## Fluorescence spectroscopy is a tool for tracing dissolved organic carbon in hot spring ecosystems

\*Hilairy Ellen Hartnett<sup>1</sup>, Joshua Nye<sup>1</sup>

## 1. Arizona State University

Dissolved organic matter (DOM) in hot spring systems is a complex, dynamic pool of molecules with multiple sources and fates. Recently, we developed a novel, validated PARAFAC model for hot spring DOM that revealed both standard humic and protein-like material as well as a fluorphore uniquely found in acidic springs (pH < 4; [1]). Here we assess dissolved carbon concentration and DOM fluorescence characteristics for ~200 hydrothermal features in Yellowstone National Park that represent a diversity of hot spring types (hydrothermal only, acid-sulfate, alkaline-chloride, metoric influenced, etc.). Bulk dissolved carbon concentrations range from low micromolar levels up to millimolar levels with higher concentrations generally associated with more acidic springs. DOM composition is quite variable across the range in pH and temperature of the springs we sampled.

Fluorescence analysis reveals multiple sources of organic carbon that can be used as tracers of terrestrial and hydrothermal carbon inputs. These additional organic tracers allow an analysis of carbon source and mixing across hot sping types. Plots of dissolved carbon content as a function of sulfate, chloride, and pH (**Fig. 1**) confirms the expected patterns in mixing that can be identified using sulfate and chloride alone [2]. However, fluorescent DOM is a sensitive tracer of surface derived organic matter and allows us to distinguish mixing between different source types even when they have similar sulfate-chloride. DOM fluorescnece also allows us to assess the extent to which mixing has occurred subsurface without terrestrial influence vs. at the surface manifestation of the spring. This new tracer provides insight to the complexity of terrestrial hydrothermal systems and may prove useful for future studies of dissolved organic matter in planetary oceans.

[1] J Nye, E Shock, H Hartnett (2020 in press) *Org. Geochem.* doi.org/10.1016/j.orggeochem.2019.103964

[2] D Nordstrom, R McCleskey, J Ball (2009) Appl. Geochem. 24(1): 191-207

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**Fig. 1:** Hot spring dissolved carbon concentration (open circles, symbol size  $\propto$  concentration; range: 15–3000  $\mu$ M) plotted in molal [SO<sub>4</sub><sup>=</sup>] vs. [Cl] space. Color scale is pH (red-orange: pH<4; yellow-green: 4<pH<7; blue: pH>7). Mixing trends and fluid types from [2] are overlain as arrows and shaded circles.