Rare Earth Element Chemistry in Surface Waters of Rivers and Streams on the North Slope of Alaska

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Background and Objectives

Changes in climate on the North Slope of Alaska and other Arctic regions have contributed to physical disturbance and thermal perturbation of permafrost landscapes, changing weather patterns, and altered hydrogeologic processes (*Lafrenière and Lamoureux, 2019*). These impacts can alter the supply of dissolved and colloidal trace elements and organic matter (OM) to surface waters and the transport of these constituents through streams and rivers during the summer thaw ('open water') season. Trace element and OM cycling, fate, and transport in surface waters is complex and can change as a function of OM degradation, changes in pH, shifts in element-OM ligand equilibrium, and aggregation/disaggregation with colloids (*Ingri et al., 2000*; *Pokrovsky et al., 2006*). Rare earth elements (REE) have been used as a tracer for element and OM cycling, fate, and transport since dissolved REE concentrations in streams and rivers are linked to the parent geology of the watershed basin and are known to vary with increasing molar mass due to interactions with inorganic and organic colloids and iron and manganese oxyhydroxide coatings on particle surfaces (*Sholkovitz, 1995*; *Stolpe et al., 2013*). This study aims to analyze the REE chemistry of the hydrologic landscape of the North Slope, which transitions between several types of hydrology including permafrost tundra-, mountain-, and lake-sourced streams and rivers, and determine what effects variables such as seasonal landscape changes, precipitation, and river discharge have on the relationship between dissolved OM, organic colloids, and REE concentrations. Data collection for this study was conducted as part of the Alaska North Slope Material Flux Study (AKMFS).

Study Area and Methods

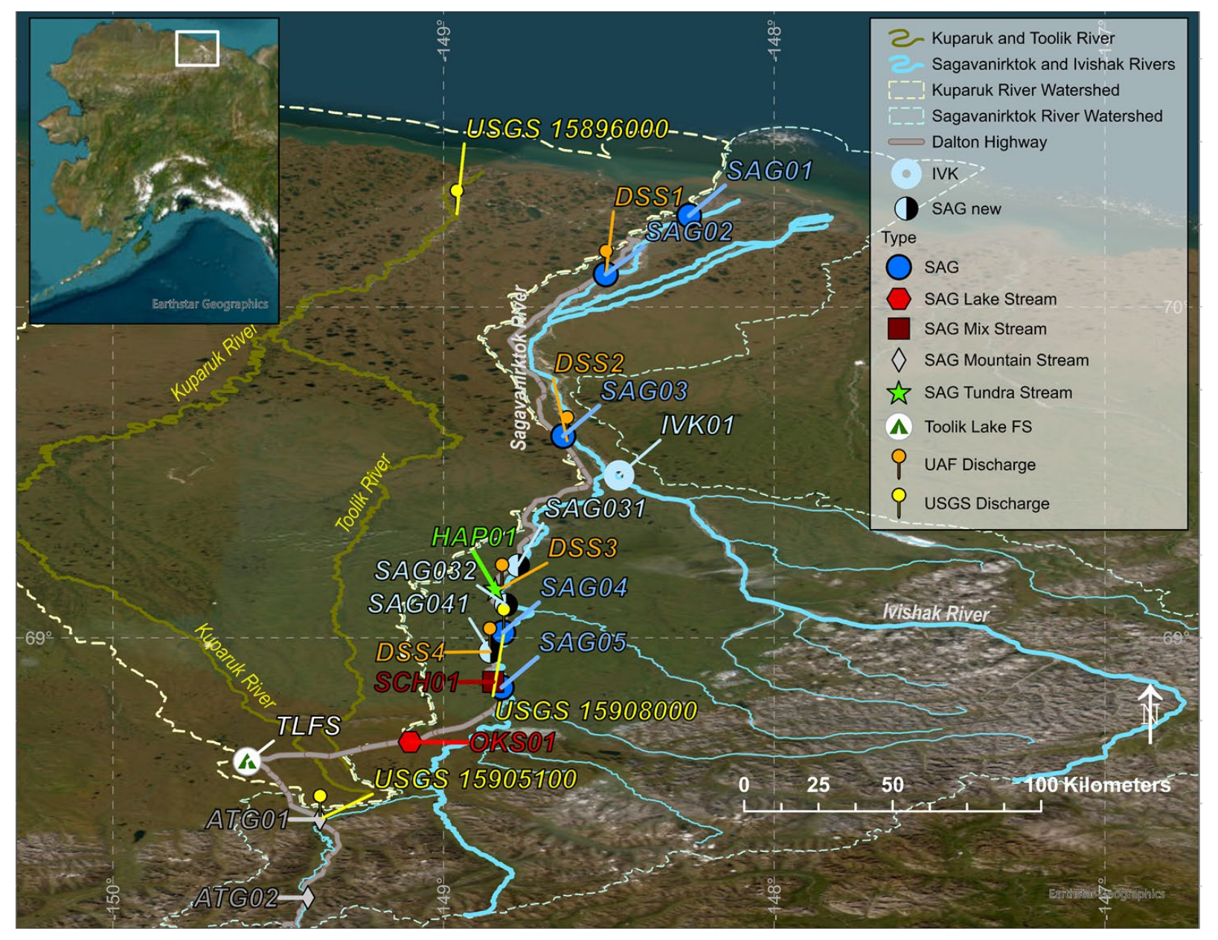


Figure 1. Study area on the North Slope of Alaska with sampling sites on the Sagavanirktok River and transitional tundra streams that feed the Sagavanirktok River. This study focuses on sites between SAG05 to SAG03. Also shown are the locations of the Sagavanirktok River USGS discharge gaging station (15908000), the Atigun River USGS discharge gaging station (15905100), and University of Alaska-Alaska Department of Transportation discharge gaging stations (DSS1-4; *Toniolo et al., 2019*). Precipitation data was measured at Toolik Field Station (TLFS) and SNOTEL site 957 (wcc.sc.egov.usda.gov/nwcc/site?sitenum=957), which is located south of site ATG02 in the Atigun Pass.

Figure 2. The AKMFS crew on the Ivishak River in August, 2022.

Table 1. River and stream discharge measurements and methods used for sampling and analysis of surface waters. Surface waters were collected using in-field syringe filtration techniques from *Smith et al., 2023 (in prep.)*.

Parameter	Method(s)
River/Stream Discharge	RiverRay/RiverPro Acoustic Doppler Current Profiler (ADCP), Sontek Flow Tracker 2 Acoustic Doppler Velocimeter (ADV), Flow Meter, USGS gaging stations
Water Temperature, Conductivity, Turbidity, pH	YSI EXO/Hach MS-5 Water Quality Monitoring Sondes
REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)	Thermo-Fisher Element XR Double-focusing Inductively Coupled Plasma Mass Spectrometer (ICPMS);125 ml bulk surface water; syringe filtration, 0.45 µm filter tip into pre-cleaned HDPE bottle
Dissolved Organic Carbon (DOC)	OI Analytical 1030D Total Organic Carbon Analyzer; 40 ml bulk surface water; syringe filtration,0.2 µm filter tip into pre-cleaned glass amber vial

Discharge data and surface water samples were collected from sites on the Sagavanirktok River and transitional tundra streams during the open water season from June – October, 2019, 2021, and 2022 (**Fig. 2**). Samples were analyzed for dissolved REE concentrations, dissolved organic carbon (DOC), and other parameters. Methods are shown and described in **Table 1**. In order to analyze the differences in REE-composition between each site, season, and year, the measured REE values were normalized by their mean concentrations in the upper continental crust (UCC) as compiled by *Piper and Bau (2013)*. The UCC-normalized concentrations for each REE, when plotted for a sample, reveal a distinct spectrum (**Fig. 3a**). In order to compare differences in individual spectra for each sampling event, the ratios between the mean UCC-normalized concentrations of the heavy REEs (HREEs; Dy, Ho, Er, Tm, Yb, and Lu) to middle REEs (MREEs; Sm, Gd, and Tb) and the MREEs to light REEs (LREEs; La, Ce, Pr, and Nd) were calculated for each sample (**Fig. 3b**). Classification by 'weight' is based on REE atomic masses (*Stolpe et al.,2013*).

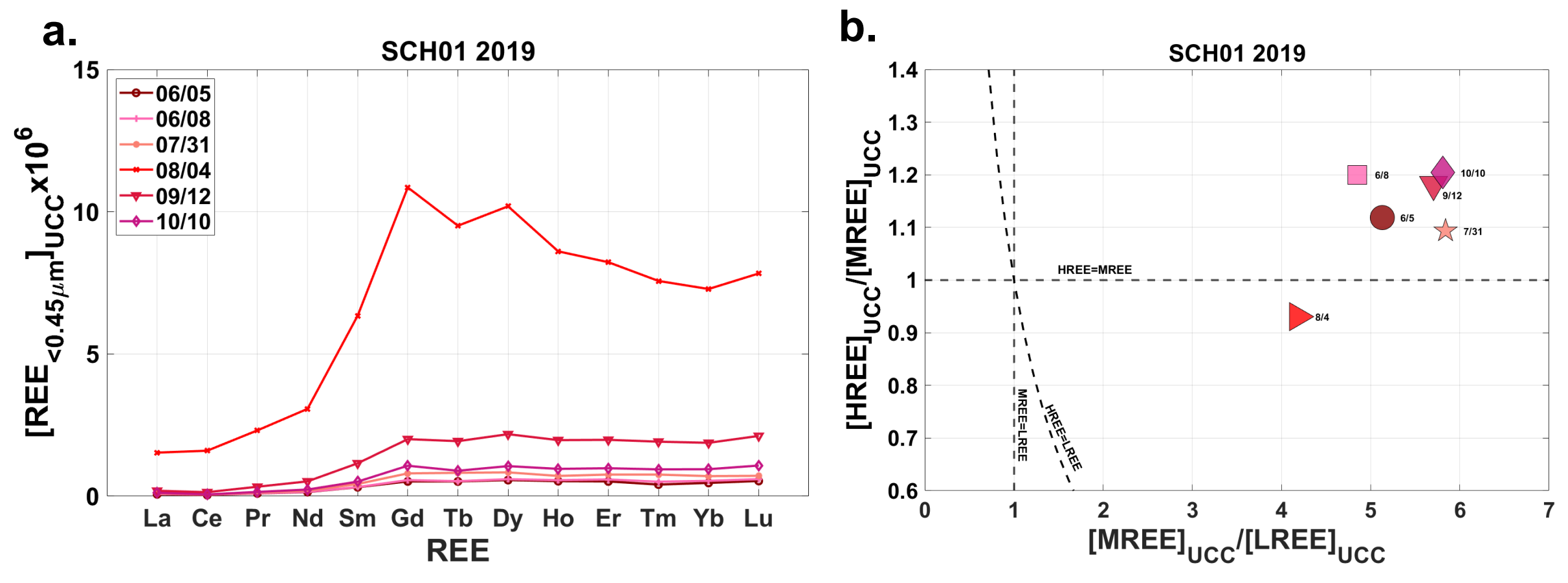


Figure 3. (**a**) UCC-normalized dissolved REE values $[REE_{<0.45\mu m}]_{UCC}$ for Schuyler Creek (SCH01) in 2019 and (**b**) Ratios of mean UCC-normalized HREE values to mean UCC-normalized MREE values ($[HREE]_{UCC}/[MREE]_{UCC}$) versus the ratios of mean UCC-normalized MREE values to mean UCC-normalized LREE values ($[HREE]_{UCC}/[MREE]_{UCC}$) for the same site and year. Dotted lines are where the mean values for each weight category are equivalent.

Results

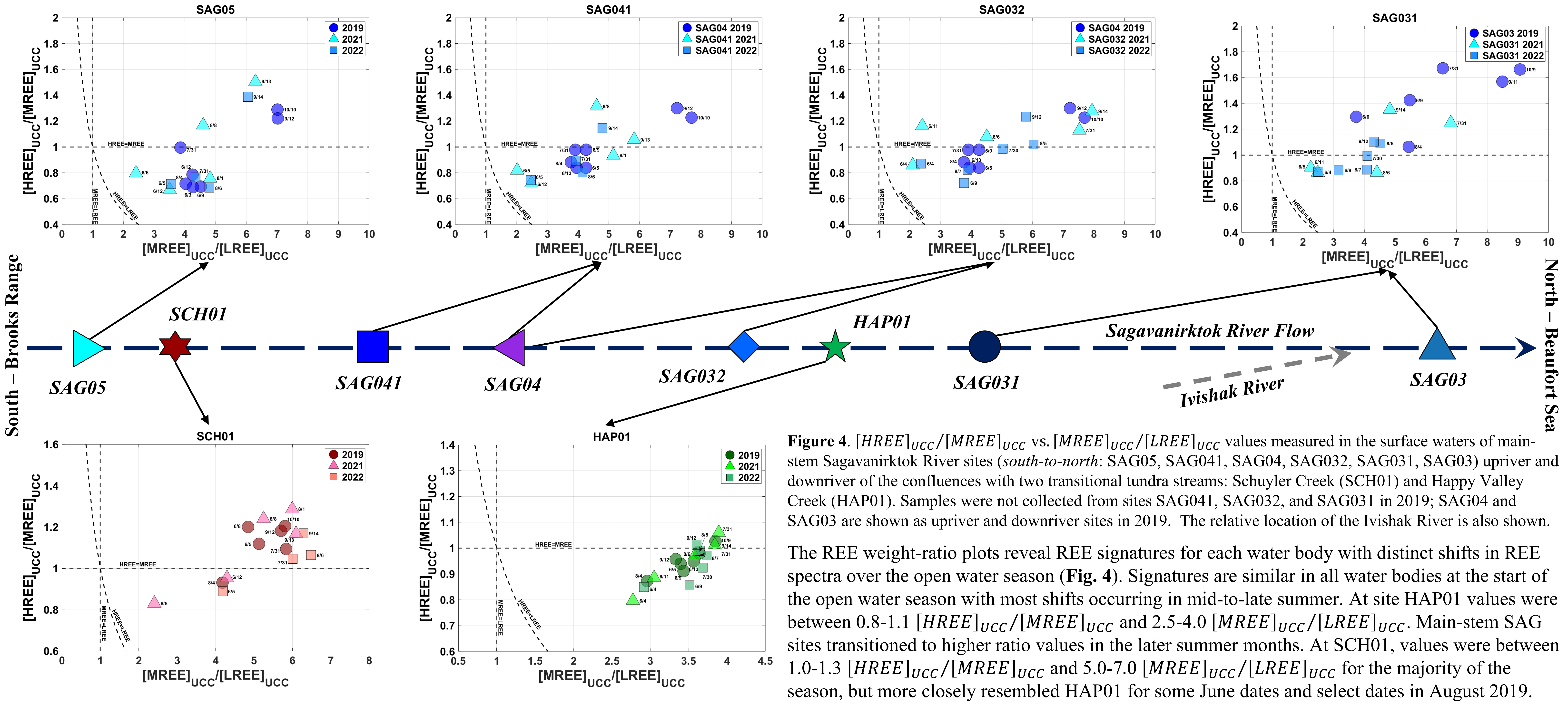


Figure 4. $[HREE]_{UCC}/[MREE]_{UCC}$ vs. $[MREE]_{UCC}/[LREE]_{UCC}$ values measured in the surface waters of main-stem Sagavanirktok River sites (*south-to-north*: SAG05, SAG041, SAG04, SAG032, SAG031, SAG03) upriver and downriver of the confluences with two transitional tundra streams: Schuyler Creek (SCH01) and Happy Valley Creek (HAP01). Samples were not collected from sites SAG041, SAG032, and SAG031 in 2019; SAG04 and SAG03 are shown as upriver and downriver sites in 2019. The relative location of the Ivishak River is also shown.

The REE weight-ratio plots reveal REE signatures for each water body with distinct shifts in REE spectra over the open water season (**Fig. 4**). Signatures are similar in all water bodies at the start of the open water season with most shifts occurring in mid-to-late summer. At site HAP01 values were between 0.8-1.1 $[HREE]_{UCC}/[MREE]_{UCC}$ and 2.5-4.0 $[MREE]_{UCC}/[LREE]_{UCC}$. Main-stem SAG sites transitioned to higher ratio values in the later summer months. At SCH01, values were between 1.0-1.3 $[HREE]_{UCC}/[MREE]_{UCC}$ and 5.0-7.0 $[MREE]_{UCC}/[LREE]_{UCC}$ for the majority of the season, but more closely resembled HAP01 for some June dates and select dates in August 2019.

Discussion

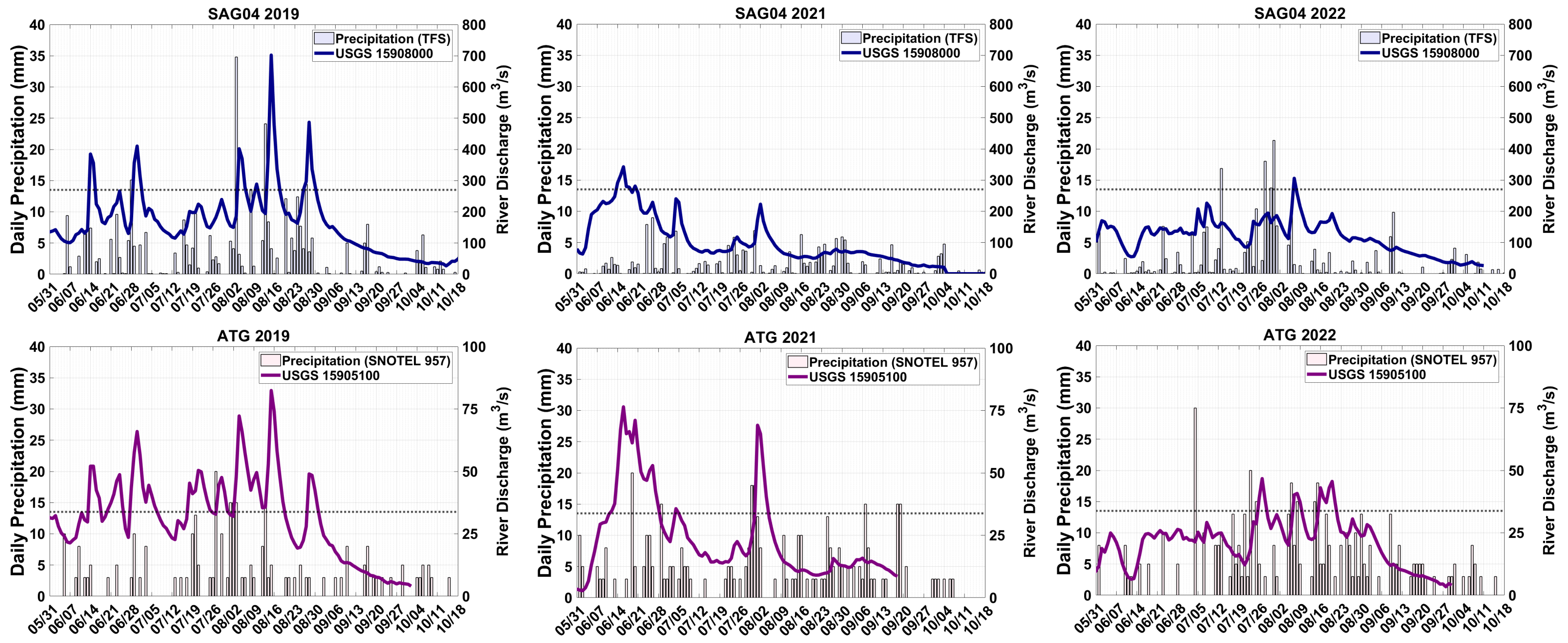
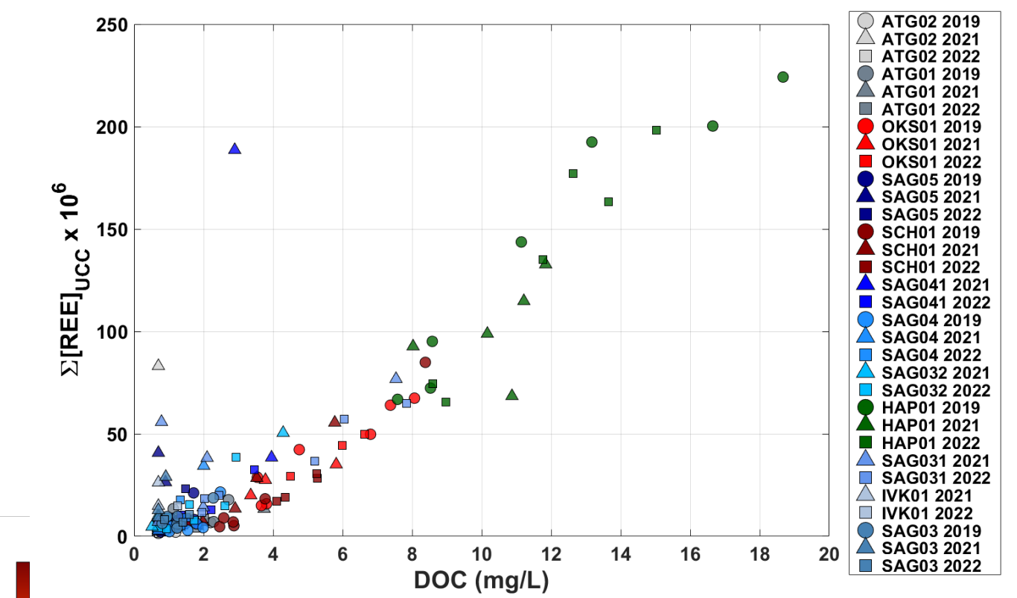


Figure 5. *Top left to right*: Sagavanirktok River discharge values (waterdata.usgs.gov/monitoring-location/15908000/) displayed with daily precipitation values at Toolik Field Station (*EDC, 2023*) for each sampling season. *Bottom left to right*: Atigun River discharge values (waterdata.usgs.gov/monitoring-location/15905100/) displayed with precipitation values at SNOTEL site 957.

Figure 6. (*Right*) Surface water total dissolved REE ($\Sigma[REE]_{UCC}$) vs. DOC concentrations measured in the Sagavanirktok River, Ivishak River and representative mountain dominated (ATG02 and ATG02), lake-dominated (OKS01), mixed (SCH01), and tundra-dominated streams in 2019, 2021, and 2022.



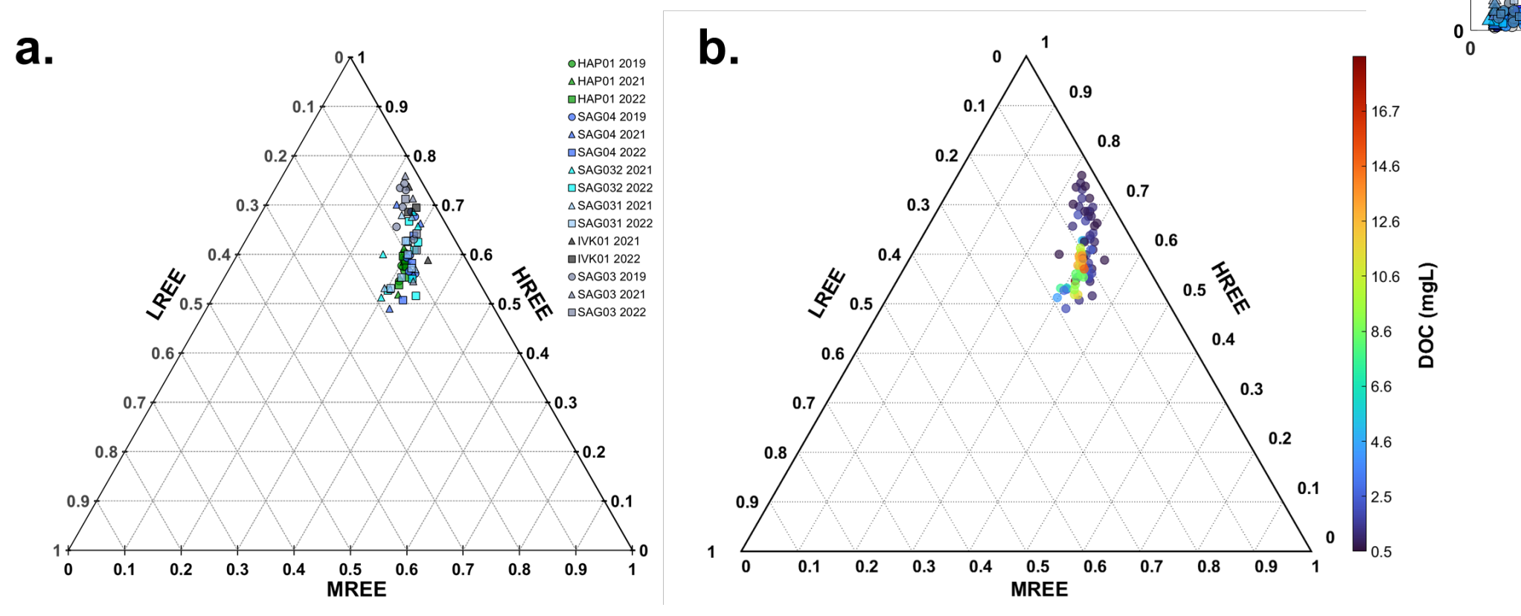


Figure 7. (*Left*) (**a**) Ternary plot of % LREE, MREE, and HREE for site HAP01 and adjacent upriver and downriver sites on the Sagavanirktok and Ivishak Rivers in 2019, 2021, and 2022 and (**b**) Contour ternary plot of DOC concentrations at the same sites.

The seasonal shift in the REE signature in each water body is unique to its biogeochemical setting. Comparison of REE weight ratios in transitional tundra streams (SCH01 and HAP01) to upriver and downriver sites on the Sagavanirktok River suggests connectivity between tundra surface waters and the main-stem river during the open water season. For SAG sites immediately downstream of transitional tundra sites (SAG041 for SCH and SAG031 for HAP), REE weight-ratios shifted toward or below the HREE=MREE line in mid-to-late summer, more close to transitional tundra sites (**Fig. 4**). This can likely be attributed to increased hydrologic connectivity during extreme precipitation and high river discharge in the open water season (**Fig. 5**). In 2019, the SAG03 site was used to represent the downriver site from HAP01. It is significantly farther downstream from HAP01 than SAG031 and is downriver of the confluence with the mountain-sourced Ivishak River (**Fig. 4**), which roughly doubles the discharge volume in the main-stem Sagavanirktok River. The slight shift in REE weight-ratios at SAG03 toward HAP01 values during a 04 AUG 2019 extreme precipitation and high river discharge event still suggests a significant influence of tundra stream waters on REE spectra in the main-stem Sagavanirktok River (**Fig. 4&5**). Seasonal and episodic inputs of OM from tundra sources during the open water season can alter stream and river chemistry and the transport of trace elements and OM (*Smith et al., 2023 (in prep.)*). Total dissolved REE values covaried with DOC in this study with a clear distinction between mountain-, tundra-, lake-, and mixed-sourced waters (**Fig. 6**). Dissolved REE concentrations in streams and rivers are linked to the parent geology of the watershed basin and vary with increasing molar mass due interactions with inorganic and organic colloids (*Sholkovitz, 1995; Stolpe et al., 2013*). The REE weight-ratio signature for mountain-dominated SAG sites were distinct from tundra-dominated HAP01 sites except when DOC concentrations (and likely colloidal OM) concentrations in the Sagavanirktok River were higher in mid-to-late summer during periods of increased hydrologic connectivity between tundra surface waters, streams, and the main-stem river (**Fig. 7a&b**).

Conclusions and Future Work

- ***Dissolved OM, likely organic colloids, play a large role in determining dissolved REE concentrations in North Slope streams and rivers***
- ***Seasonal and episodic inputs of OM from tundra sources during the open water season can alter stream and river chemistry and the transport of trace elements and OM***
- ***If extreme precipitation and high discharge events during the open water season become more frequent, trace element and OM fluxes through the Sagavanirktok River and other Arctic Rivers may become more variable***

Acknowledgements: *This project was supported by the Strategic Environmental Research and Development Program (SERDP; RC19-1382, PI: Gallaher). The 2019-2022 Alaska North Slope Material Flux Study (AKMFS) Teams includes: Tom Douglas, Amanda Barker, Dragos Vas, Stephanie Saari, Kate Liddle Broberg, Patricia Nelsen, Lauren Bosche, Brad Baxter, Leroy Hessner, and Taylor Sullivan (CRREL); Matt O'Banion, Chris Oxendine, Jakeb Prickett, and Jordan Laughlin (USMA); and USNA Midshipman and USMA and USCGA Cadets. Thanks to Horatio Toniolo, University of Alaska, Fairbanks (UAF), and the NSF-sponsored support staff at Toolik Field Station (https://toolik.alaska.edu/). Special thanks to Alan Schiller (USM) and Chris Osburn (NCSU) for sample analysis; Jerry Lucas and Luis Rodriguez (USNA) for logistical support; and the many people at BP Exploration Alaska, ConocoPhillips Alaska, Hilcorp, and Alaska Clean Seas, especially Chris Hall and Royce O'Brien, who helped facilitate this work.*

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