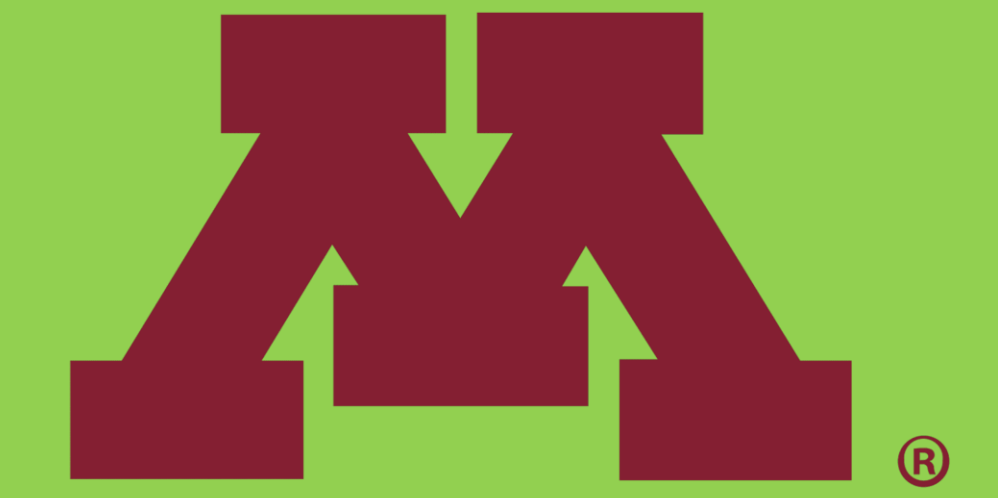


# Glaciers Provide a Source of Organic Matter to Stimulate Aquatic Biogeochemical Processes

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## Abstract

Glaciers export dissolved organic matter (DOM) to downstream ecosystems in meltwater. A stream's DOM pool is influenced by input from surrounding soils and vegetation whereas glacial meltwater has the addition of glacially-derived DOM to the bulk DOM pool. Current data availability studying DOM in glacial streams is largely limited to polar and mid-latitude glaciers as studies of DOM content of equatorial glacier-fed streams are extremely limited. Here, we use fluorescence spectroscopy to characterize how the optical properties of dissolved organic matter evolve along a glacial stream that flows from the Hermoso glacier on Volcan Cayambe, Ecuador. Results show that DOM characteristics change as the meltwater flows from higher elevation pure glacier meltwater to lower elevation streams that flow through different types of vegetation cover. Specifically, the DOM evolves from protein-like and microbial-like near the glacier terminus to more fulvic acid-like downstream near the vegetated area of the watershed. The transformation from protein-like to humic-like prior to the establishment of developed soils suggests that in-stream biogeochemical processes involving dissolved organic matter are occurring and that glaciers play a crucial role in providing DOM to aquatic ecosystems by stimulating the aquatic carbon cycle.

## Introduction

Earth's hydrologic cycle is heavily influenced by glaciers and their meltwater<sup>1</sup>. Glacially-derived dissolved organic matter (DOM) is a bioavailable and potentially important organic carbon source for downstream ecosystems, providing a source of nutrients for heterotrophic metabolism<sup>2</sup>. Recent studies have indicated that climate change could alter the process by which nutrients are exchanged between glaciers and aquatic ecosystems, due to changes in the flux of meltwater to these streams<sup>3</sup>. Studies characterizing the role of DOM in freshwater and marine ecosystems, as well as water treatment facilities have used fluorescence spectroscopy as a technique to monitor biogeochemical processes involving DOM by monitoring temporal and spatial changes in fluorescing organic moieties (fluorophores) in the bulk DOM pool<sup>4,5</sup>. Subsequent statistical analyses of the fluorescence dataset by parallel factor analysis (PARAFAC) enables the contribution of unique fluorophores to the total fluorescence of DOM<sup>5</sup>. While high-latitude glaciers have been examined at greater depth, biogeochemical transformations of DOM in mid to low-latitude glacier meltwater has been overlooked.

Here, we investigate DOM transformations in meltwater from Hermoso glacier, Volcan Cayambe, Ecuador (Figure 1). The proglacial stream flows from the glacier terminus through patches of herbs and grasslands, moss, and a polylepis forest near the bottom of the catchment. Understanding how glacially-derived nutrient supply affects biogeochemical processes within glacial streams is crucial when assessing the way glacial ecosystems function.

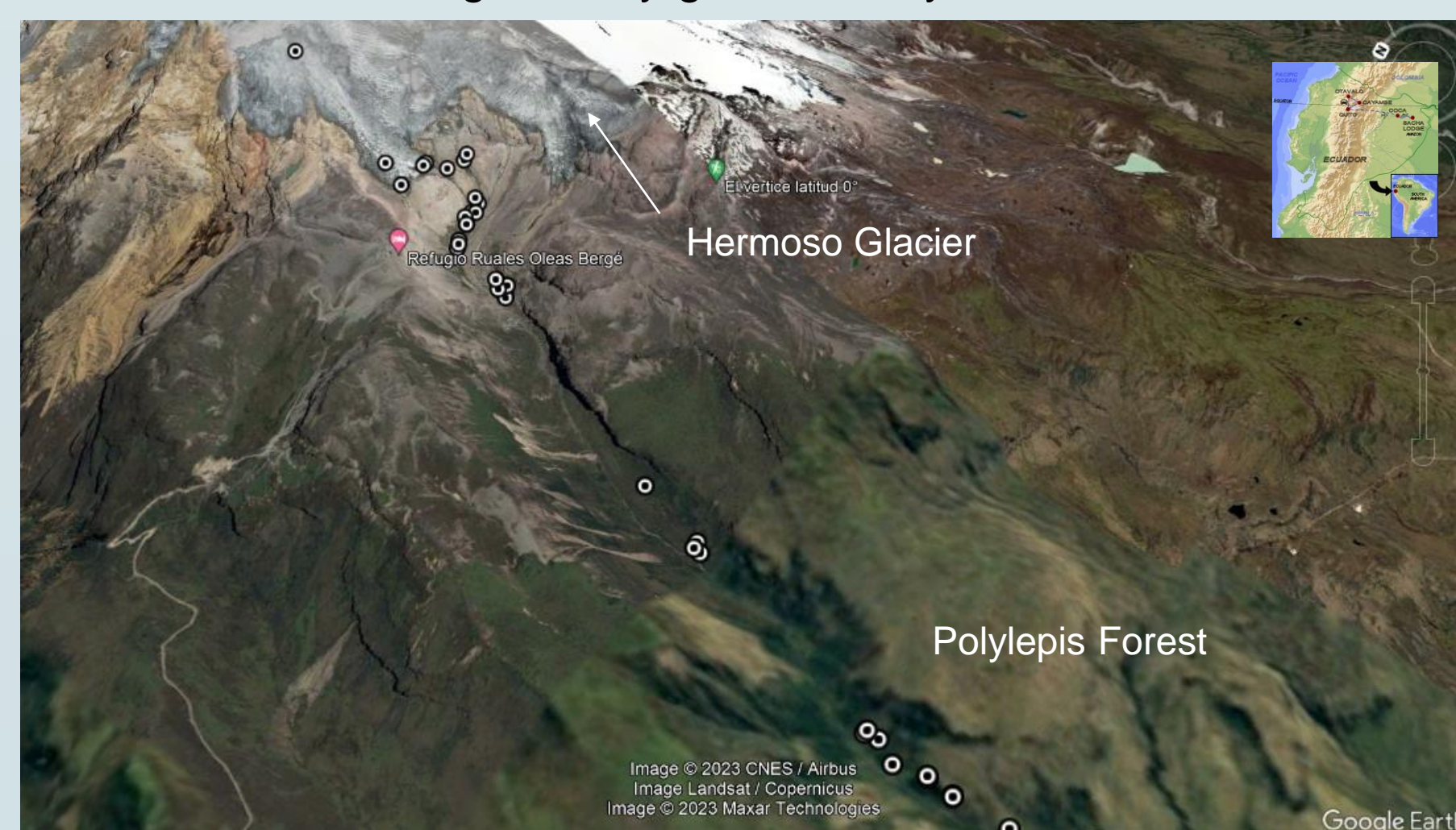


Figure 1: Sample sites along glacial stream amongst Volcan Cayambe, Ecuador.

## Methods

- Water samples were collected from the glacier snowpack, glacier ice, rain, and proglacial streams throughout the watershed during June and October of 2022.
- Samples were filtered through sterilized glass fiber filters to remove any sediment or particulate matter. Filtrate was stored in pre-combusted (480 °C for 8 hours) amber borosilicate glass vials and transported to the University of Minnesota to be analyzed.
- 62 filtered water samples were analyzed for total fluorescence (excitation-emission spectra; EEMs) with an Aqualog scanning fluorometer (Horiba, Irvine, USA) from 240-450 nm excitation and 250-800 emission wavelengths at a 1 nm interval and 10 second integration time. EEMs were blank subtracted and normalized to the water Raman curve area that was acquired daily.
- PARAFAC analysis was applied to the EEM data set to identify individual fluorophores and quantify their contribution to individual EEMs. This model was verified by split-half analysis and was found to be valid at a 95% confidence interval. Fluorophore "components" identified in the PARAFAC model were compared to similar fluorophores that have been reported previously (Table 1).

Excitation (nm)	Emission (nm)	Fluorophore identification
200 - 250	330 - 350	Tryptophan-like protein
200 - 250	350 - 500	Fulvic acid-like
250 - 280	250 - 380	Microbial-like
280 - 400	380 - 500	Humic-like

Table 1: Fluorophores identified by excitation and emission regions, divided into 4 groups<sup>6</sup>.

## Results

The PARAFAC model used in this study identified four different fluorophore "components" that describe 96% of the variance in the EEM dataset: humic-like, fulvic acid-like, microbial-like, and protein-like. Component 1 corresponds to fulvic acid-like, 2 is microbial-like, component 3 shows protein-like DOM, and 4 is humic-like.

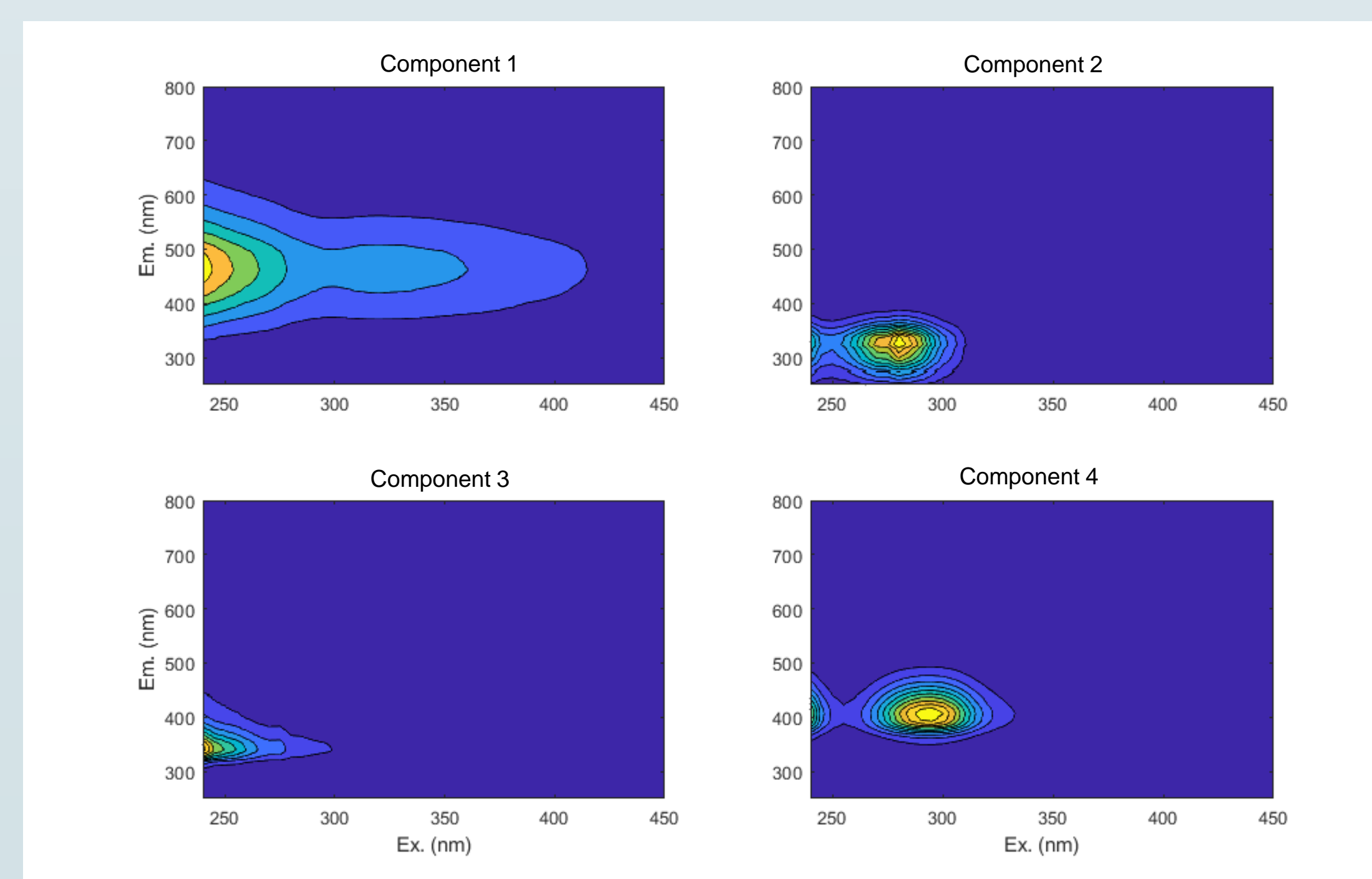


Figure 2: Four-component model identified by the excitation-emission (EEM) maximum fluorescence and the organic moieties that they are associated with.

## Results

Groups	Sum of Scores	Average Score	Ratio Relative to Maximum Component
Fulvic Acid (comp 1)	3938	64	1.1
Microbial (comp 2)	4327	70	1
Protein (comp 3)	2943	48	1.45
Humic (comp 4)	1942	31	2.25

Table 2: Distribution of scores model on the four different components identified by the PARAFAC analysis.

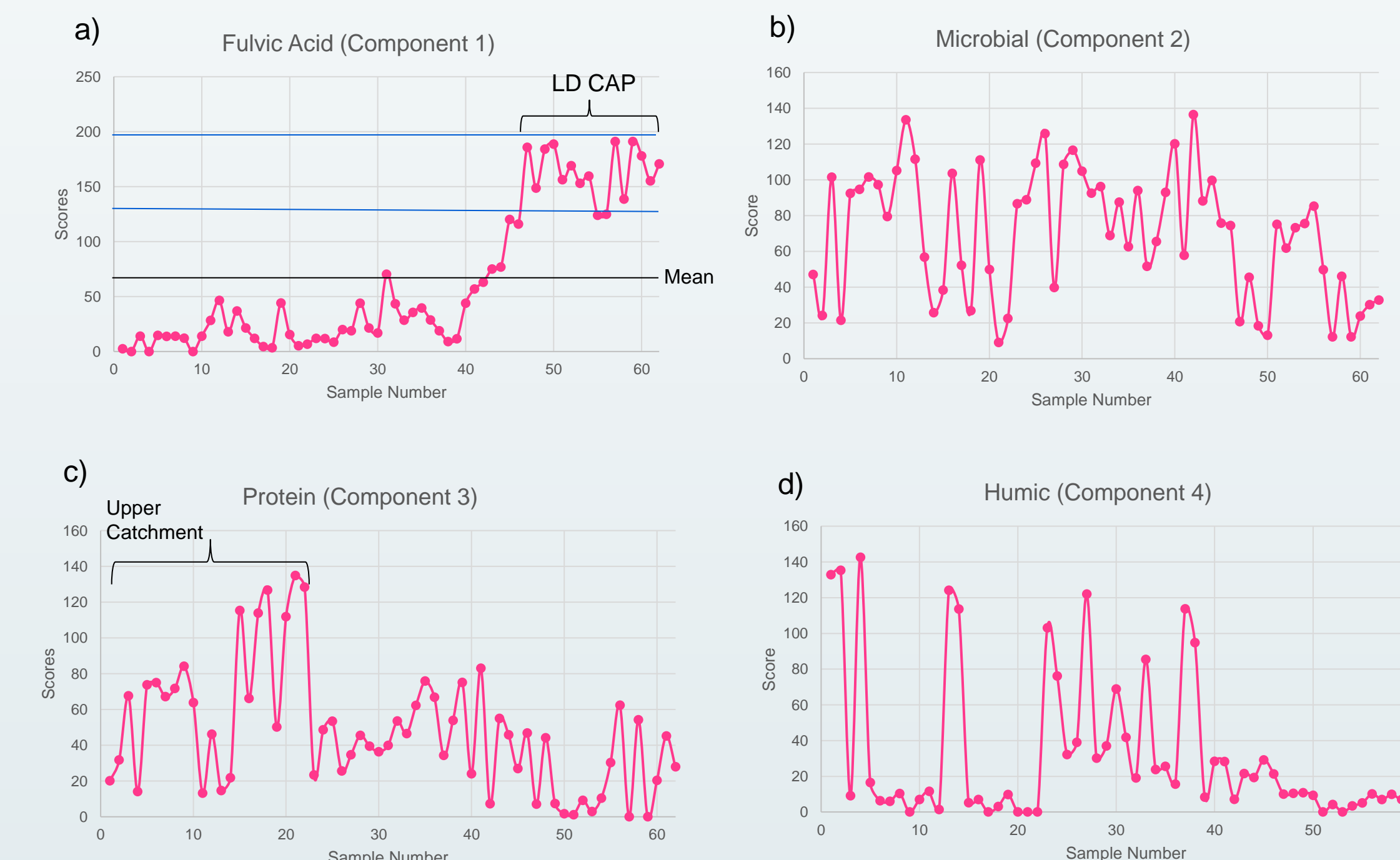
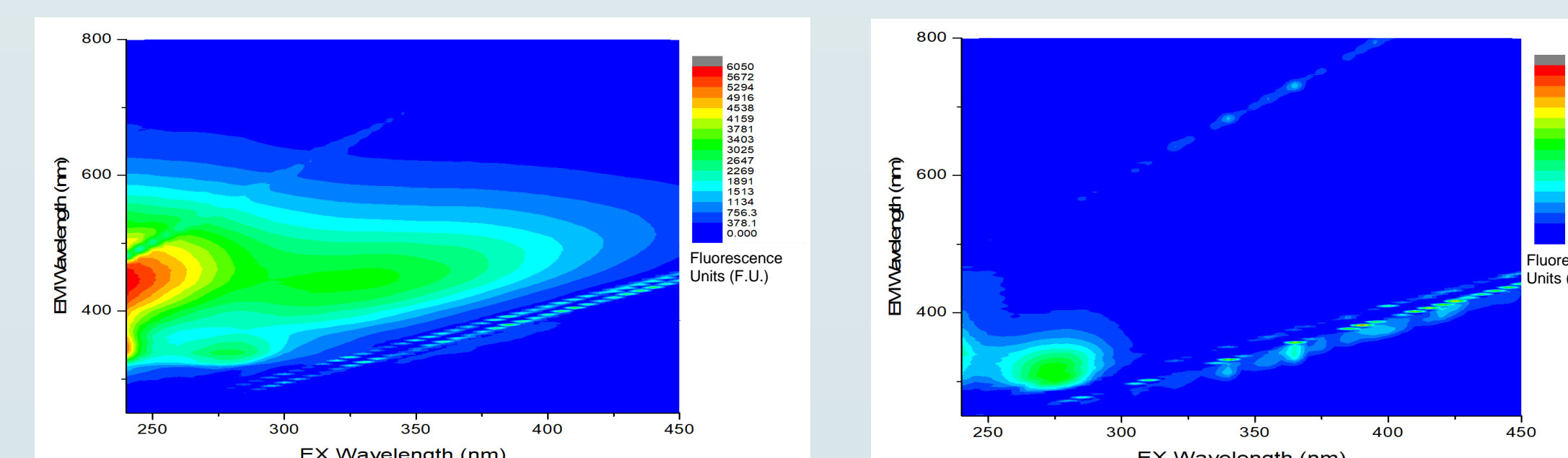


Figure 3: Fulvic acid-like, microbial-like, humic-like, and proteinaceous components plotted to show their change in overall fluorescence down the glacial stream.

LD Wet 5 – Component 1      Hermoso Snow – Component 2



LD 511 – Component 3      LD-GM – Component 4

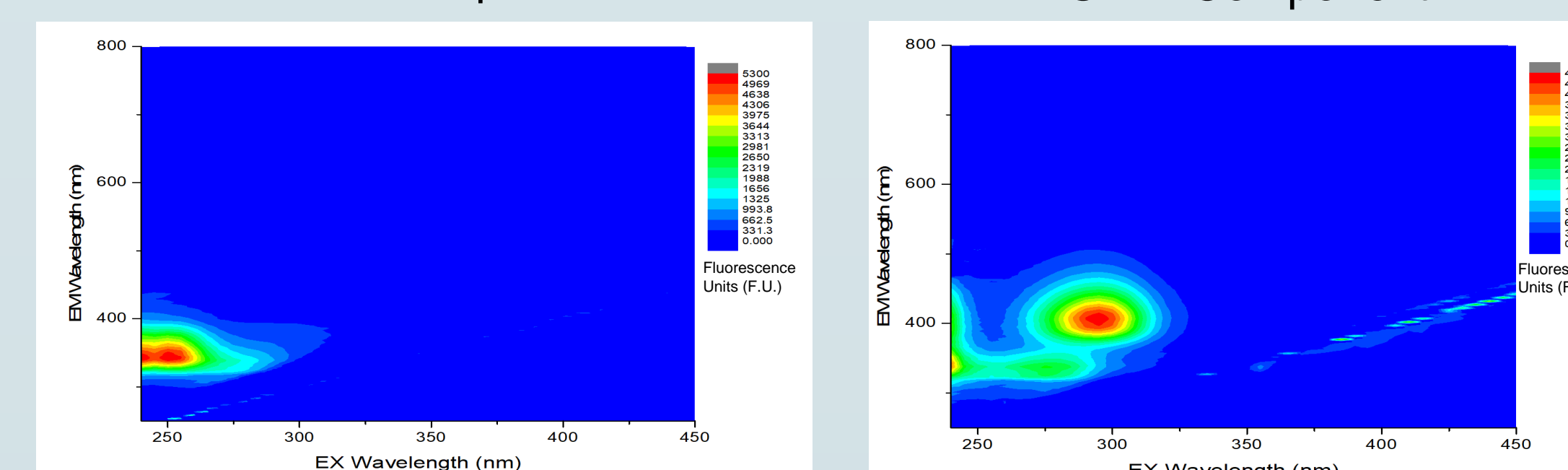


Figure 4: Four-component model showing samples that score highly on the four different components.

## Discussion and Conclusions

- The microbial-like component dominates the Hermoso glacier and its downstream ecosystems, with a component sum up to 2.25 times higher than the mean scores of protein, fulvic acid, and humic-like DOM (Table 2). The microbial-like fluorophore is the most common in the data set, suggesting that it is ubiquitous across the ecosystem (Figure 3b).
- Beginning near the glacier terminus, coinciding with precipitation, snow, and ice, samples show a larger abundance of microbial-like and protein-like components prior to the vegetated areas of the stream (Figures 3a, 3b).
- DOM contents near the bottom of the catchment showed the largest variability from the rest of the sample set. The 15 samples collected at the bottom of the catchment showed particularly high scores (nearly 2 standard deviations away from the mean) of fulvic acid-like components compared to the samples collected closer to the glacier (Figure 3a).
- The shift to a higher abundance of fulvic acid-like fluorescence begins to increase rapidly by a factor of 4 prior to the appearance of the polylepis forest (Figure 3a).
- Humic-like results were hypothesized to be greater among the more vegetated areas of the stream, considering the age and development of the different soil types. However, based on the findings, humic material showed the lowest mean scores among all samples, appearing most in the sulfur springs and a few sites closer in proximity to the Hermoso glacier (Figure 3d).
- The transition from protein-like to fulvic acid-like fluorescence could suggest a transformation from labile to more recalcitrant forms of organic matter<sup>8</sup>. The evolution of DOM throughout the glacial stream is indicative of active biogeochemical processes within the stream.
- As surfaces are recolonized after glacial retreat, different areas along the stream produce different sources of DOM to be metabolized.

## Acknowledgements and References

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