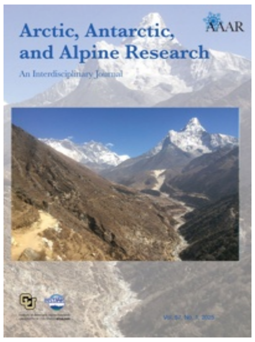

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Chemical signatures of microbial life in an ecological end-member: Shifting hydroclimate and sediment fluxes influence DOM biogeochemistry in Lake Fryxell, a permanently ice-covered lake in the McMurdo Dry Valleys of Antarctica

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ABSTRACT

The ice-covered lakes in the McMurdo Dry Valleys (MDV) of Antarctica provide end-member ecosystems for understanding the production of dissolved organic matter (DOM) in aquatic ecosystems in the absence of vegetation on the landscape and under resource and nutrient constraints. Given these constraints, DOM in MDV lakes is derived solely from microbial phototrophs and heterotrophic bacteria, contrasting with the dominant terrestrial sources in temperate regions. Previous research developed fluorometric approaches for characterizing DOM, including in MDV lakes. In this study we leveraged these approaches along with contemporary molecular-based techniques to elucidate changes in DOM composition across the depth profile for Lake Fryxell in the MDV. The results showed that the presence of organic molecules containing sulfur increased at depth where anoxic conditions prevailed. To evaluate the influences of climate-induced rising lake levels and multiple flood events in the MDV, we compared recent and historical samples. The results indicated a remarkable consistency in source-related fluorescence metrics over time, whereas a twofold decrease in sulfur content of the fulvic acid fraction was observed in samples from above and below the oxycline. Biogeochemical processes associated with the influx of iron oxide–rich sediments during flood events may have contributed to this change, and similar processes may stimulate biogeochemical cycling and remineralization in temperate lakes during seasonal transitions.

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Antarctica; limnology; biogeochemistry; DOM; nutrient cycling; lake metabolism

Introduction

Dissolved organic matter (DOM) plays a major role in driving biogeochemical and physical processes in natural waters. The humic DOM fraction can influence the structure and function of aquatic environments by absorbing visible and ultraviolet (UV) light, shuttling electrons to support microbial metabolism, reacting with metal ions through complexation, and sorption to particulates, especially metal oxides. Furthermore, some labile DOM fractions provide a substrate for microbial growth. Elucidating changes in the chemical characteristics of DOM can indicate ecosystem-scale changes in biogeochemical cycles, allowing resolution of the discrete roles that DOM can play (Jaffe et al. 2008; Battin et al. 2009). Studying such changes can also improve our understanding of the persistence of organic matter across aquatic ecosystems over time (D'Andrilli et al. 2022).

From a lake ecosystem perspective, DOM can originate from allochthonous sources in the terrestrial landscape that drain into a lake or from autochthonous sources within the lake itself. In temperate regions, many lakes are ice-covered in winter and autochthonous DOM sources from under-ice phytoplankton growth and microbial processes may become more important than allochthonous sources at that time (Rue et al. 2019). In addition, during winter when lake water columns are stable, DOM can accumulate in the bottom waters through diffusion from lake sediments (Aiken et al. 1996).

The permanently ice-covered lakes in the Ross Sea Region of Antarctica, including the McMurdo Dry Valleys (MDV) of South Victoria Land, offer an excellent limnological setting to investigate the biogeochemistry of DOM in lakes under ice-covered conditions

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(McKnight, Aiken, and Smith 1991; Aiken et al. 1996). The MDV are located in an ice-free region of Antarctica and comprise alpine glaciers, expanses of barren ground, and glacial meltwater streams that flow during the summer into ice-covered, closed-basin lakes in the valley floors. The DOM in the inflow streams is derived from perennial microbial mats in the streams and organic matter stored in the hyporheic zone, and the concentrations are low, typically less than 1 mg C/L (Aiken et al. 1996; Torrens, Gooseff, and McKnight 2022). Thus, autochthonous production of DOM derived from phytoplankton and extensive benthic microbial mats is the main source of DOM in the lakes (McKnight, Aiken, and Smith 1991; Aiken et al. 1996). These microbial exudates and senescence of microbiota represent a regenerating and bioavailable pool of DOM, which may serve an important ecological role in the absence of terrestrially derived organic matter inputs.

Beginning in the 1990s, research conducted in the MDV led to development of spectroscopic approaches for characterizing the DOM sources in aquatic ecosystems (McKnight et al. 2001; Cory and McKnight 2005). These approaches have been employed in numerous studies, and the resulting tools have proven invaluable in characterizing aquatic carbon cycling across lentic and lotic environments. They have been equally helpful in resolving processes in some temperate alpine lakes analogous to the Antarctic lakes where lake ice cover persists for most of the year (Miller et al. 2009; Mladenov et al. 2011; Rue et al. 2019). These approaches have also been applied to characterize DOM quality in numerous proglacial, saline, and other lakes in another region of East Antarctica (Kida et al. 2019, 2023). Additionally, the DOM in MDV lakes is of interest due to its persistence and evolution being influenced by historical climatic changes. In particular, the humic DOM can persist for thousands of years while being altered by physical and biogeochemical processes (Aiken et al. 1996; Doran et al. 2014; Cawley et al. 2016). Events preserved in the geologic record reveal that evapoconcentration of certain MDV lakes resulted in formation of brine pools, whereas others became overlain by freshwater or persisting ice cover (Lyons 2004). These shifts in freshwater input and solute chemistry are manifested in the DOM pool as ecological legacies (Cawley et al. 2016; Khan et al. 2016) and therefore act as indicators of landscape change.

The chemistry of DOM in lakes can also integrate episodic biogeochemical events, such as floods. In the MDV, the influx of sediment during summers with high flow events can play a large role in driving lake biogeochemistry (Foreman, Wolf, and Priscu 2004). Because these lakes are meromictic and productivity is constrained by limited light and nutrients, the streamflow-induced scouring of algal biomass as particulate organic matter (POM) inputs and its degradation may provide a source of POM and DOM to support the lake foodwebs (Cullis, Stanish, and McKnight 2014). Likewise, sediments transported into the lakes represent a source of redox-active materials such as iron oxyhydroxides (Harnish et al. 1991). Under reducing conditions, the fulvic acid fraction of DOM can be utilized by bacteria as an electron shuttle for the reduction of iron oxyhydroxides. As first posited by Howes et al. (1992) and later shown by Fulton et al. (2004), these redox processes can support chemotrophic productivity as well as enhance carbon cycling. Building on the conceptual framework of Fulton et al. (2004), Figure 1a represents the observed historical conditions as sediment settles through the water column, transitioning through the oxycline, with the Fe and Mn in oxyhydroxides becoming mobilized into the dissolved phase through reductive dissolution under anoxic conditions. This influx of sediment can drive increasing concentrations of the dissolved reduced Fe and Mn species below the oxycline. In turn, upward diffusion of ferrous iron (Fe^{2+}) across the oxycline can result in oxidation to ferric iron (Fe^{3+}) and precipitation as iron oxyhydroxides. These reactions can potentially involve humic DOM in electron shuttling reactions or by sorption onto iron and manganese oxyhydroxides (Fulton et al. 2004). Figure 1b shows how these conditions may have changed in response to the observed warming hydroclimate beginning in the early 2000s (Gooseff et al. 2017). There have been more frequent high-flow events, which are represented by increased stream flow, greater sediment transport, and POM scouring events in these streams. Through this dynamic cycling of Fe and Mn in the oxycline, DOM may be sorbed onto precipitating oxides and then released below the oxycline, and thus the chemical characteristics of the DOM pool may have changed as well. In addition, increasing moat development (Stone et al. 2024) has resulted in increased exposure of the upper water column to continuous high light intensity in summer, which may have enhanced both photoautotrophy and DOM photodegradation (Bégin et al. 2020).

To understand the biogeochemical relationships in these lake ecosystems where ice cover is dominant, it is informative to observe DOM both quantitively and qualitatively (Mopper et al. 2007; Chin et al. 2023). For example, characterization of the molecular formula of a broad array of individual compounds in bulk DOM and the humic fraction of DOM by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has supported interpretation of the hydrologic

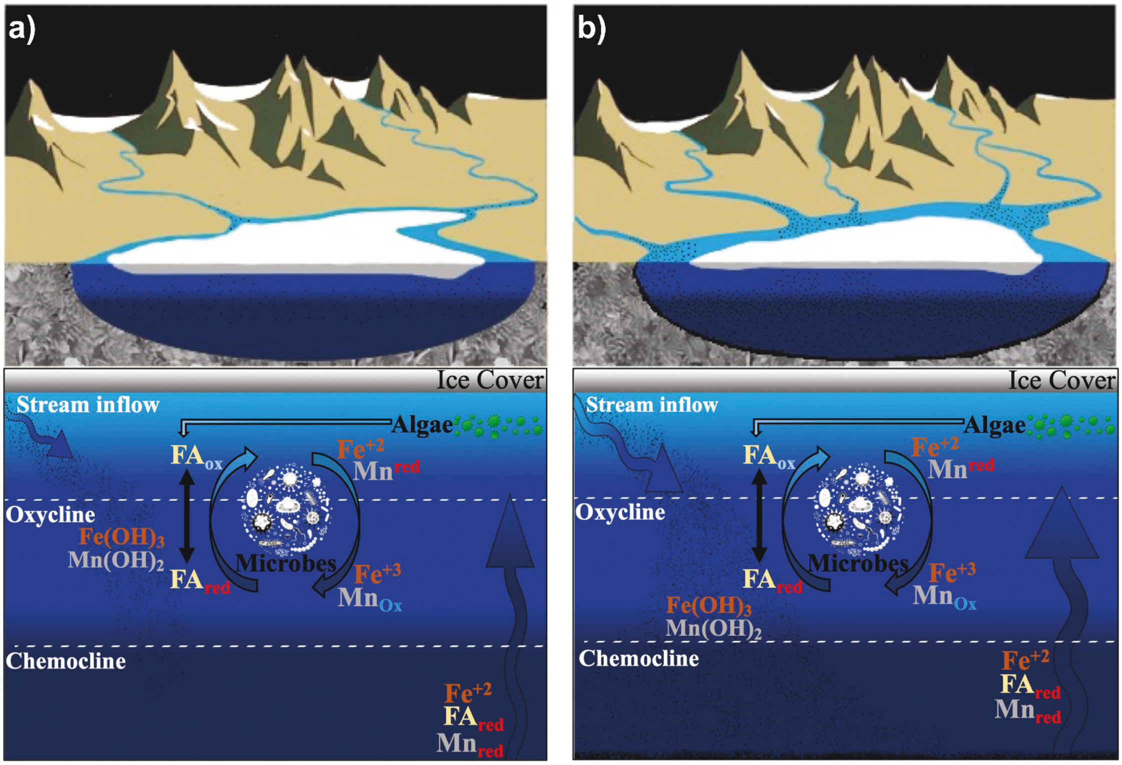

Figure 1. Conceptual diagram adapted from Fulton et al. (2004) showing the potential role of humic DOM reduction in iron (Fe) and manganese (Mn) cycling and lake productivity in the oxycline and chemocline of Lake Fryxell transitioning from (a) historical conditions to (b) those of increased landscape connectivity, littoral zone, flooding events, and sediment fluxes.

and biogeochemical controls on DOM chemical complexity in an urban stream and a subalpine lake (Rue et al. 2017, 2019). These analytical capabilities provide a means to advance the understanding of DOM biogeochemistry beyond the scope of earlier studies of the MDV lakes in the 1990s.

In this study, we revisited the finding of Aiken et al. (1996) that the sulfur content of the fulvic acid fraction in Lake Fryxell, an MDV lake, was much greater at depth below the oxycline than above the oxycline (8 versus 2.1 percent). We evaluated the hypothesis that this difference would have persisted and be reflected in a greater abundance of sulfur-containing organic molecules determined by FT-ICR-MS in a fulvic acid sample from the bottom water than in one from the above the oxycline. An alternative hypothesis that we considered was that ongoing lake level rise, enhanced scouring in streams, and expanded littoral zones, as well as increased inputs of POM and sediment inputs, have altered carbon cycling in Lake Fryxell such that the chemical characteristics of the DOM have become more uniform across the oxycline or changed over time. For this study, we evaluated the composition and diversity of organic compounds present in the DOM throughout the depth profile of Lake Fryxell. We employed established spectroscopic and fluorescence methods and isolated fractions of the DOM pool using the same resin-based method used in the previous study and another method that isolates a broader range of organic molecules (Minor et al. 2014). We used ultra-high-resolution mass spectrometry to identify the distribution of organic molecules with varying composition (Sleighter and Hatcher 2007). These results provide new knowledge into the diversity and structure of DOM under contrasting biogeochemical conditions in a MDV lake.

Site description

With limited precipitation, strong katabatic winds, and consistent cold temperatures, the MDV are an end-member ecosystem in the Long-Term Ecological Research (LTER) Program of the National Science Foundation. Extensive monitoring of the lakes and their inflow glacial meltwater streams has been conducted since 1993 (Figure 2a; McKnight and Gooseff 2023; Priscu 2023). Streamflow is driven by glacial melt during the summer and occurs for four to twelve weeks each year (Wlostowski et al. 2016). Water is lost from the lakes by ablation of the permanent ice cover. The lakes have been steadily rising since the initial exploration in

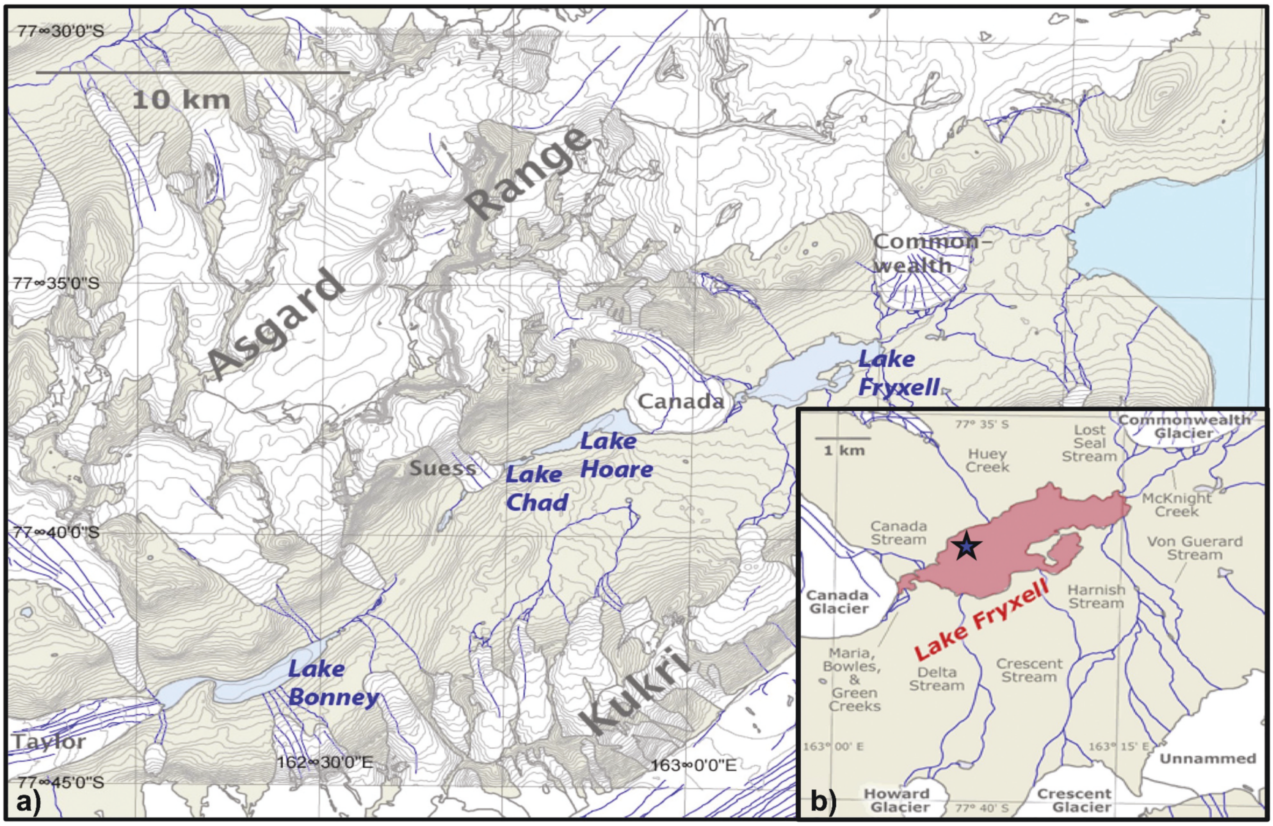

Figure 2. (a) Map of lakes located in Taylor Valley, within McMurdo Dry Valleys region of Antarctica. (b) inlay map of glaciers and streams contributing to Lake Fryxell and with starred sampling site location (-77° 36′ 37.0794″S, 163° 7′ 27.9474″E).

the early 1900s by Scott and Taylor (Bomblies, McKnight, and Andrews 2001).

The MDV lakes serve to integrate the broader landscape (Lyons et al. 1998). Absent terrestrial vegetation, the soil is almost free of organic matter. The major ions in stream water are derived from marine salts and weathering of sediment in the hyporheic zone of the streams (Green, Angle, and Chave 1988; Gooseff et al. 2002). The perennial microbial mats of the stream benthos fix carbon through photosynthesis and take up nutrients, which regulates nutrient transport to the lakes (Kohler, Stanish et al. 2015). The DOM concentrations in the streams are low, typically less than 1 mg C/L (Torrens, Gooseff, and McKnight 2022). During high flows the microbial mats are scoured, providing a flux of POM into the lakes (Cullis, Stanish, and McKnight 2014; Kohler, Chatfield et al. 2015). As such, low-flow summers have lesser inputs of solutes, POM, and sediment to the lakes.

Among the most interesting aspects of the MDV lakes is that most are closed-basin systems with no outlet and remain perennially covered by ice between 4 and 7 m thick (Obryk et al. 2016). This ice cover limits not only the input of light but also physical mixing, rendering a highly stratified environment (Spigel and Priscu 1998). In Lake Fryxell, these conditions result in supersaturated dissolved oxygen concentrations in the upper water column and anoxic conditions below the chemocline at 12 m, below which sulfate steadily decreases approaching the benthos as sulfate-reducing bacteria convert it to hydrogen sulfide (Sattley and Madigan 2010). The melting of the lake margin and stream input both generate a degree of mixing in the upper water column, as well as increased productivity in the littoral zone. Dynamic planktonic communities persist under the ice cover and are responsive to shifting stream inputs (Patriarche et al. 2021). In contrast, the lake bottom waters remain isolated and anoxic. The microbial communities in these bottom waters are highly adapted to meeting energetic metabolism demands using redox-active materials including Fe, Mn, sulfur, as well as DOM (Karr et al. 2005; Lau, Hupfer, and Grossart 2017).

Compared to temperate regions, lakes in the MDV have a truncated foodweb and a harsh physicochemical gradient that require adaptive strategies for biota to survive (Wharton et al. 1993; Spigel and Priscu 1998). Though solar radiation and associated primary production may serve as the engine that drives temperate lake ecosystem structure and function, MDV lakes experience sustained periods of total winter darkness, with summers marked by light of limited intensity from a thick and permanent ice cover as well as relatively nutrient-poor landscapes providing low fluxes of bioavailable solutes (McKnight et al. 2000; Laybourn-Parry et al. 2002). These conditions favor communities that can effectively meet their metabolic demands under these shifting constraints (Vick and Priscu 2012; Vick-Majors, Priscu, and Amaral-Zettler 2014; Dillon et al. 2020; Panwar et al. 2020). Therefore, adaptive traits such as motility and metabolic strategies such as chemoautotrophy and mixotrophy serve critical roles in these ecosystems (Roberts et al. 2000; Dolhi et al. 2015; Sherwell et al. 2022). Therefore, McMurdo Dry Valley (MCM) lakes are likely sensitized to fluxes of sediments, solutes, and POM, which annually replenish inorganic and organic pools of nutrients necessary to support lake metabolism (McKnight et al. 1999; Lyons et al. 2016; Dubnick et al. 2017). Moreover, because these lakes do not turn over seasonally, strong physiochemical gradients persist and inputs of redox-active substances like DOM, Fe, and Mn may closer resemble a basic form of a battery capable of storing charge and shuttling electrons. The upward diffusion of reduced dissolved species from below the oxycline further represents a flow of potential energy, which fosters a dynamic interface where organisms can utilize these resources to meet catabolic or anabolic metabolism demands (Del Giorgio and Cole 1998; Carlson, Del Giorgio, and Herndl 2007).

Lake Fryxell receives inflow from nine streams (Figure 2) and has among the highest dissolved organic carbon (DOC) concentrations of lakes in the MDV. Concentrations of DOC and major cations are generally highest in the bottom waters and decrease progressively to the ice interface (Figure S1). The anions chloride and sulfate largely follow this trend above the oxycline, and chloride continues to increase with depth below the oxycline (Figure S1). However, under the anoxic conditions below the oxycline at 12 m, the sulfate concentrations steadily decrease due to biotic processes (Sattley and Madigan 2006, 2010). Furthermore, Aiken et al. (1996) reported a ^{14}C age of the humic carbon as 99 percent modern in the upper water column and 68 percent modern in the bottom waters, corresponding to an average of 2,500 years old, which may be older than the formation of ice cover (Lyons et al. 1998). Results of Khan et al. (2016) indicate that this stratification of young and old DOM remained stable for at least 25 years. Their results showed that the preservation of pyrogenic carbon in the DOM pool in the bottom waters is sourced from ancient long-range wildfire deposition and the more recently produced pyrogenic carbon in the lake surface water has the signature of modern fossil fuel combustion. Long-term observations of Lake Fryxell have also noted decreasing DOC concentrations in the upper water column over the last 25 years, likely due to increased meltwater input and steady DOM production. This largely defines diffusion as the primary mechanism by which DOM is transported within the water column, with its production from detrital decay from accumulated POM in the benthos being a larger source than dissolved stream input (Aiken et al. 1996; Takacs, Priscu, and McKnight 2001).

Materials and methods

Sample collection and preparative DOM isolation

On 23 January 2018, water samples were collected using a Niskin bottle from ten depths (5, 6, 7, 8, 9, 10, 11, 12, 15, and 19 m) of Lake Fryxell in the area of its maximum depth (20 m) at the precise location (−77°36′37.0794″ S, 163°7′27.9474″ E) where the limnology team also conducts annual monitoring in support of the long-term MCMLTER record (Doran 2013; Lyons and Priscu 2014). Previous sampling at the same depths during the summer of 2017–2018 showed that the oxycline occurred between the 10- and 11-m depths and a deep chlorophyll *a* maximum concentration occurred above the oxycline at the 9- and 10-m depths (Table 1). A small

Table 1. Lake characteristics and metrics of DOM quality from spectroscopy analysis and Cory-McKnight PARAFAC model output of Lake Fryxell whole water samples.

	DO (mg/L)	Chl-*a* (µg/L)	DOC (mg/L)	Fe (µg/L)	Mn (µg/L)	$SUVA_{254}$	FI	HIX	BIX	Protein (%)	RI
5 m	28.9	0.88	1.1	9.9	0.8	2.43	1.62	1.88	0.97	18	0.42
6 m	28.8	2.29	1.9	1.1	0.2	1.57	1.62	2.20	0.95	17	0.42
7 m	26.3	3.37	2	0.6	0.1	1.74	1.69	2.53	1.02	15	0.39
8 m	32.7	4.47	2.9	0.9	0.1	1.90	1.77	3.13	1.05	13	0.36
9 m	29.8	12.3	4.8	1.7	0.2	1.59	1.80	3.50	1.03	12	0.37
10 m	15.1	17.4	5.9	3.5	15.2	1.61	1.85	4.10	0.99	11	0.38
11 m	7.3	3.27	8	52.2	232	1.19	1.87	4.70	0.96	9	0.40
12 m	0.0	0.77	9.6	25.6	199	1.70	1.86	4.52	0.94	10	0.41
15 m	0.0	0.51	15.3	4.9	49.2	1.85	1.82	4.07	0.94	10	0.40

Dissolved oxygen concentrations as mg/L (DO); Chlorophyll a concentrations as ug/L (Chl-a); Dissolved organic carbon concentration as mg/L (DOC); Dissolved iron (Fe) and manganese (Mn) concentration in µg/L; Specific UV Absorbance at 254 nm (SUVA254); Fluorescence Index (FI); Humification Index (HIX); Biological Index (BIX); Percentage of Protein-like fluorophores present (Protein %); Redox Index (RI). Chl-*a*, DOC, Fe, and Mn were determined for samples collected on 2 January 2018. Chl-*a* and DOC data are from the MCM-LTER database (https://mcm.lternet.edu/power-search/data-set). DO was determined by the Winkler titration method (1888) for samples collected on 6 December 2017.

aliquot of field sample was passed through Whatman 47-mm 0.45-μm cellulose acetate and acidified with trace metal–grade nitric acid for inductively coupled plasma–mass spectrometry analysis of dissolved Fe and Mn concentrations (Creed, Brockhoff, and Martin 1994). Following filtration of the remaining water samples through precombusted Whatman 47-mm GF/F filters, a multitiered analysis on whole water and specific DOM fractions was completed using both spectroscopy and ultra-high-resolution mass spectrometry. The filtered waters from the oxic zone at 8 m and the anoxic zone at 19.5 m were processed for isolation of the fulvic acid fraction of the DOM pool using XAD-8 macroporous resins following the method of Thurman and Malcolm (1981). After passing a fixed volume (1–2 L), depending on DOC concentration, through the column, the sorbed hydrophobic fraction was eluted using a 0.1 M NaOH solution and then acidified to pH 2. The sample was then reconcentrated on a smaller XAD-8 column, followed by a deionized (DI) water rinse and then eluted. The resulting eluate was desalted using a BioRad MP-50 cation exchange that had been protonated using a 0.1 M HCl solution, followed by a rinse with DI water to recover any solution stored interstitially. The final desalted volume was shell-frozen in a freeze-dryer flask and then placed in a Labconco freeze dryer to remove the water and concentrate the fulvic acid into a solid phase. The estimated recovery of the fulvic acid fractions from the 8-m depth varied between 13.7 and 30 percent of the DOC concentration measured on a Shimadzu TOC-V. These low recovery values agree with those previously reported (McKnight, Aiken, and Smith 1991; Aiken et al. 1996; Khan et al. 2016). From the 19.5-m depth, recovery of the fulvic acid fraction was between 51 and 53 percent. A humic acid fraction, which is defined as the fraction that precipitates at pH 2, was not recovered in processing the samples, which was also the case in the previous study (Aiken et al. 1996). Once concentrated in solid form, the fulvic acids were analyzed for elemental composition by dry mass to determine total sulfur content by Huffman Hazen Laboratories using a thermogravimetric method (Huffman and Stuber 1985).

DOM isolation involving solid-phase extraction (SPE) from Agilent Bond Elut 0.5-g cartridges containing a styrene-divinylbenzenepolymer (PPL) resin was also employed. The SPE method using PPL resin selectively sorbs both polar and nonpolar substances (Dittmar et al. 2008) and recovers a larger fraction of the DOM pool than the XAD-8 resin. This method provides an important secondary method as well as a diagnostic tool through which to compare trends observed in the fulvic acid fraction (Chin et al. 2023). SPE-PPL (SPE-DOM) extraction was performed across more depths to characterize a wider class of molecules such as carbohydrates that are not otherwise isolated by XAD-8. However, low DOC concentrations near the surface required integrating the eluates for the 6- and 7-m samples, as well as the 8- and 9-m samples, to ensure adequate recovery. Cartridges were first rinsed with 15 mL of MeOH, followed by protonation with 25 mL of a 0.01 M solution of HCl. Sample volumes between 1 and 2 L of water were passed through the cartridges, followed by 10 mL of DI water to remove any residual salts. To prevent oxidation of DOM sorbed to the SPE-PPL resin, an N_2 gas stream was passed through until dry (Mopper et al. 2007; Minor et al. 2014). Each cartridge was eluted with MeOH to resolubilize the recovered DOM and then dried again to a solid phase under N_2 gas (Li et al. 2016).

Spectroscopy and spectrometry

Fluorescence spectroscopy is a reliable method of observing changes in the chromophoric fraction of DOM in whole water as well as the humic DOM isolated with SPE-PPL and XAD-8 resins (Minor et al. 2014). Through established metrics that indicate degrees of humification (humification indiex, HIX), biological contribution (biological index, BIX), and the overall contribution of microbial and terrestrial sources (fluorescence index, FI), this information can identify important biogeochemical processes influencing DOM (Gabor et al. 2014). Whole water collected across the Lake Fryxell depth profile was filtered through precombusted Whatman GF/F filters, after which DOC concentrations were measured on a Shimadzu TOC analyzer followed by absorbance at 254 nm on an Agilent 8453 spectrophotometer to estimate bulk chromophore aromaticity by normalizing to DOC concentration to establish the specific UV absorbance metric ($SUVA_{254}$). The absorption spectrum was used to correct for inner-filter effects (Miller et al. 2010) in the fluorescence spectroscopy analysis that followed on a Horiba Jovin Yvon FluoroMax-4. Due to limited fulvic acid yield, spectroscopy was not performed on the fulvic acids. Because of the use of MeOH in SPE-PPL as well as subsequent carryover into the solid phase, spectroscopic analysis was also not completed on the SPE-DOM isolates.

Following the method of Cory and McKnight (2005), the fluorescence scans from filtered, undiluted whole water were collected between 240 and 450 μm excitation and 300 and 500 μm emission following postprocessing in MATLAB 2022 to correct for inner-filter effects and instrument correction using Raman and blank scans to produce excitation emission matrixes (EEMs). From these EEMs, qualitative indicators of DOM were calculated. These included FI, a metric of relative contribution of allochthonous and autochthonous; HIX, a metric for the degree of polycondensation in the humic substance; and BIX, a metric regarding the relative contribution of fresh biological and microbial sources (Gabor et al. 2014). Secondary parallel factor analysis (PARAFAC) was performed on the corrected EEMs using a thirteen-component Cory-McKnight model, which was created from thousands of freshwater samples from numerous diverse sources to identify common fluorophores among them (Cory and McKnight 2005). Because this model was developed using Lake Fryxell samples, it was suitable for use to provide loadings of discrete components and facilitated further metrics such as the redox index (RI; Gabor et al. 2014). This is calculated by dividing the sum of reduced quinone-like components over the total quinone-like fluorophores. The RI in particular offers evidence of microbially mediated electron shuttling by probing the redox state of the involved moieties (Mladenov et al. 2008; Beggs, Summers, and McKnight 2009; Miller et al. 2009).

The high-resolution mass spectrometry of the SPE-DOM and fulvic acids was completed at the Environmental Molecular Science Lab (EMSL) within the Department of Energy's Pacific Northwest National Lab (PNNL) campus. A 12-Tesla Bruker solariX FT-ICR -MS with a Bruker ESI interface was used, with each sample run in triplicate along with an International Humic Substances Society fulvic acid standard collected from the Suwannee River for internal instrument quality assurance/quality control purposes (Chin et al. 2023) as well as to ensure data repeatability and reproducibility as outlined by Kido Soule et al. (2010). These raw spectra were analyzed using the Compound Identification Assignment algorithms (Minor et al. 2014) over a mass range of 200–700 m/z associated to known DOM moieties (Sleighter et al. 2007). The Compound Identification Assignment application provides elemental ratios of Carbon (C), Oxygen (O), Hydrogen (H), Nitrogen (N), Sulphur (S), and Phosphorus (P) of specific heteroatoms present in molecular peaks observed throughout the raw spectra, and from these data van Krevelen diagrams can be made using H:C and O:C ratios to distinguish structure in addition to stoichiometric content (Kim, Kramer, and Hatcher 2003). Using the FTICR R Exploratory Data Analysis (FREDA) toolset developed by the EMSL Molecular Science Computing Data Analysis & Visualization Division, these visualizations were created with the compounds identified and resultant molecular formulae used calculate comparative DOM metrics. These include the nominal oxidation state of carbon (NOSC; LaRowe and Cappellen 2011) to understand its thermodynamic favorability in microbial metabolism and overall aromaticity structure using the modified aromaticity index (Koch and Dittmar 2006, 2015; Graham et al. 2017):

$$AI_{mod} = \frac{1 + C - 0.5O - S - 0.5(N + H + P)}{C - 0.5O(O - N - S - P)}$$

$$NOSC = 4 - \frac{4C + H - 3N - 2O + 5P - 2S}{C}.$$

Results

Water chemistry

The depth profiles of DOC, sulfate, and chloride concentrations in Lake Fryxell (Figure S1) highlight the relatively stable water column, which is primarily mediated through diffusive transport. The DOC concentrations in 2018 were roughly 20 percent lower at the bottom waters than those reported by McKnight, Aiken, and Smith (1991) in 1988, indicating a potential diluting influence of the increased streamflow. There was an increase in DOC at the 8-m depth compared to the DOC at 7 m. This increase corresponded with an increase in chloride and sulfate. At increasing depth, sulfate and chloride concentrations rose in proximity to the oxycline boundary at 10 m. However, below the oxycline the chloride continued to increase, whereas sulfate started to decline at 15 m and dropped substantially at the bottom waters. This pattern suggests that under more reducing conditions below the oxycline, sulfate was being used as an electron acceptor, potentially yielding hydrogen sulfide (H_2S). Analysis of the water quality samples collected concurrently showed that the concentrations of dissolved Fe and Mn were generally low above the oxycline, ranging from 1 to 15 μg/L, whereas below the oxycline at the 11- and 12-m depths peaks occurred in both Fe and Mn concentrations (Table 1).

DOM spectroscopy

As previously reported (McKnight et al. 1994), the $SUVA_{254}$ values in Lake Fryxell were generally low compared to typical values for temperate lakes (Table 1). The highest value for $SUVA_{254}$ occurred near the water–ice interface, which may be indicative of production of fresher DOM from photoautotrophy. The lowest value occurred at 11 m, immediately below the oxycline and aligned with the peaks in both dissolved Fe and Mn concentrations, suggesting a scavenging of more aromatic DOM by sorption reactions associated with the dynamic cycling of oxyhydroxides occurring in that zone (Figure 1).

The FI values ranged between 1.62 and 1.87. Overall, these high values highlight that microbial contributions influenced the pool of humic substances at all depths (Table 1). The variation in FI with depth is an indication of the range in FI that can be associated with microbial sources of DOM, given that terrestrial vegetation is not present in the MDV. The lowest FI values occurred in the upper water column above the oxycline and may reflect more recent production by phytoplankton growth. Blue shifting in the excitation emission matrix spectroscopy, reflecting a shift toward lower molecular weight and polycondensed compounds (Coble 1996), at increasing depth below the oxycline further supports these patterns (Figure S2).

The HIX values were in the low range and were lowest near the surface (1.88) and increased with depth. The highest HIX value of 4.7 was aligned with the peaks in Fe and Mn concentrations. These shifts suggest a substantial degree of alteration of the fluorescent DOM pool in the zone below the oxycline (Table 1). The BIX values were generally high compared to values reported for temperate ecosystems, suggestive of high biological activity (Gabor et al. 2014) and matched with the BIX values reported by Kida et al. (2019) for numerous lakes in another ice-free region of East Antarctica. In contrast to the variation in FI and HIX values, the BIX values exhibited a limited range with slightly higher values in the 7- to 9-m zone above the oxycline. The percentage of protein-like fluorescence was greatest in the upper water column at 18 percent and then exhibited a progressive twofold decrease with depth. This pattern indicates production of fresher DOM in the upper water column and is consistent with the depthwise increase in HIX. The variation in RI appeared to align with the variation in BIX, with values indicating more oxidized DOM occurring in the 7- to 10-m zone above and immediately within the oxycline.

DOM spectrometry

From immediately below the ice cover to the oxycline boundary there was a decreasing presence of nitrogen and sulfur-containing heteroatoms as well unsaturated hydrocarbons in the SPE-DOM isolates (Table 2; Figure S3). Conversely, there was an increasing presence of phosphorus groups in the amino acid and protein region. Below the oxycline, there was a large incorporation of sulfur groups (CHOS) into the DOM pool. At depth there was an increasing prevalence of more complex compounds (CHONS, CHOSP, CHONSP) comprising 36 to 40 percent of the total pool. These changes correspond to more heteroatoms shifting into the condensed aromatic and unsaturated hydrocarbon regions. Relative to above the oxycline, there was a shift toward more groups in the carbohydrate region at depth, which were also enriched in sulfur (Figure S3).

In the fulvic acids isolated above the oxycline (9 m) there were more CHO and CHON groups, and below the oxycline at 19 m there was a strong shift to CHOS heteroatoms from 8 to 17.3 percent (Figure 3b). This difference also accompanied an increased presence of these groups in the unsaturated hydrocarbon regions, where ancient pyrogenic carbon is still being preserved in the DOM pool (Figures 3c,d). It should be noted that molecules appearing in the lignin region of the van Krevelen diagram do not exclusively refer to plant-like material but rather represent a region with more aromatic structure that are resistant to further degradation (D'Andrilli et al. 2013). In terms of the similarity between these samples (Figure 3a), the largest common shared peaks also corresponded to this region, whereas the most dissimilarities were in hydrocarbon regions associated with pyrolysis and increased polycondensation. This finding further affirms the persistent fingerprints of modern fossil fuel combustion in the surface waters and legacy black carbon wildfire in the benthos DOM (Khan et al. 2016).

Regarding the variability in calculated qualitative metrics of DOM from FT-ICR-MS data, values for NOSC and AI-mod were far more responsive to the changing conditions across the depth profile in the SPE-DOM than in the fulvic acids. The oxidation state and aromaticity of carbon in the SPE-DOM changed across the depth profile (Table 2) by upwards of 40 percent, further revealing the influence of

Table 2. Values for NOSC, AI-mod, and percentages of formulae assignments (CHO, CHON, CHOS, CHOP, CHONS, CHONSP) from FT-ICR-MS analysis of fulvic acids and SPE-PPL DOM collected across the Lake Fryxell depth profile.

Method	Depth (m)	NOSC	AI-mod	CHO (%)	CHON (%)	CHOS (%)	CHOP (%)	CHONS (%)	CHONP (%)	CHONSP (%)
SPE-PPL	6–7m	−0.307	0.061	43.4	24.7	12.4	13.4	2.8	1.4	0.4
	8–9m	−0.314	0.061	44.3	23.1	12.2	13.4	2.6	1.7	0.7
	10m	−0.295	0.054	46.1	33.0	12.7	13.9	1.9	1.3	0.4
	11m	−0.317	0.058	45.0	20.2	13.1	15.6	1.9	1.8	0.5
	12m	−0.135	0.062	31.7	26.5	20.8	6.0	10.7	2.1	0.7
	19.5m	−0.185	0.073	33.6	21.4	22.6	5.1	9.5	2.6	1.7
Fulvic acid	9m	−0.262	0.058	60.8	24.8	10.1	2.0	1.7	0.1	0.3
	19m	−0.269	0.063	55.3	18.2	20.9	2.4	2.2	0.2	0.1

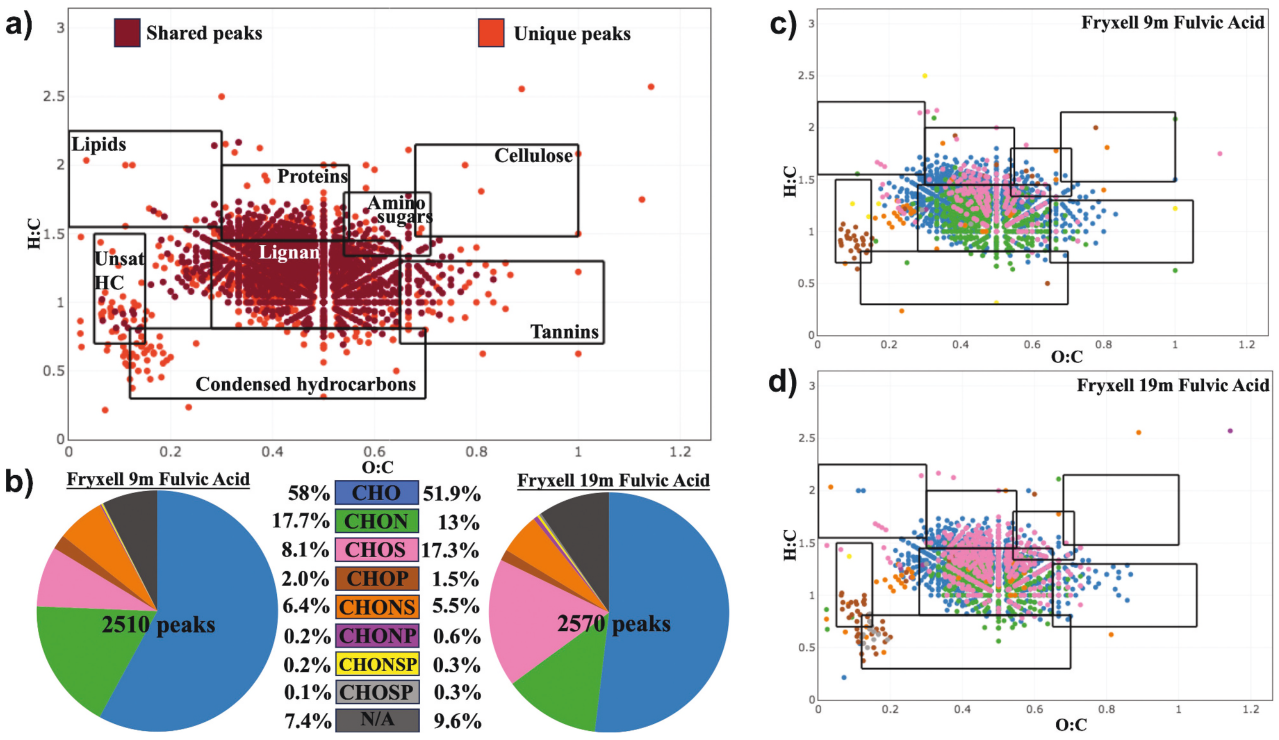

Figure 3. (a) Van Krevelen Diagrams of shared and unique peaks of the Fulvic Acids isolated from Lake Fryxell at the 9 meter and 19 meter depth with compound class regions identified. (b) Distributed composition by assigned molecular formulae of 9 meter and 19 meter Fulvic Acid samples. (c) Van Kevelen Diagram of Fulvic Acid collected from Lake Fryxell at the oxic 9 meter depth. (d) Van Krevelen Diagram of Fulvic Acid collected from Lake Fryxell at the anoxic 19 meter depth.

differing environmental conditions above and below the oxycline. In contrast, the fulvic acids varied less than 4 and 8 percent, respectively (Table 2). Above the oxycline, NOSC values (−0.2950:−0.317) of SPE-DOM also reflected conditions free of thermodynamic limits favoring aerobic carbon microbial oxidation (NOSC > −0.6), and below the oxycline where sulfate acts as the dominant electron acceptor these values remained below the sulfidic threshold (NOSC < −0.3) to remain energetically viable for microbial respiration (Boye et al. 2017). There are less apparent patterns in the AI-mod values, even across oxic and anoxic conditions, and trends appeared more corollary to those observed in spectroscopic metrics of DOM "freshness" (BIX) or redox state (RI). This comparison also emphasizes the usefulness in utilizing both spectrometric and spectroscopic-based methods.

Due to the limited nature of mass spectrometry in providing quantitative information beyond the diversity and structure of identified heteroatoms, secondary analysis of the fulvic acids was performed to measure the sulfur content directly, which also reproduced an analysis from Aiken et al. (1996) to provide possible comparative information in terms of total sulfur content. These data were obtained by Huffman Laboratories using a similar thermogravimetric approach as previously and showed a 1 percent content of sulfur by mass at 9 m and 4 percent at 19 m, which affirms the increasing incorporation of sulfur into the fulvic acids relative to depth (Figure 3) and complements patterns observed in heteroatom composition (Table 2).

Discussion

Contemporary observations

Through synthesizing these results based on a growing body of relevant research, our findings affirm and extend those made previously and offer new insight from contemporary analytical capabilities. In particular, the results from mass spectrometry provide new information regarding the diversity of organic molecules comprising DOM present across the depth profile of Lake Fryxell. The pronounced shift toward sulfur-containing compounds in the SPE-PPL sample at 12 m, just below the oxycline, confirms our initial hypothesis based on the greater sulfur content of the fulvic acid at depth reported by Aiken et al. (1996). The clear transition between the 11- and 12-m depths suggests that the major transitions in the lake related to greater stream inflows have not overwhelmed the pronounced influence on DOM composition imposed by the biogeochemical transitions at the oxycline. This shift also highlights a transition toward a redox-driven metabolism mediated by sulfate as the most favorable terminal electron acceptor present below the oxycline (Lau, Hupfer, and Grossart 2017; Lau et al. 2018).

In addition, the presence of phosphorus-containing compounds in the SPE-DOM isolates from zones of the water column where primary production was occurring, along with the dominance of phosphorus-containing compounds in the protein-like region of the van Krevelen diagram (Table 2; Figure S3), indicates that these compounds may be released as exudates by the growing phytoplankton community (Roth-Rosenberg et al. 2021) or by the release of extracellular materials from cell lysis (Säwström et al. 2007; Filippova et al. 2016). The deep chlorophyll maxima of 17.4 µg/L present at 10 m, a common trait of highly stratified and nutrient-limited lakes (Karpowicz et al. 2024), also corresponded to a prevalence (33 percent) of N-containing heteroatoms. Below the oxycline, there was a shift to the phosphorus-containing compounds occurring in the condensed aromatic and hydrocarbon region of the van Krevelen diagram. This shift may indicate that the algal exudates became progressively degraded by microbial heterotrophic processes at this depth. In addition, fresher DOM from photoautrophy may be diffusing down from above to exert a possible priming effect on this degradation (Bianchi 2011; Logue et al. 2015; Laffet, Prentice, and Tremblay 2023). The corresponding changes in the NOSC values confirmed that the SPE-DOM pool remained thermodynamically suitable to support microbial respiration across oxic and anoxic conditions. Overall, the differences in DOM composition between the oxic and anoxic zones largely appeared in the broader DOM fraction isolated with SPE-PPL resin. In particular, the fulvic acid components did not exhibit a substantive shift in the diversity of heteroatoms, a shift in the presence of phosphorus-containing compounds, or a strong a shift in NOSC. This contrast further suggests that nonchromophoric compounds account for the differences observed in the SPE-DOM fractions (Kivilä et al. 2023).

A less conclusive pattern occurred with the AI-mod, with similarly high aromaticity of SPE-DOM near the surface and benthos. This may reflect contrasting processes in terms of bacterial uptake of more labile aliphatic compounds initially exuded by phytoplankton growth (Hach et al. 2020). More energetically viable substrates that can be anaerobically respired by heterotrophic bacteria may be preferentially removed from the SPE-DOM pool (Gibson and Harwood 2002; Kellerman 2015; Lau and Del Giorgio 2020). In contrast, the fulvic acids isolated from above and below the oxycline showed minimal changes in AI-mod. Cumulatively, these findings highlight the value of exploring chemically distinct and operationally defined DOM fractions, such as fulvic acids, as well as a broader DOM pool containing both polar and nonpolar compounds. These results also suggest that the evolution and cycling of nonhumic DOM plays a particularly important role under the resource and mixing constraints associated with ice cover (Roiha, Laurion, and Rautio 2015; Rue et al. 2019).

One source of DOM in the MDV lakes could stem from phage-induced lysis of bacteria and the release of extracellular products (Tuomi et al. 1995; López-Bueno et al. 2009). It has been shown across lacustrine Antarctic systems that carbon flows through the microbial loop but seasonally shifts toward the viral shunt (Evans et al. 2021) in transitions from the austral summer to the period of winter darkness. During these transitions, an estimated 60 percent or more of contributions to the DOC pool originate from viral lysis (Säwström et al. 2007). These DOM sources may additionally appear in the van Krevelen diagram, particularly in regions associated with lipids, proteins, amino sugars, and carbohydrates. There is also a notable presence of phosphorus-containing heteroatoms in the protein region in portions of the water column of Lake Fryxell associated with high planktonic activity, which is absent in the fulvic acids. This potentially captures a dynamic pool of labile DOM (Thompson and Cotner 2018; Cotner, Anderson, and Osburn 2022), one also previously unaccounted for in Lake Fryxell (Takacs, Priscu, and McKnight 2001). In contrast, the bottom waters may contain more recalcitrant aromatic compounds that may be preserved under anoxic conditions and are utilized by microbial communities with more metabolic plasticity (Vick-Majors, Priscu, and Amaral-Zettler 2014; Picazo et al. 2021).

In general, the spectroscopic characterization of DOM from Lake Fryxell highlights the influence of DOM production and alteration in this ice-covered lake ecosystem. Closer to the surface, there appears to be greater production of fresh DOM indicated by the higher $SUVA_{254}$, percentage of protein-like fluorescence, lower HIX, and lower FI (McKnight et al. 2001; Cory and McKnight 2005). At depth as light dims, shutting down photosynthetic activity, there is less production of DOM by phototrophs, as well as more alteration of DOM from heterotrophic activity, supported by the concomitant increasing HIX values (Stadler, Ejarque, and Kainz 2020). Together these depth profiles reflect the various processes altering the DOM pool, possibly explaining the persistence of legacy DOM at depth over time (Bastviken et al. 2004). It is particularly important to note that the FI values in this study are consistent with values from prior studies (McKnight et al. 2001; Cory and McKnight 2005), despite Lake Fryxell having dramatically increased in volume, with a resulting diluting influence on DOC concentrations (Khan et al. 2016). Furthermore, the FI and BIX values are in the same range as those found by Kida et al. (2019) for numerous lakes and streams in the Lutzow-Holm Bay and Amundsen Bay area also in East Antarctica. In contrast, the $SUVA_{254}$ and HIX values reported by Kida et al. (2019) were much lower than those found in this study for Lake Fryxell.

Finally, these results for Lake Fryxell resemble those from a study of DOM, phytoplankton, and nutrient dynamics during winter in a subalpine lake in the Rocky Mountains (Rue et al. 2019). This study also evaluated SPE-DOM and fulvic acid isolates, utilizing both spectroscopy and FT-ICR-MS to characterize the DOM pool. Although limited changes were observed in spectroscopic metrics over time and depth, there were evolving changes to the molecular diversity of the fulvic acid isolates and SPE-DOM under the ice cover, with phosphorus-containing compounds becoming more predominant in the upper oxic zone and sulfur-containing compounds in the anoxic bottom waters.

Comparison to prior study

The sulfur contents of the fulvic acids reported by Aiken et al. (1996) were 2.1 percent above the oxycline and 8 percent below the oxycline. These sulfur contents are significantly higher than those measured in this study (1 and 4 percent, respectively). The sulfur content of fulvic acid from Lake Vida, another MDV lake, was found by Cawley et al. (2016) to be 1.1 to 1.2 percent, comparable to current values for Lake Fryxell. The decrease in sulfur content observed in the fulvic acid collected for this study compared to that reported by Aiken et al. (1996) shows that in just thirty years a large change occurred in a pool of legacy DOM previously thought to be chemically stable. This comparison also suggests that the DOM in the bottom water is chemically reactive and possibly transitioning from humic DOM fractions into other nonhumic fractions by microbial processes.

The results from ultra-high-resolution mass spectrometry show a larger presence of CHONS and CHONSP heteroatoms, particularly in the protein, amino acid, and carbohydrate in the SPE-DOM isolates that do not appear in the fulvic acids. Though the study of Lake Vida by Cawley et al. (2016) found similar sulfur composition for the DOM, the mean ^{14}C age of the Lake Vida fulvic acids is older than that of Lake Fryxell. The observed shift in sulfur content indicates that the recent climatological change in the MDV is a likely driver for the changes in the biogeochemical cycling of sulfur in the anoxic bottom waters. These decreases in the sulfur content of the fulvic acids could be biotically driven from increasing organic matter deposition (Kujawinski et al. 2009). Alternatively, these trends could be abiotically influenced from competitive interactions with Fe, which is deposited by high-flow events, scavenging the hydrogen sulfide before it can be assimilated by reaction with DOM (Raven et al. 2016; Pohlabeln et al. 2017; Longnecker et al. 2020; Gomez-Saez et al. 2021). In these anoxic, isolated bottom waters, the reducing conditions favor speciation and formation of stable iron–sulfide complexes (Foreman, Wolf, and Priscu 2004). Overall, these findings suggest possible cascading effects on the pool of dissolved organic sulfur compounds driven by rapid lake level rise accompanied by the increased flux of reactive sediments and organic matter.

Conclusions

Employing multiple means of DOM isolation and DOM characterization has provided a deeper understanding of DOM cycling in Antarctic lakes (D'Andrilli et al. 2013; Minor et al. 2014). These results support prior inferences about processes controlling autochthonous contributions and alterations of DOM throughout the Lake Fryxell depth profile (Howes et al. 1992; McKnight et al. 1993, 2001) and contribute new insight regarding DOM molecular composition, diversity, and persistence throughout the water column (Kellerman et al. 2018). These insights include the contrasting presence of phosphorus- and sulfur-containing compounds as a function of redox conditions and the thermodynamic stability of DOM across these conditions to support microbial respiration. In general, the detailed FT-ICR-MS results resolved the more qualitative aspects of the DOM character that were indicated by the spectroscopic results. For example, the changes with depth in the RI were consistent with those observed in the NOSC and AI-mod values of the DOM isolated by SPE-PPL resin. Cumulatively, these patterns highlight a response in the oxidation state of DOM in regions of the water column where biological activity is highest. Additionally, our study highlights the value of studying both fulvic acid and a broader DOM pool to understand these dynamic changes. For future studies of lakes in the MDV, these results suggest some key drivers of coupled biogeochemical processes that may influence metacommunity dynamics (Danczak et al. 2020).

There exist few environments on Earth where allochthonous contributions of DOM to aquatic ecosystems are absent. This renders the MDVs of intrinsic research value for identifying the signatures in the DOM pool of microbially mediated production, transformation, and degradation of DOM. These systems may offer helpful perspectives toward resolving divergent views among freshwater, marine, and soil science communities on the potential for degradation of microbial processes to produce humic DOM (Kothawala et al. 2021; D'Andrilli et al. 2022; Freeman et al. 2024). As more surveys of Antarctic lakes reveal a continuum of end-member environments and controls on DOM chemodiversity, the relative importance of climate history to legacy landscapes may become better resolved (Kida et al. 2019, 2023). This study also highlights the value of long-term monitoring and collection of preserved humic samples. The ratios of sulfur present in fulvic acids isolated from surface and bottom from our 2017–2018 study and those from twenty-five years earlier (Aiken et al. 1996) were both 4:1. However, the twofold reduction in sulfur content suggest that the mechanisms driving the incorporation of sulfur into the DOM pool may be sensitive to the flood events that drove the increase in lake volume over that period. As the shifting climate increases the landscape connectivity of these Antarctic polar deserts, the coupling of hydrological and biogeochemical processes may continue to change the chemical composition of DOM in the lakes (Foreman, Wolf, and Priscu 2004; Herbei et al. 2016; Dillon et al. 2020).

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