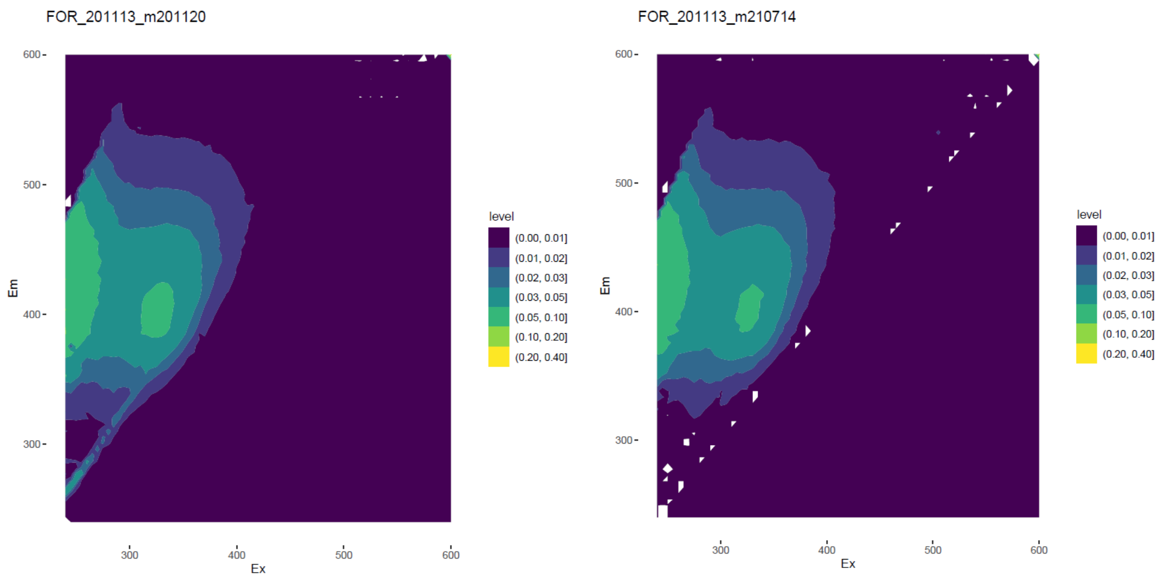
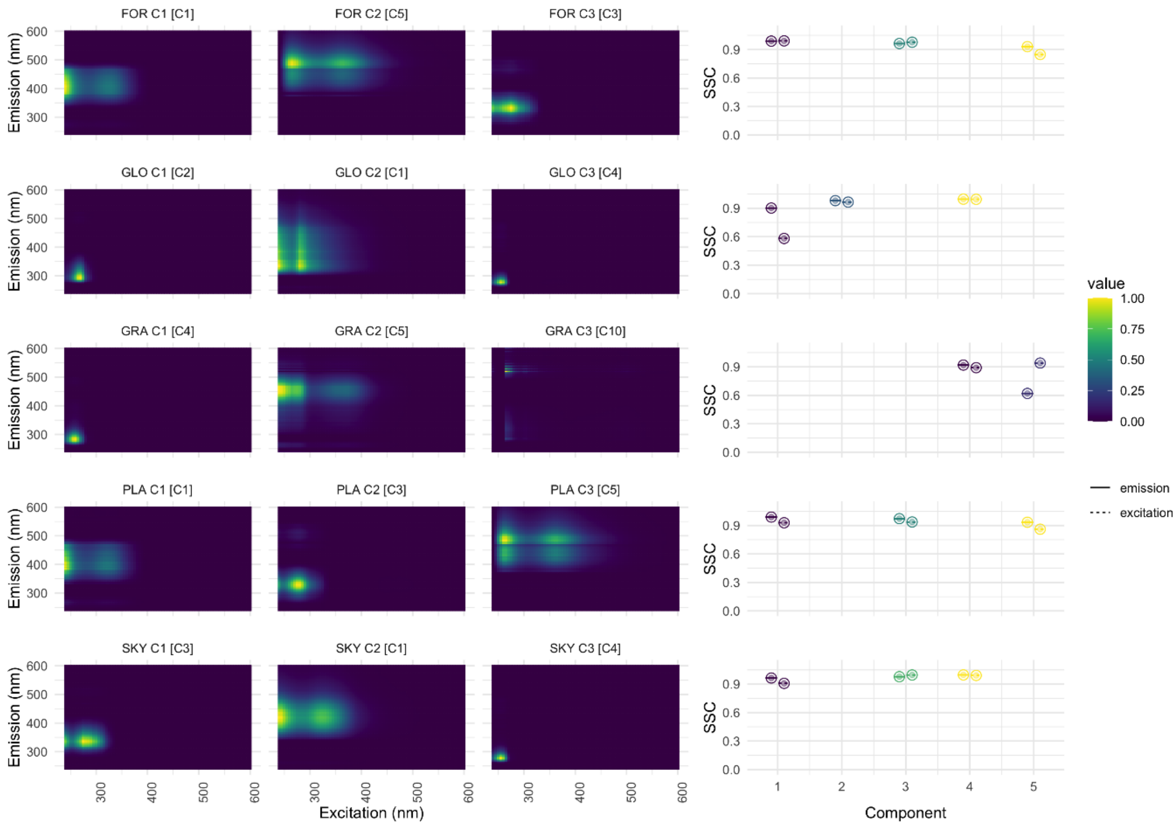
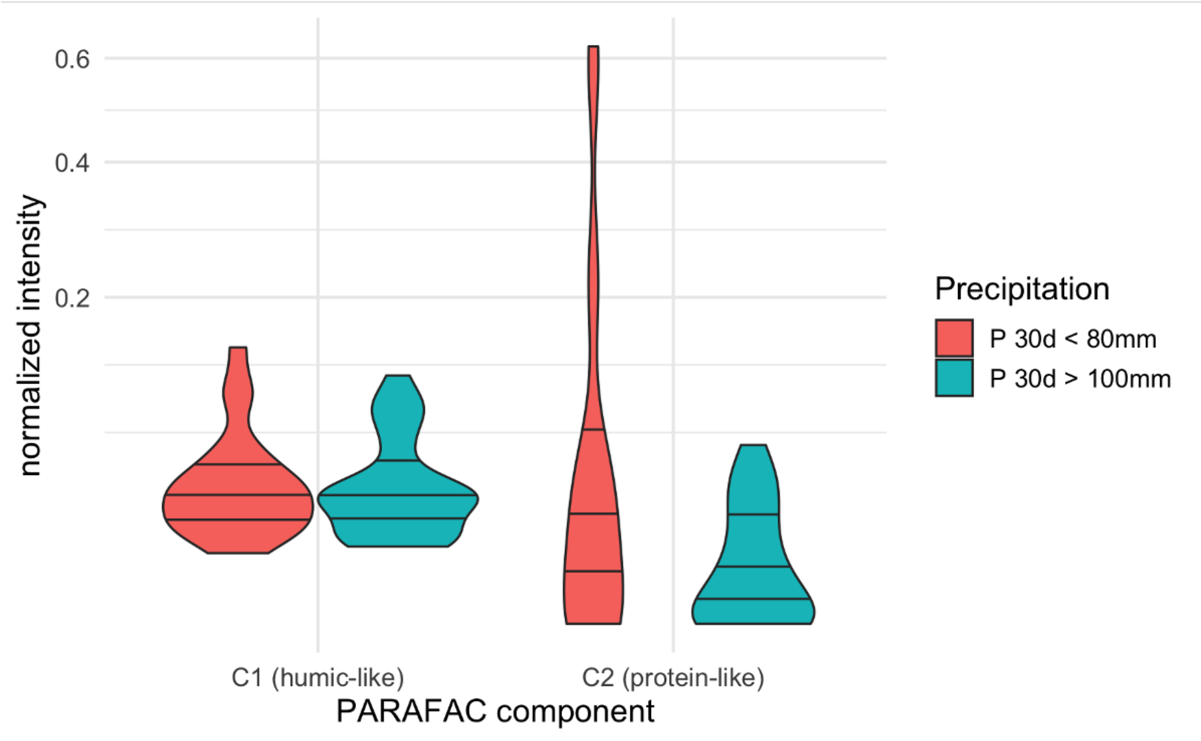


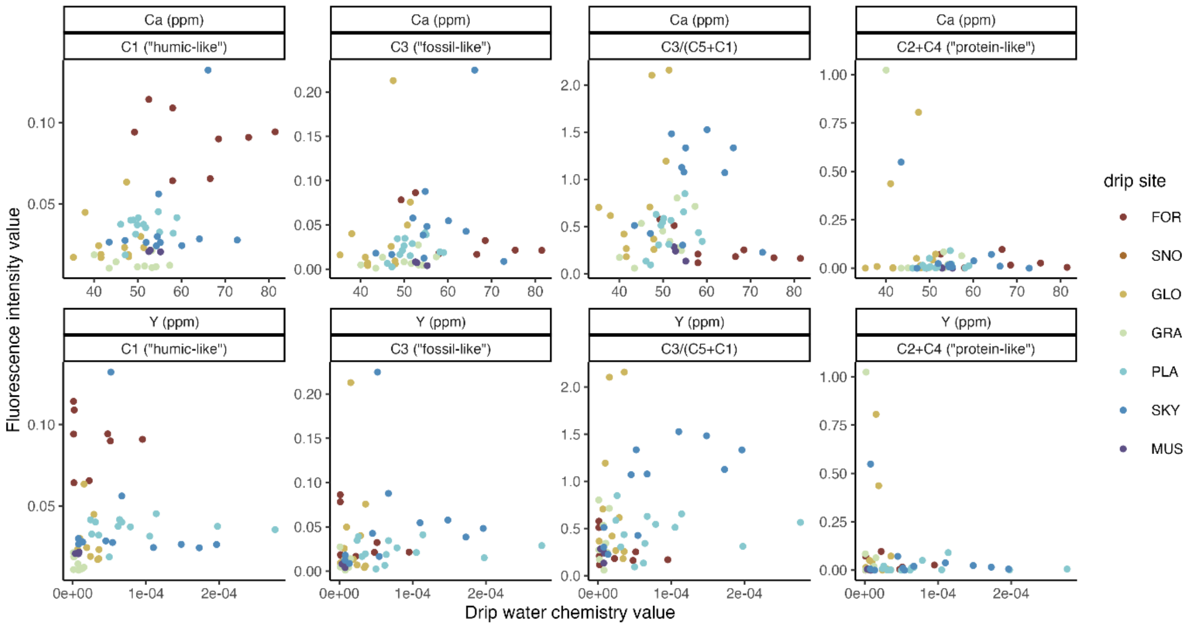
Supplementary Figure 1. The effect of storage time for the drip water sample FOR, collected on 13 November 2020. The Excitation-Emission matrix (EEM) on the left was acquired on 20 November 2020, and the one on the right on 14 July 2021.



Supplementary Figure 2. Performed parallel factor analysis (PARAFAC) model cross-validation. Results from the location-wise three components PARAFAC model reveal the presence of all five peaks as dominant features in single locations. Therefore, the 5-component model can represent the variability of the entire dataset to a large degree. Featuring high shape-sensitive congruencies (SSC) (Wünsch et a., 2019) values from 0.6-0.99, variability in the single locations is very similar to the full five-component model. Specifically, the model for *FOR* is most similar to components C2, C5, C3; for *GLO* to C2, C1, C4; for GRA to C4, C5, (+Outlier); for *PLA* to C1, C3, C5 and for *SKY* to C3, C1, C4.



Supplementary Figure 3. Simplified to a humic-like and a protein-like component, the difference in intensity distribution in protein-like fluorescence between wet and dry conditions over the entire dataset is significant.



Supplementary Figure 4. Graphical representation of relationships between fluorescence (C1,C3,C3/(C5+C1),C2+C4) and selected drip water geochemistry parameters. Drip water chemistry data (Ca and Y concentration) is re-used from the study Kost et. al, 2022. For numerical values of spearman rank correlation coefficients, see Tab. 3. Top row shows a comparison of fluorescence with the drip water Ca concentration, an alternative indicator of the extent of dissolution of karst bedrock. Bottom row shows a comparison of fluorescence with the total drip water Cu concentration, as an alternative indicator for the presence of colloidal organic complexes.

Supplementary Table 1. Description of vegetation and conditions above each drip location.

Location (Abbreviation)	Vegetation above sampling location and Observations in the cave
Forest (FOR)	Forest-dominated with *Quercus robur*, *Quercus ilex*, *Castanea sativa* and *Eucalyptus* trees. Below the trees also Fern (*Polypodiopsida*), brambles (*Rubus fruticosus*) and gorse (*Ulex europaeus*). Roots of *Eucalyptus* trees are observed at the cave ceiling close to the sampling location.
Snowball (SNO)	Forest-dominated with *Quercus robur*, *Quercus ilex*, *Castanea sativa* and *Eucalyptus* trees. Below the trees also Fern (*Polypodiopsida*), brambles (*Rubus fruticosus*) and gorse (*Ulex europaeus*). Roots of *Eucalyptus* trees are observed at the cave ceiling close to the sampling location.
Gloria (GLO)	Intermediate vegetation cover, dominated by *Ulex europaeus* and *Polypodiopsida*. Two isolated trees (*Eucalyptus* and *Quercus robur*) and a doline are close by. Roots of *Eucalyptus* trees are observed at the cave ceiling close to the sampling location.
Gravel (GRA)	Intermediate vegetation cover, dominated by *Ulex europaeus* and *Polypodiopsida*. Two isolated trees (*Eucalyptus* and *Quercus robur*) and a doline are close by. The cave ceiling close to the sampling location is filled with helictites and eccentric soda straws. Additionally, roots of *Eucalyptus* trees are present.
Skyscraper (SKY)	Pasture-dominated vegetation cover. Grazing animals (sheep, cattle) have been observed regularly. Several sinkholes and an uvala are nearby.
Playground (PLA)	Pasture-dominated vegetation cover. Grazing animals (sheep, cattle) have been observed regularly. Several sinkholes and an uvala are nearby.
Mushroom (MUS)	Intermediate vegetation cover, dominated by *Ulex europaeus* and *Polypodiopsida*.

Supplementary Equation 1.

Beer's law:

$$\alpha(\lambda) = 2.303\ A(\lambda)/l$$

where $\alpha = absorption\ (m^{-1})$, A=Absorbance, l=cuvette pathlength (m) and $\lambda = wavelength\ (nm)$.