canada, *Water Resources Research*, 27, 1975–1986, <https://doi.org/10.1029/91WR00504>, 1991.
- 720 Xue, G., Cai, Y., Cheng, P., Lechleitner, F. A., Zhang, H., Zheng, Y., Wei, Y., Huang, S., Yang, L., Cheng, X., Lu, Y., Zhou, J., Ma, L., Cheng, H., and Edwards, R. L.: The Climate Control of Soil Organic Carbon Dynamics Inferred From Speleothem Radiocarbon Ages, *Geophysical Research Letters*, 50, e2022GL101875, <https://doi.org/10.1029/2022GL101875>, 2023.
- 725 Yin, J.-J., Tang, W., Wang, Z., Pu, J., Lan, G., Yang, H., Wu, X., and Li, J.: Deciphering the hydroclimatic significance of dripwater $\delta^{13}\text{CDIC}$ variations in monsoonal China based on modern cave monitoring, *Journal of Hydrology*, 603, 126882, <https://doi.org/10.1016/j.jhydrol.2021.126882>, 2021.
- MeteoSwiss, <https://www.meteoswiss.admin.ch/> (last access: 26 August 2024), 2024.