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RESEARCH ARTICLE

Temporal variability of dissolved organic matter composition in the hypersaline Mono Lake, California

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Abstract

Saline lakes are generally characterized by high productivity and accumulation of organic matter, contributing to the global carbon cycle. Mono Lake is an endorheic lake in California (USA) whose geochemistry and microbial community composition have been extensively studied. Less is known about the dissolved organic matter (DOM) composition in this system. Here, we investigated the molecular composition of DOM in Mono Lake using ultrahigh resolution mass spectrometry (FT-ICR MS) to capture patterns of variability in DOM during a transition from monomictic to meromictic conditions in 2017–2018. Dissolved organic carbon (DOC) concentrations were up to twofold higher at ~ 10–15 m in monomictic compared with meromictic conditions. Lake DOM in spring and summer of 2017 was enriched in nitrogen-containing formulae and higher proportions of unsaturated aliphatics, lipid- and protein-like compounds, likely associated with phytoplankton-derived inputs. During fall 2017, lake DOM revealed a more terrestrial signature, and enrichment in sulfur-containing formulae, presumably due to changes in redox condition in the water column. Following prolonged stratification (2018), DOM composition was also influenced by phytoplankton inputs and by the strong redox gradient observed in the lake, with increased relative abundance of S-containing compounds immediately below the pycnocline. During the shift in limnological conditions, Mono Lake DOM remained less aromatic and more reduced than DOM observed in other saline endorheic lakes. These findings shed light on organic carbon cycling in hypersaline lakes, which is important to better constrain contributions of inland aquatic ecosystems to the carbon cycle.

Keywords Dissolved organic matter · Endorheic saline lakes · FT-ICR MS · Mono Lake, California

Introduction

Saline lakes are inland aquatic environments distributed across all continents, representing ~ 40% of total water volume stored in lakes and ~ 50% of total inland water surface area (Wetzel 2001; Messager et al. 2016). Many of these ecosystems are situated in hydrologically enclosed basins in arid regions and have long residence times, resulting in efficient recycling of nutrients compared with freshwater lakes (Waiser and Robarts 2000; Isaji et al. 2019). This nutrient dynamic plays an important role in the high primary productivity often observed in saline lakes, which in turn contributes to the high concentrations of dissolved organic carbon (DOC) reported in these systems (Salm et al. 2009; Xu et al 2024). Recent studies have shown that DOC concentrations in hypersaline lakes are ~ 2–3 times greater than in freshwater and less saline lakes (Wen et al. 2018; Yang et al. 2020) and can be up to 5 times greater in bottom waters compared with surface waters (Butturini et al. 2020). These findings suggest that saline lakes, in particular hypersaline lakes, contribute to organic matter preservation, having the potential to act as a carbon sink. In addition, saline lakes can have intense CO_2 exchanges with the atmosphere, potentially playing an important role in the global carbon cycle (Duarte et al. 2008; Tranvik et al. 2009; Osburn et al. 2011). Despite having significant contributions to both local and global carbon cycle, much remains to be learned about dissolved organic matter (DOM) composition in hypersaline lakes (Butturini et al. 2020, 2022).

Mono Lake is a large, 160 km^2 endorheic lake located in California (USA) at the western edge of the Great Basin. It

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is well-known for its unique geochemical features, including pH ~ 10, salinity ~ 85 ppt, and DOC greater than 5000 µM. The hydrologic budget in Mono Lake is primarily driven by freshwater inputs derived from Rush Creek and Lee Vining Creek, which provide ~ 15×10^7 m^3 $year^{-1}$ (Keevil et al. 2022), and evaporation (~ 1 m $year^{-1}$; Vorster 1985). Hydrologically, Mono Lake is typically monomictic, being characterized by thermal stratification during early spring and summer and a complete water column overturn during winter (Melack and Jellison 1998). However, since early 1980s, Mono Lake has experienced recurrent episodes of prolonged stratification (meromictic conditions) due to large variations in freshwater inputs, which are mainly associated with large snowmelt runoffs from Sierra Nevada (Jellison and Melack 1993a, b). Following meromictic conditions, Mono Lake often accumulates reduced species (i.e., sulfide, ammonia, methane, and arsenite) in bottom waters (Hollibaugh et al. 2005), associated with changes in redox conditions that can have a profound effect on the ecology and biogeochemistry of the lake (Melack et al. 2017). During prolonged stratification, the strong redox gradient creates favorable conditions for sulfur-reducing bacteria to thrive in bottom waters, thereby sulfate reduction is one of the main anaerobic pathways in remineralization of organic matter in this lake (Scholten et al. 2005; Sorokin et al. 2011; Edwardson and Hollibaugh 2017). This system is characterized by high primary production (269–1060 g C m^{-2} $year^{-1}$; Jellison and Melack 1993a, b), which is mainly sustained by a green algae *Picocystis* sp. strain ML. Seasonal variation in phytoplankton abundance is mainly influenced by grazing by the endemic brine shrimp *Artemia monica*, which is an important food source for several migratory birds (Wiens et al. 1993).

Many previous studies have shown shifts in microbial community composition throughout the water column as a result of limnological changes in Mono Lake (Hollibaugh et al. 2001; Edwardson and Hollibaugh 2017; Stamps et al. 2018), including microbial succession from sulfate oxidizers to sulfate reducers during a transition period from monomictic to meromictic conditions from 2017 to 2018 (Phillips et al. 2021). Although geochemical characteristics and microbial communities in Mono Lake have been studied extensively, much remains to be learned about the composition of organic matter (OM) in this system, which could potentially help shape microbial diversity and community composition. In this study, we investigated the molecular composition of DOM in Mono Lake during the 2017–2018 transition from monomictic to meromictic conditions using ultrahigh resolution mass spectrometry (FT-ICR MS). Our primary objectives were to provide a detailed characterization of DOM composition and to identify key biogeochemical processes modifying DOM composition in a hypersaline soda lake during changes in limnological conditions.

Materials and methods

Sample collection

Samples were collected along a vertical profile at Mono Lake at Station 6 (37° 57.44′ N, 119° 1.89′ W; Fig. 1), which is located near the deepest part of the south basin. A profile was collected in May, June, and September of 2017 and in May, June, and October of 2018. As in Ref. 57, we refer to these as spring, summer, and fall of 2017 and 2018. For each sample collection, conductivity, temperature, and dissolved oxygen were measured using a SeaBird SBE 19 CTD cast to 35 m depth. These data are publicly available in the US Geological Survey data release (Miller et al. 2020) and are shown in Supplementary Fig. S1. About five or six discrete water samples were collected from each profile at depths ranging from 0.5 to 35 m (see Table S1 for details) using a 5-L Niskin bottle as described by Phillips et al. (2021).

Samples from potential contributors to the DOM pool in Mono Lake, such as Rush Creek ($n = 1$), Lee Vining Creek ($n = 1$), and a dominant phytoplankton species (*Picocystis* sp.) ($n = 1$), were also collected in 2018. Lake samples collected in spring 2018 were used to isolate and cultivate *Picocystis* sp. as described in Ref. 60. Briefly, *Picocystis* sp. strain ML was grown in batch culture at the University of Georgia. The stock and experimental cultures were maintained at 20 ± 1 °C under photosynthetic active radiation (PAR) of 65 µmol photons m^{-2} s^{-1} and a 14:10 light:dark cycle in Erlenmeyer flasks (stock culture in 1 L and experimental cultures in 5 L). The pH was kept at 9–10. We note that cyanobacteria can also play an important role in Mono Lake (Melack et al. 2017; Phillips et al. 2021), but cultures were not available for analysis.

Within hours of collection, water samples (3–5 L) were filtered (0.7 µm Whatman GF/F filters combusted at 450 °C for 5 h and 0.2 µm Pall Supor membranes) and aliquots (~ 60 mL) were collected using acid-washed Nalgene high-density polyethylene (HDPE) amber bottles for DOC concentration measurements (Halewood et al. 2022). These samples were immediately stored at −20 °C and further analyzed at the University of Georgia. Remaining filtrates (~ 1.5–2 L stored in acid-washed polycarbonate bottles) were acidified to pH ~ 2 (using concentrated HCl), and DOM was isolated using solid-phase extraction (SPE) cartridges filled with styrene–divinylbenzene polymer (Agilent Bond Elut PPL, 1 g) and then eluted with methanol as described in Ref. 9. After elution, DOM samples were concentrated using ultrapure nitrogen gas and stored in glass vials (combusted at 450 °C for 5 h) at –20 °C under dark conditions for Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis.

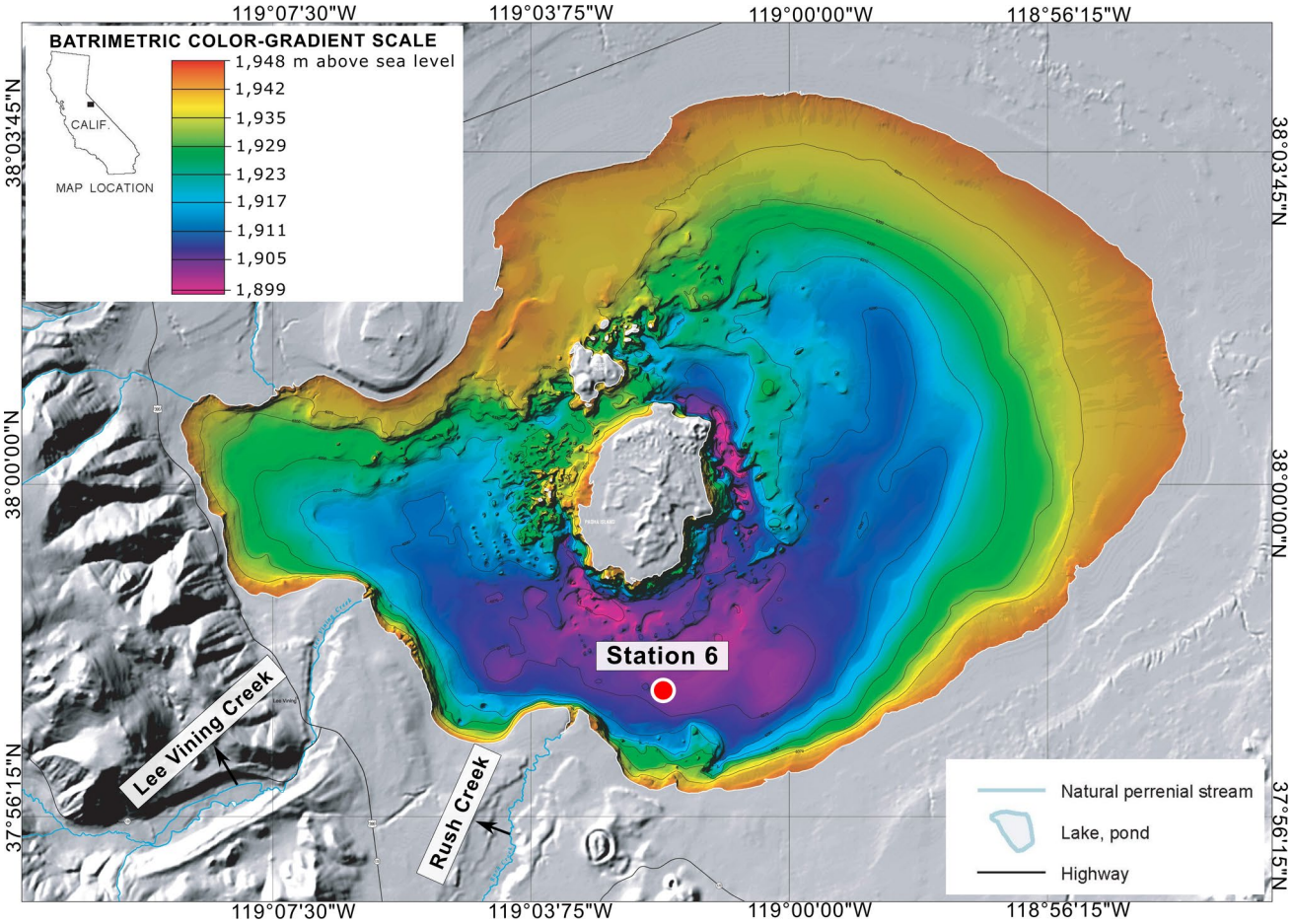

Fig. 1 Digital bathymetric model of Mono Lake, California, showing the sampling site (Station 6; 37° 57.44′ N, 119° 1.89′ W) where depth-profile samples (0–35 m) were collected seasonally in 2017 and 2018. Additional samples that could contribute to the DOM pool in the lake were collected in 2018, including creeks (Lee Vining and Rush Creek) and the dominant phytoplankton species (*Picocystis* sp.). Source: Modified from Raumann et al. (2002) publicly available from the US Geological Survey National Geologic Map database (https://ngmdb.usgs.gov/Prodesc/proddesc_52722.htm)

Bulk measurements and FT-ICR MS analysis

DOC concentrations were measured with a Shimadzu TOC-L_{CPH} analyzer (Halewood et al. 2022). A potassium hydrogen phthalate calibration curve was used as standard. Before and during DOC analysis of our samples, internal blanks and Milli-Q water blanks (18.2 MΩ) were run on the instrument. Analytical accuracy and precision were tested against deep-sea reference material (Hansell 2005) and were better than 5%.

Molecular composition of the DOM extracts (yielding a DOC concentration of 100 ppm in methanol) was analyzed by negative mode electrospray ionization (–ESI) using a custom-built hybrid linear ion trap 21 Tesla Fourier transform-ion cyclotron resonance mass spectrometer (FT-ICR MS) at the National High Magnetic Field Laboratory (NHMFL, Florida State University, Tallahassee, FL, USA) (Hendrickson et al. 2015; Bahureksa et al. 2022). A total of 100 broadband scans were accumulated per sample. Mass spectral peaks with a minimum signal-to-noise ratio of 6 were exported to peak lists, phase-corrected, and internally calibrated on the basis of a "walking" calibration method (Xian et al. 2010; Savory et al. 2011). Molecular formulae were assigned using PetroOrg software (Corilo 2017) with an iteration table that included $C_{1–100}$, $H_{1–200}$, $O_{1–30}$, $N_{0–4}$, $S_{0–2}$, and $P_{0–1}$ as described previously by McKenna et al. (2024). Assignments with error greater than 0.2 ppm were discarded. The peak intensity of each molecular formula was normalized by the sum peak intensities of the total assigned peaks for that sample (Letourneau and Medeiros 2019; Behnke et al. 2021; Medeiros 2022). Not all compounds present in the DOM are captured by our analysis, as it is limited by the extraction efficiency of the SPE cartridges and by biases in the electrospray ionization (Dittmar et al. 2008; Ohno et al.

2016). In this study, DOM composition refers specifically to the fraction of DOM captured by our approach.

We calculated stoichiometric ratios (e.g., O/C and H/C, where C, H and O are the number of carbon, hydrogen and oxygen atoms in a given molecule, respectively) and indexes such as double bond equivalents (DBE) and aromaticity index (AI^*) (Koch and Dittmar 2006, 2016) to better constrain the chemical characteristics of DOM. Those metrics were used further to categorize all assigned molecular formulae into compound classes as described by Seidel et al. (2014) and Rivas-Ubach et al. (2018). Briefly, molecular formulae were categorized into the following compound classes: polycyclic aromatics (PCAs; $AI^* > 0.66$), highly aromatic compounds (HACs; $0.66 \geq AI^* > 0.50$), highly unsaturated compounds (HUCs; $AI^* \leq 0.50$ and $H/C < 1.5$), unsaturated aliphatic compounds (UAs; $2.0 > H/C \geq 1.5$), saturated compounds (SCs; $H/C \geq 2.0$ or $O/C \geq 0.9$), nitrogen unsaturated aliphatic compounds (NUACs; $2.0 > H/C \geq 1.5$, $N > 0$), (7) lipids ($O/C \leq 0.6$, $H/C \geq 1.32$, $N/C \leq 0.126$, $P/C < 0.35$, $N/P \leq 5$), proteins ($0.6 \geq O/C > 0.12$, $2.5 > H/C > 0.9$, $0.7 \geq N/C \geq 0.126$, $P/C < 0.17$, $N \geq 1$ and $1 \geq O/C > 0.6$, $2.5 > H/C > 1.2$, $0.7 \geq N/C \geq 0.2$, $P/C < 0.17$, $N \geq 1$), and carbohydrates ($O/C \geq 0.8$, $2.7 > H/C \geq 1.65$, $N = 0$). Although this characterization is not unambiguous and there may exist alternative structures for a given molecular formulae, it provides a helpful overview of likely structures behind the identified formulae (Seidel et al. 2014).

Normalized intensities of molecular formulae were also used to calculate indices to assess processes that can transform the DOM pool, such as photodegradation (I_{photo}; more photodegraded DOM holds lower I_{photo} values; Bercovici et al. 2023). Additionally, given the redox gradient found in Mono Lake and the importance of sulfur-containing compounds to this lake's biogeochemistry (e.g., Edwardson and Hollibaugh 2017), we also tracked the distribution of molecular formulae containing S as follows. First, we identified 193 molecular formulae containing S that were present in all lake samples. Next, for each sample, we computed the sum of the intensity of those 193 molecular formulae (Sum*S*). We also computed the sum of the intensity of 40 molecular formulae that were present in all samples and that have been previously identified as being stable and of low terrestrial character (Mar; Medeiros et al. 2016). We then calculated the ratio of the sums of these intensities (Sum*S*/(Sum*S* + Mar)), which we refer to generically as S_{index}. The S_{index} increases with the relative abundance of S-containing DOM. Note that this approach is similar to that used by Knoke et al. (2024) for identifying sulfurized mangrove porewater-derived DOM from an estuary in Amazonia. We chose to use the generic S_{index} here instead of Knoke et al.'s (2024) index (I_{SuP}) because the latter was developed using samples from a mangrove environment, which is characterized by different vegetation than Mono Lake. However, the patterns of variability in Mono Lake data captured by Knoke et al.'s (2024) I_{SuP} index and the S_{index} used here are nearly identical (Supplementary Tables S2 and S3), and the two indices are highly correlated with each other ($r = 0.94$, $p < 0.05$).

We assessed the relative intensity of molecular formulae that are part of the island of stability (IoS; Lechtenfeld et al. 2014), a set of formulae that have been identified previously as being persistent in DOM from diverse aquatic systems, including rivers (Behnke et al. 2021; Kurek et al. 2022), groundwater, freshwater and saline lakes (Kellerman et al. 2018), and the ocean (Lechtenfeld et al. 2014). The relative abundance of compounds that are part of the IoS have been found to be correlated with DOC age in diverse aquatic systems (rivers, lakes, and ocean; Lechtenfeld et al. 2014; Kellerman et al. 2018). There is substantial overlap between these molecular formulae and carboxylic-rich alicyclic molecules (CRAM) (Lechtenfeld et al. 2014; Kurek et al. 2022), which are known to be potentially recalcitrant organic compounds in marine systems (Hertkorn et al. 2006). As summarized by Kurek et al. (2022), FT-ICR MS resolves mixture with thousands of possible isomers for each molecular formulae (Hertkorn et al. 2008), and as such it possible that different compounds contribute to the IoS in Mono Lake compared with other environments. Despite this, comparisons between samples are still useful as DOM formulae from different aquatic systems have been shown to share many structural features (Zark and Dittmar 2018). The range of IoS content for Mono Lake (~ 15–18%; Supplementary Tables S2 and S3) is similar to those reported for several rivers and lakes (~ 14–22%; Kellerman et al. 2018; Kurek et al. 2022).

We also used an index developed by Bercovici et al. (2023) to assess bio-formation and transformation of the DOM pool associated with a natural microbial community of phyto- and bacterioplankton (I_{bio}; larger I_{bio} indicates more bio-formation and transformation). The index was developed using results from a mesocosm experiment studying the natural microbial formation and reworking of DOM using artificial seawater and a coastal North Sea water inoculum (Osterholz et al. 2015). The relevance of using this index in Mono Lake is addressed in the discussion section. Lastly, the nominal oxidation state of carbon (NOSC) proposed by LaRowe and Van Cappellen (2011) was calculated and further used to compare Mono Lake DOM composition with other aquatic systems.

Statistical analyses

The patterns of variability in DOM composition in our samples were investigated using principal component analysis (PCA) of the FT-ICR MS data, as in Refs. 65 and 39. Prior to PCA, FT-ICR MS data were normalized by the standard

deviation between samples and mean centered. Normalized peak intensities of all assigned molecular formulae were used to compute the PCA. All components reported here are statistically significant at the 95% confidence level (Overland and Preisendorfer 1982). Parameters that could be driving changes in DOM composition were fit to PC ordinations post hoc using a linear model (Lechtenfeld et al. 2014; Pan et al. 2023), which is a simplification since relationships may be nonlinear. Bray–Curtis dissimilarity analyses were computed on FT-ICR MS normalized intensities to provide an additional measure of molecular differences between Mono Lake DOM samples. We note that we have also used principal coordinate analysis (PCoA) based on Bray–Curtis dissimilarity matrices to describe relationships among samples (e.g., Osterholz et al. 2016; Knoke et al. 2024), and results were quantitatively similar to those shown here for the principal component analysis (see "Discussion").

Results

DOC concentration and molecular composition of DOM in Rush Creek and Lee Vining Creek and in a *Picocystis* sp. culture

We analyzed the DOM composition of three contributors to the DOM pool in Mono Lake: autochthonous production by *Picocystis* sp., and DOM present in Rush Creek and Lee Vining Creek. Rush Creek and Lee Vining Creek contribute substantially to total runoff to Mono Lake (LADWP 1995) and had DOC concentrations of 91 ± 1 µM and 39 ± 2 µM during our sampling, respectively (Supplementary Table S1). The DOC concentration in the *Picocystis* sp. culture was 963 ± 2 µM (Supplementary Table S1).

A total of 8024 molecular formulae were assigned to *Picocystis* sp. DOM, while 8150 and 5709 molecular formulae were assigned to Rush Creek and Lee Vining Creek DOM, respectively, after FT-ICR MS analysis. Variability patterns in DOM composition were captured by principal component analysis (PCA) of FT-ICR MS data with assigned formulae, which included Mono Lake samples ($n = 30$), *Picocystis* sp. culture ($n = 1$), and creek samples (Lee Vining and Rush Creeks; $n = 2$). The analysis separated these samples into three groups (Fig. 2a). The dominant principal component (PC1) explained ~ 41% of the total variance of FT-ICR MS data. High positive values in PC1 were associated with Lee Vining Creek and Rush Creek samples (orange dots in Fig. 2a). The two samples were located close together in PC space, indicating that they had similar DOM composition. These samples were relatively enriched with molecular formulae with low to medium H/C ratios (H/C < 1.5; red dots in Fig. 2b), showing a pattern typical of terrestrial DOM signature (Sleighter and Hatcher 2008; Medeiros et al. 2015b). Most of the molecular formulae enriched in the creek samples contained C, H, and O atoms only (CHO, ~ 69%), with most being categorized as highly unsaturated (HUCs: ~ 79%), highly aromatic (HACs: ~ 17%), and polycyclic aromatic compounds (PCAs: ~ 3%) (orange bars in Supplementary Fig. S2c, d). Contrastingly, *Picocystis* sp. extract was associated with high positive values in PC2 (green dot in Fig. 2a), which explained 10% of the total variance of FT-ICR MS data. Compared with Mono Lake and creek samples, the *Picocystis* sp. extract was relatively enriched with N- (CHON: ~ 41%) and S-containing formulae (CHOS and CHONS: ~ 11%), with most molecular formulae being categorized as highly unsaturated (HUCs: ~ 62%) and unsaturated aliphatics (without or with nitrogen; UAs and NUAs: ~ 29%) and protein-like compounds (~ 8%) (green bars in Supplementary Fig. S2c and S2d, e). This molecular composition is broadly consistent with freshwater phytoplankton-derived DOM (Bittar et al. 2015).

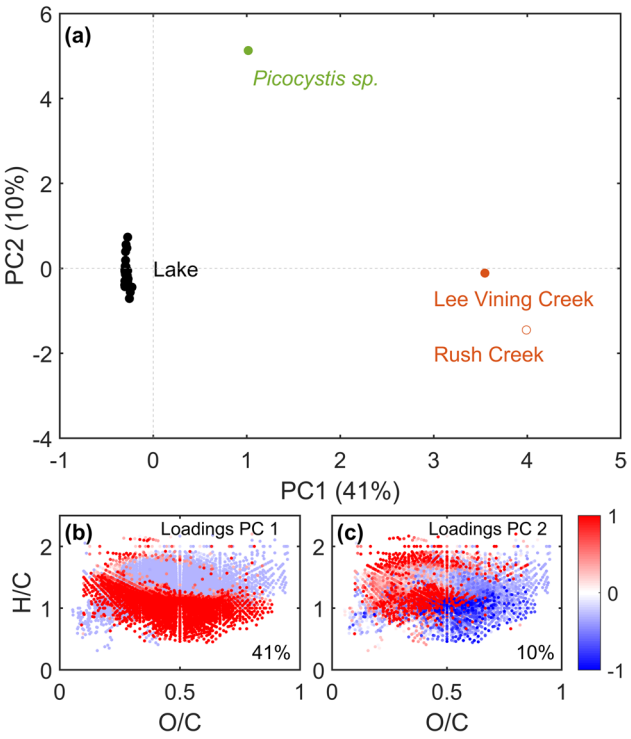

Fig. 2 **a** Principal component analysis of DOM composition based on > 13,000 molecular formulae found in Mono Lake, *Picocystis* sp., Rush Creek and Lee Vining Creek. van Krevelen diagrams with loadings of **b** PC1 and **c** PC2 are also shown

Variability patterns in DOC concentration and DOM composition within Mono Lake

PC analysis performed with FT-ICR MS data from lake samples, creeks, and *Picocystis* sp. clearly separated samples into three clusters, allowing us to distinguish DOM

composition of the lake from that of the contributors (Fig. 2a). To address changes in DOM composition within the lake, additional PCA analyses were performed considering only lake samples (i.e., without considering samples from the creeks or from the *Picocystis* sp. culture). Analyses were pursued independently for 2017 and 2018, and patterns of variability are described in detail in "Monomictic conditions (2017)" and "Meromictic conditions (2018)" sections, respectively.

Monomictic conditions (2017)

Density profiles showed the seasonal development of a shallow pycnocline from summer to fall in 2017 (Fig. 3a–c). A shallow oxycline was also developed, with low dissolved oxygen being observed below 3–5 m in summer and fall (Fig. S1a). DOC concentrations varied substantially among seasons and throughout the water column, ranging from approximately 8100 to 21,300 µM (Fig. 3a–c; Table S1), which is on the same order of DOC concentration previously reported at Mono Lake (Domagalski et al. 1989; Humayoun et al. 2003) and in other saline lakes (Butturini et al. 2020, 2022). Highest concentrations were found during spring (average of 15,400 µM) and summer of 2017 (average of 13,300 µM) (Fig. 3a, b) and were up to twofold greater at some depths than during the fall, when DOC concentrations varied less with depth (ranging from ~ 8100 to ~ 10,000 µM; Fig. 3c). In all seasons, the largest DOC concentrations were observed between 15 and 20 m.

Temporal and vertical changes in DOM composition in the lake in 2017 were identified by PCA and Bray–Curtis dissimilarity analysis using the FT-ICR MS-derived dataset. Samples tended to spread along both PC1 and PC2 axes and showed a clear separation between spring and summer relative to fall samples (Fig. 4a). While samples from fall 2017 were characterized by negative PC1 and PC2 scores, samples from spring and summer were characterized by either positive PC1 or PC2 scores, or both. PC1 captured a pattern of variability in which samples with positive PC1 scores (i.e., all samples from spring and those from 10, 20, and 27 m depth in summer) were relatively enriched in molecular formulae with low O/C ratios (O/C < 0.5, red dots in Fig. 4b). These molecular formulae were dominated by N-containing formulae (CHON, ~ 57%; red bars in Fig. 4c) and high proportions of highly unsaturated (HUCs), unsaturated aliphatic (UAs), and nitrogen-containing unsaturated aliphatic (NUAs) compounds (Fig. 4d). Lipid- and protein-like compounds accounted for ~ 8% of the formulae with positive PC1 loadings (Fig. 4e). Samples with negative PC1 scores (primarily samples collected during fall), on the other hand, were relatively enriched with formulae with negative PC1 loadings (blue dots in Fig. 4b). These were characterized by comparatively higher contributions of S-containing formulae (CHOS = ~ 17% and CHONS = ~ 9%) (blue bars in Fig. 4c). Additionally, these formulae had lower proportions of N-containing formulae (CHON: ~ 45%) and unsaturated aliphatic compounds (UAs: ~ 6% and NUAs: ~ 3%) compared with those with positive loadings.

The analysis also revealed a second mode of variability that was statistically significant. Most summer and a few spring samples (20 m and 30 m) clustered at regions associated with positive values of PC2 (Fig. 4a), capturing a pattern of relative enrichment of formulae with positive PC2 loadings (Fig. 4f). Most of these formulae contained N and/or S (red bars in Fig. 4g), and they were primarily highly unsaturated (HUCs) and unsaturated aliphatics (UAs and NUAs; ~ 62% and ~ 30%, respectively, Fig. 4h). These samples were also relatively enriched in P-containing formulae (CHOP; red bars in Fig. 4g). In contrast, fall 2017 samples and a few samples from spring (10 m and 25 m) and summer (20 m) of 2017 presented negative values in PC2. The mode captured a relative enrichment in formulae with negative PC2 loadings (Fig. 4f). Most of these formulae contained N (~ 55%; blue bars in Fig. 4g), being primarily highly unsaturated compounds (HUCs: ~ 74%; Fig. 4h). A smaller fraction of the molecular formulae that were enriched in fall samples were categorized as unsaturated aliphatic compounds (UAs and NUAs) compared with the formulae enriched in most samples collected in spring and fall (Fig. 4h).

Bray–Curtis dissimilarity analysis was used as a complementary tool to PCA analysis, providing a quantitative assessment of dissimilarity in DOM molecular composition in the lake. This analysis revealed a high degree of dissimilarity between spring and fall samples (up to 61%, Supplementary Fig. S3a). Summer samples that were associated with negative values of PC1 (0.5 m and 15 m; Fig. 4a) showed high dissimilarity values to spring samples (up to 55%; Supplementary Fig. S3a). Similar to our PCA analysis, molecular dissimilarities within seasons were also observed in the Bray–Curtis analysis. For instance, fall samples collected at 15 m and 20 m had similar PC scores (Fig. 4a), which indicates that DOM is molecularly similar, and had the lowest degree of dissimilarity (25%, Supplementary Fig. S3a). Those samples were distant from the fall sample collected at 18 m in principal component space, and they had the highest degree of dissimilarity within all fall samples (37% and 39%, respectively; Supplementary Fig. S3a).

We calculated several DOM indices for each sample to assess potential processes behind temporal and vertical differences in DOM composition. To obtain a measure of the relative contribution of *Picocystis* sp. and creek-derived DOM, we computed the sum of the intensity of all formulae characteristic of those sources (Supplementary Fig. S2) and divided by the sum of the intensity of all molecular formulae assigned for each sample and multiplied by 100, yielding a percentage. We also computed the relative importance of

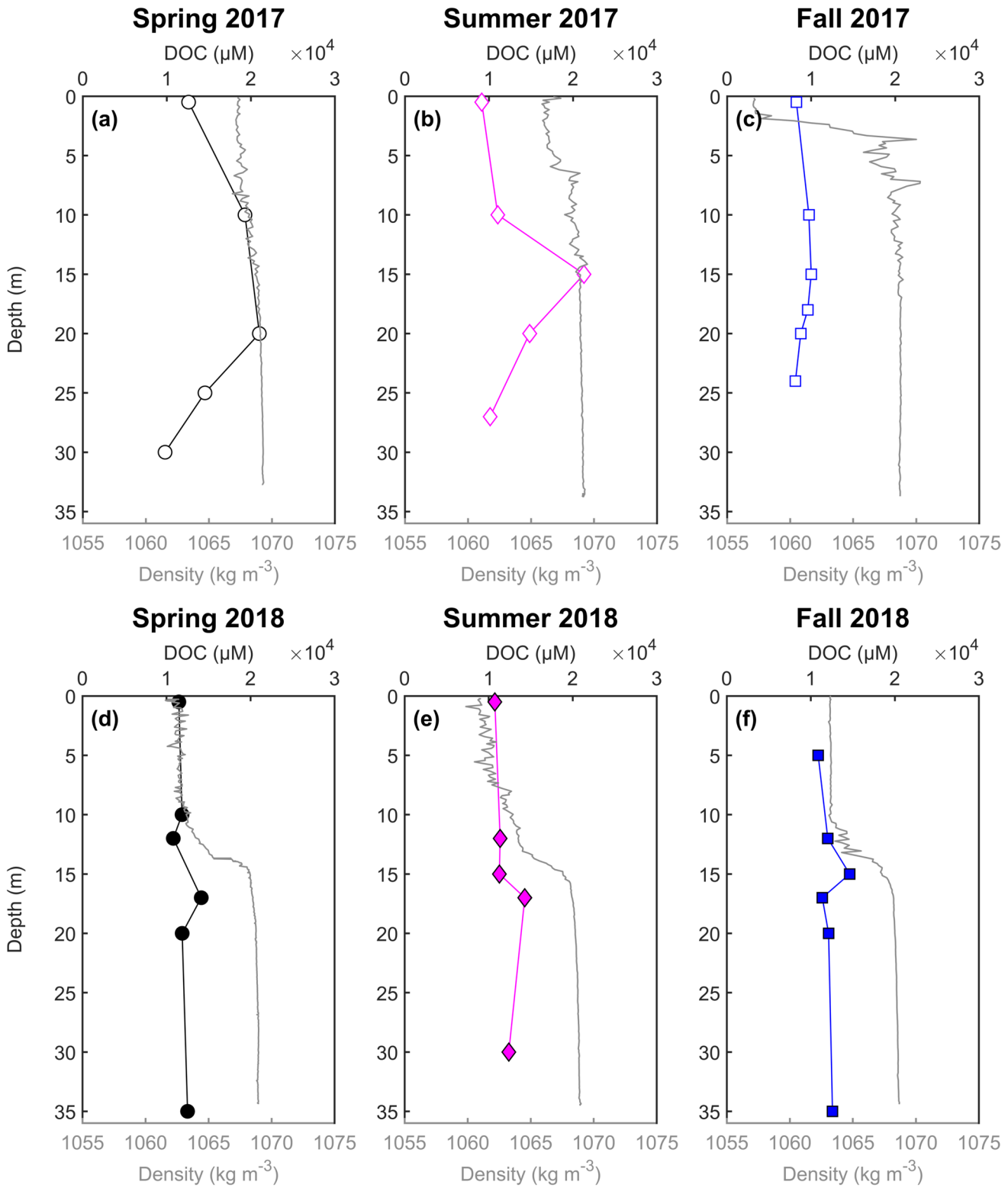

Fig. 3 Vertical distribution of DOC concentration at Station 6 during spring, summer, and fall of 2017 (**a**–**c**) and 2018 (**d**–**f**). Density data were calculated on the basis of in situ measurements of salinity and temperature at the time of sampling, which are publicly available from the US Geological Survey data repository (https://catalog.data.gov/dataset/a-two-year-water-column-time-series-of-geochemical-data-during-a-limnological-shift-i-2017)

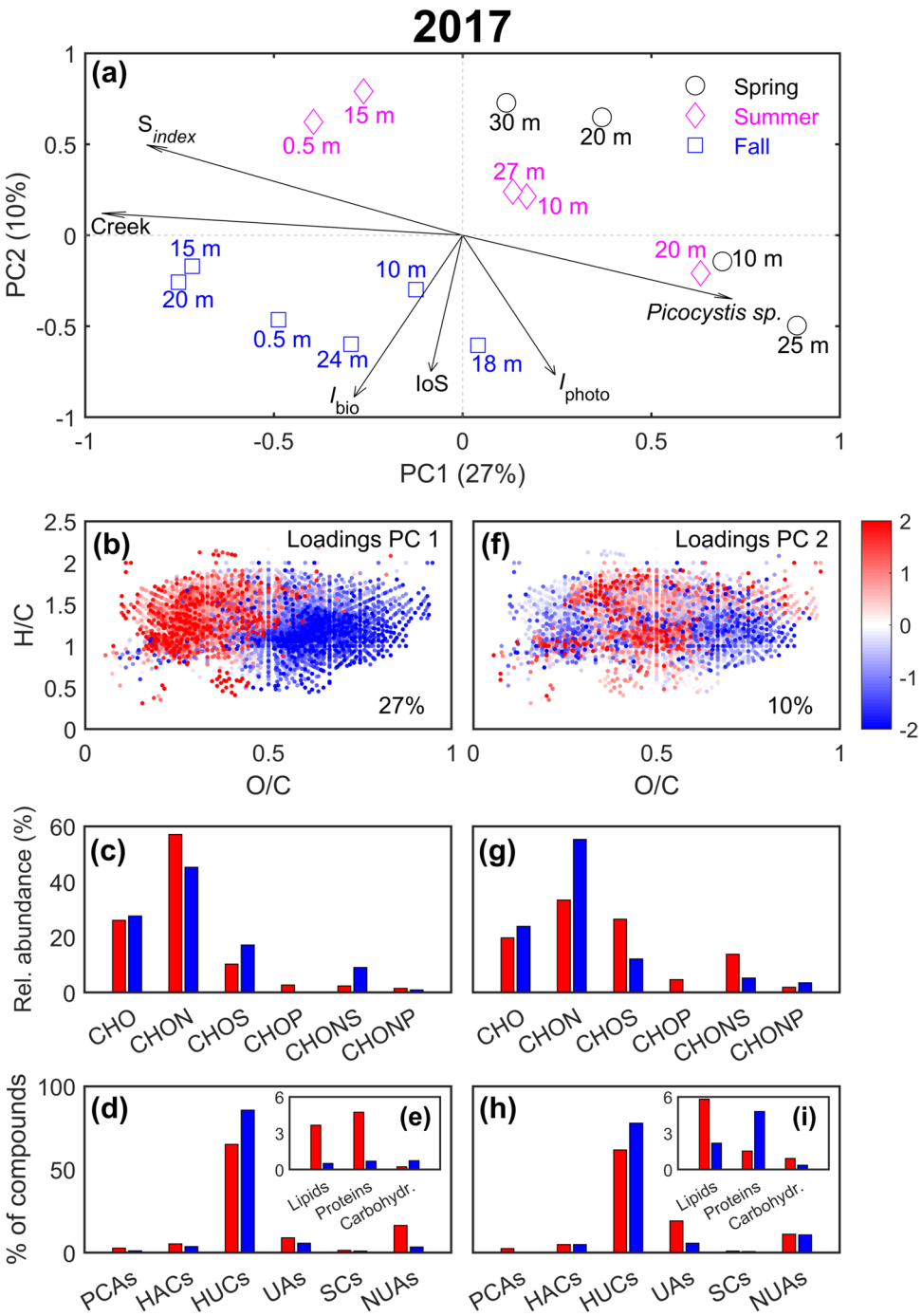

Fig. 4 **a** Principal component analysis of DOM composition for samples collected during spring, summer, and fall 2017. Indices (black vectors) were fit post hoc to the scores of the PCA. **b** van Krevelen diagram color coded with PC1 loadings. **c–e** Chemical characteristics and major compound classes of molecular formulae with positive (red) and negative (blue) PC1 loadings. **f** van Krevelen diagram color coded with PC2 loadings. **g–i** Chemical characteristics and major compound classes of molecular formulae with positive (red) and negative (blue) PC2 loadings. *PCAs* polycyclic aromatics, *HACs* highly aromatic compounds, *HUCs* highly unsaturated compounds, *UAs* unsaturated aliphatics, *SCs* saturated compounds, *NUAs* N-containing unsaturated aliphatic compounds

sulfur-containing compounds (S_{index}), process-specific indices (I_{photo} and I_{bio}), and the contribution of IoS compounds. Overall, the relative contribution of formulae enriched in the *Picocystis* sp. culture ranged from 0.4% to 2.3% of total intensity and was generally higher at depth (Fig. 5a; Supplementary Table S2). The highest contributions of *Picocystis* sp. formulae were detected during spring and during summer at depth. These contributions were significantly correlated with the dominant principal component (Fig. 4a). Vertical profiles of the relative contribution of creek-derived DOM approximately mirrored the contribution of *Picocystis* sp. (Fig. 5b) and were negatively correlated with PC1 (Fig. 4a). S_{index} indicated a pattern of a larger influence of sulfur-containing compounds at some depths during fall and summer, and a smaller influence during spring (Fig. 4a). All fall samples were also associated with a larger contribution of IoS compounds. Most summer and a few spring samples were associated with smaller I_{photo}, while I_{bio} was increased in fall samples. Thus, photodegradation, bio-formation and transformation, and the relative contribution of stable compounds

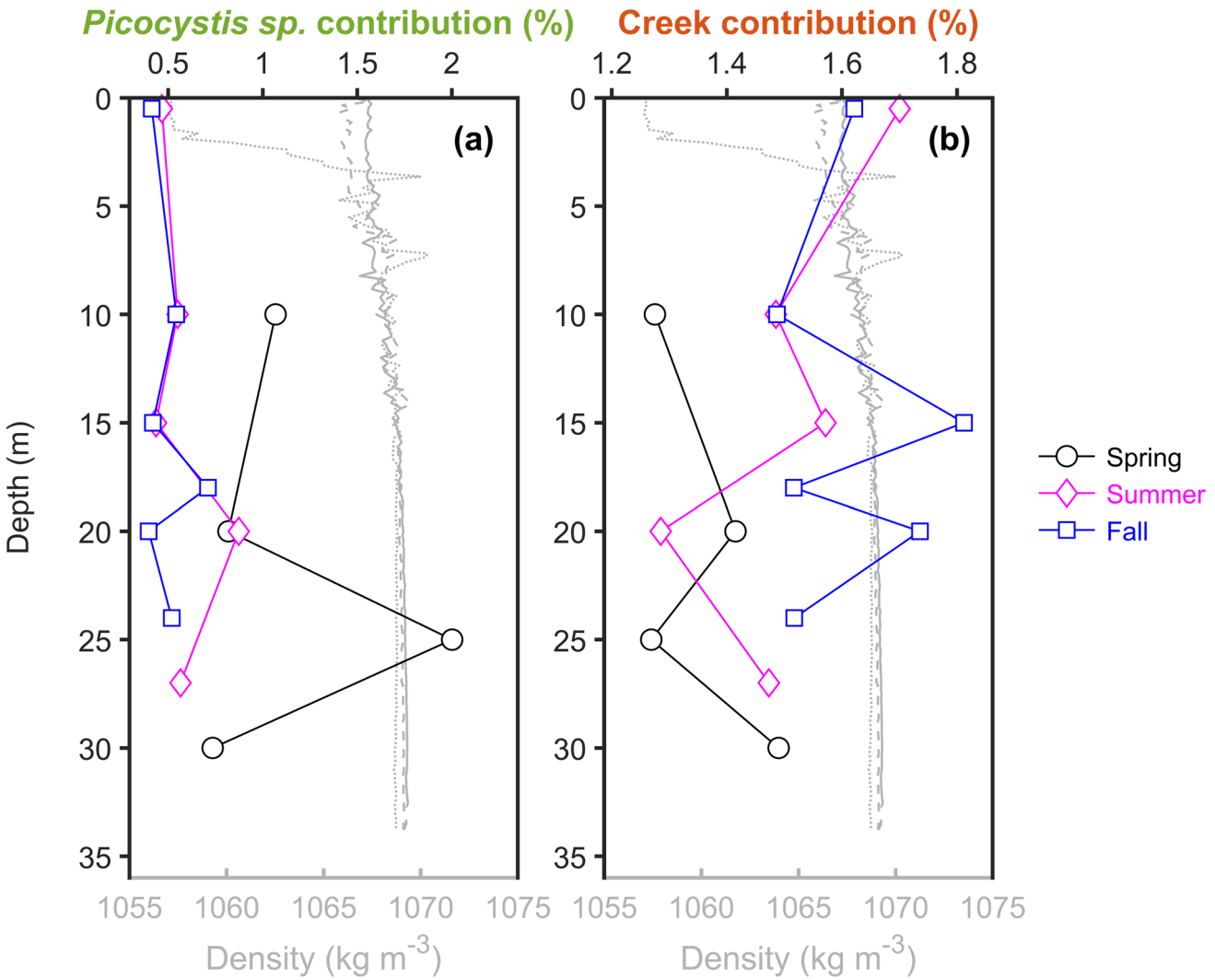

Fig. 5 Vertical profiles of contributions of **a** *Picocystis* sp. and **b** creek-derived organic matter to the DOM pool for samples collected during 2017. Dashed, solid, and dotted lines (in grey) represent the density profiles for spring, summer, and fall seasons, respectively. Near-surface stratification was only observed during fall. Density data were calculated on the basis of in situ measurements of salinity and temperature at the time of sampling, which are publicly available from the US Geological Survey data repository (https://catalog.data.gov/dataset/a-two-year-water-column-time-series-of-geochemical-data-during-a-limnological-shift-i-2017)

may have contributed to changes in DOM composition in the lake.

Meromictic conditions (2018)

A pycnocline, centered at around 12–14 m (Fig. 3d–f), was observed in all seasons during 2018. An oxycline was also observed at a slightly shallower depth (Fig S1b). DOC concentration varied less between seasons under meromictic conditions when compared with monomictic conditions, averaging ~ 12,000 µM (Table S1). In all seasons, DOC concentrations increased immediately below the pycnocline, with highest concentrations between 15 and 17 m (ranging from ~ 14,100 to ~ 14,600 µM; Fig. 3d–f; Table S1).

The changes in DOC concentration in the lake were accompanied by changes in DOM composition (Fig. 6a). The highest positive PC1 scores were observed in surface and bottom waters during spring, near the surface during summer, and at 17 m during fall. The mode captured a pattern where molecular formulae relatively enriched in those samples (shown in red in Fig. 6b) generally contained N (CHON: ~ 62%) and were categorized as highly unsaturated (HUCs: ~ 63%) and unsaturated aliphatics compounds (UAs and NUAs: ~ 31%) and included significant contributions of protein-like (~ 8%) and lipid-like compounds (~ 3%) (Fig. 6c–e). In all seasons, the lowest PC1 values were found in samples collected immediately below the pycnocline (~ 15–17 m; Fig. 6a), indicating that these samples were

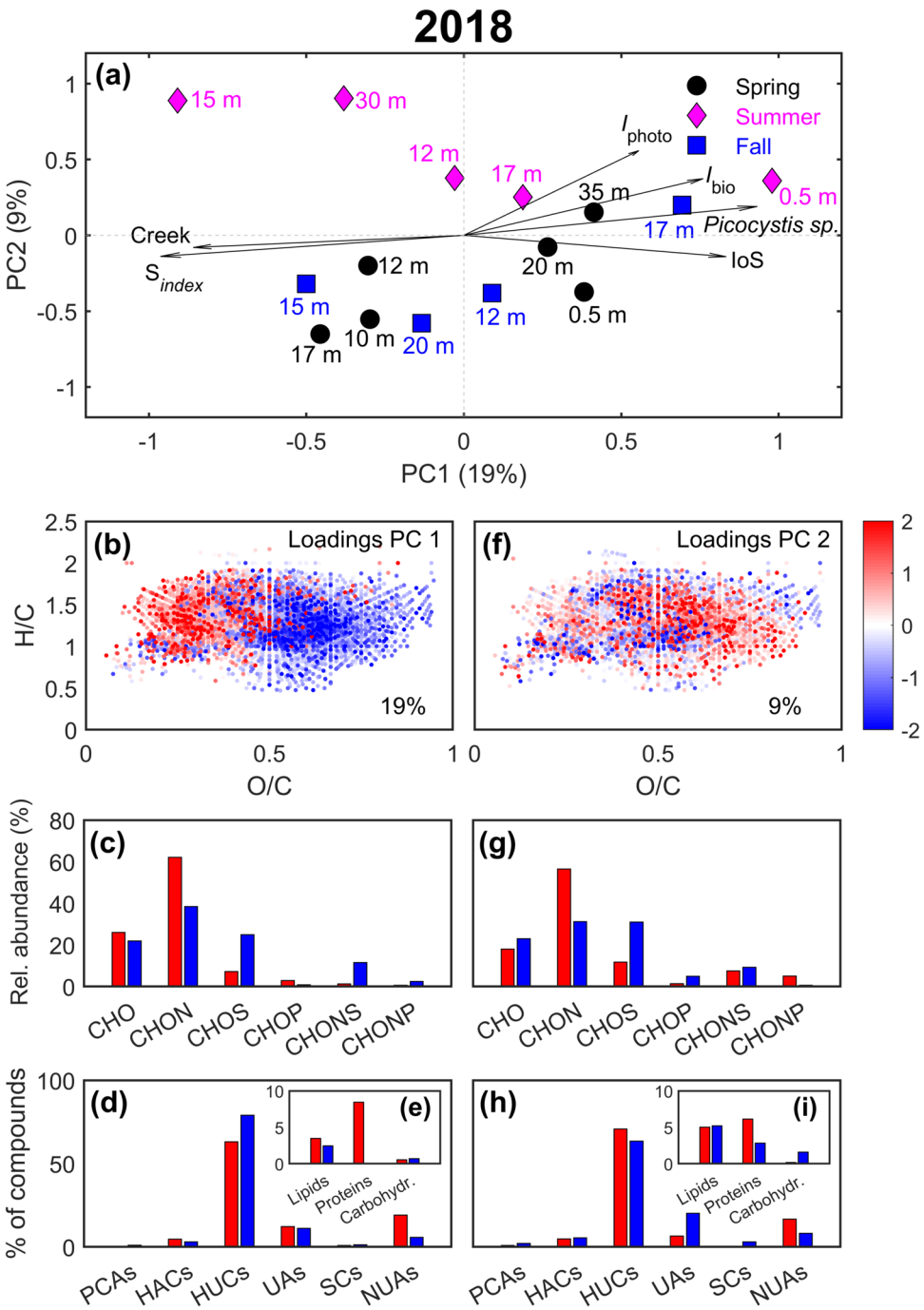

Fig. 6 **a** Principal component analysis of DOM composition for samples collected during spring, summer, and fall 2018. Indices (black vectors) were fit post hoc to the scores of the PCA. **b** van Krevelen diagram color coded with PC1 loadings. **c–e** Chemical characteristics and major compound classes of molecular formulae with positive (red) and negative (blue) PC1 loadings. **f** van Krevelen diagram color coded with PC2 loadings. **g–i** Chemical characteristics and major compound classes of molecular formulae with positive (red) and negative (blue) PC2 loadings. *PCAs* polycyclic aromatics, *HACs* highly aromatic compounds, *HUCs* highly unsaturated compounds, *UAs* unsaturated aliphatics, *SCs* saturated compounds, *NUAs* N-containing unsaturated aliphatic compounds

relatively enriched in S-containing formulae (CHOS and CHONS: ~ 36%; Fig. 6c).

Differences in DOM composition between the profiles collected in different seasons were captured by PC2. This principal component separated samples collected in summer from those collected during spring and fall (Fig. 6a). Summer samples were associated with positive values in PC2, with a pattern of relative enrichment in N-containing formulae (CHON and CHONP: ~ 61%), higher contributions of highly unsaturated (HUCs: ~ 71%), unsaturated aliphatic compounds (UAs and NUAs: ~ 23%), as well as lipids- (~ 5%) and protein-like (~ 6%) compounds (red bars in Fig. 6g–i). Contrastingly, most samples collected during spring and fall were associated with negative values of PC2 and thus they were relatively enriched in formulae with negative PC2 loadings (Fig. 6f). Compared with the formulae enriched during summer, the mode captured a pattern where those enriched during spring and fall had more S and P (CHOS and CHOP: ~ 36%; blue bars in

Fig. 6g) and had slightly higher proportions of unsaturated aliphatic (UAs: ~ 28%; blue bars in Fig. 6h).

Molecular dissimilarities in DOM composition assessed via Bray–Curtis analysis revealed high degree of dissimilarity within summer samples. During this season, the highest degree of dissimilarity was observed between surface waters and the sample collected at 15 m (56%; Supplementary Fig. S3b). These samples had the largest difference in PC1 scores (Fig. 6a). The sample collected in surface waters during summer 2018 was also compositionally different when compared with spring and fall 2018, with degree of dissimilarity up to 51% for both season (Supplementary Fig. S3b).

We also investigated the contributions of DOM sources and processes to better understand the potential mechanisms responsible for shaping the DOM pool in Mono Lake during prolonged stratification. Samples collected during spring 2018 had slightly increased contributions of *Picocystis* sp. at the surface and near the bottom, with a local minimum near the pycnocline, although vertical variations were quite small (Fig. 7a). The highest contribution of *Picocystis* sp. formulae during summer was observed near the surface. Contributions from creek-derived DOM were generally higher just above the pycnocline (Fig. 7b). The contributions of both *Picocystis* sp. and creek-derived DOM were significantly correlated with PC1 scores (Fig. 6a). PC1 scores were also significantly correlated with process-specific indices (I_{photo} and I_{bio}), abundance of sulfur-containing compounds (S_{index}), and the contribution of IoS compounds, suggesting that variations in DOM composition in the water column was associated with DOM sources and cycling. In all seasons, S_{index} was generally higher near the pycnocline (Fig. 6a; Supplementary Table S3).

Discussion

To investigate changes in DOC concentration and DOM composition in Mono Lake, samples were collected at multiple depths along a vertical profile in spring, summer, and fall of 2017 and 2018. We also analyzed samples from two creeks that contribute to the total runoff to the lake, and from a culture of *Picocystis* sp. strain ML, an important phytoplankton species in Mono Lake (Winkler 1977; Jellison and Melack 1993a, b). Given that a single profile was collected during each season, our sampling cannot fully resolve seasonal variability, as observations may have been influenced by short-term variability. Additionally, our creek sampling cannot capture temporal variability in DOM composition, since a single sample was collected in each creek.

Mono Lake was characterized by nearly vertical, homogeneous density in spring and summer 2017, with the establishment of a shallow pycnocline and oxycline by fall 2017. In contrast, a pycnocline centered around 12–14 m was observed for all profiles collected in 2018. Our results showed that changes in limnological conditions were accompanied by changes in DOC concentration in Mono Lake.

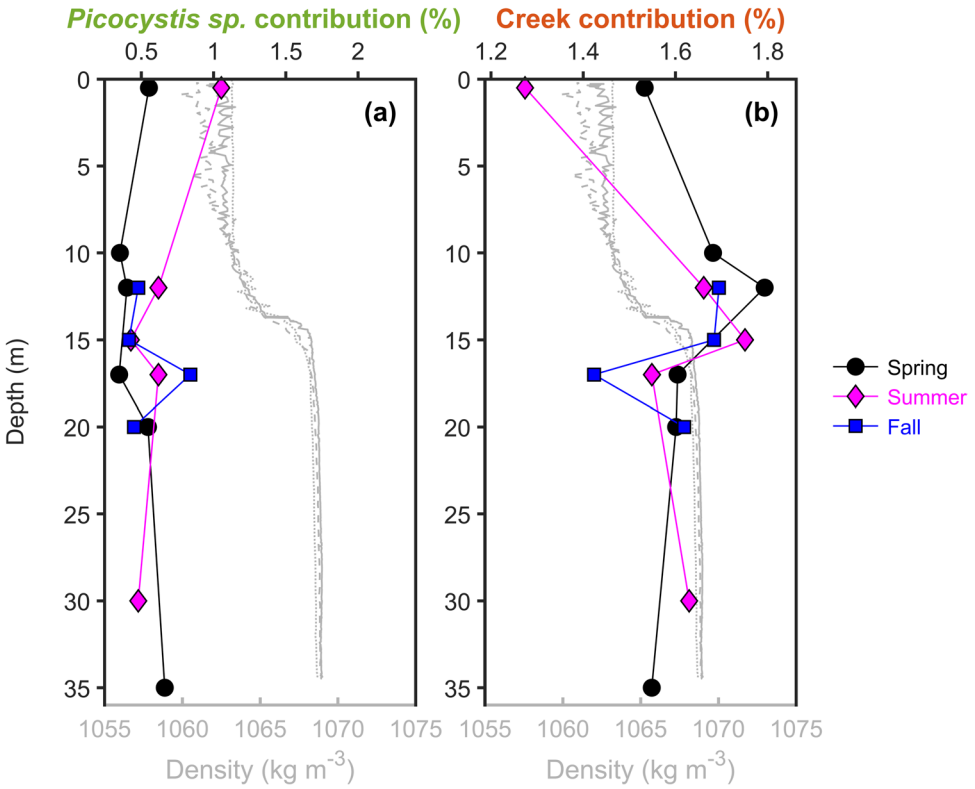

Fig. 7 Vertical profiles of contributions of **a** *Picocystis* sp. and **b** creek-derived organic matter to the DOM pool for samples collected during 2018. Dashed, solid, and dotted lines (in grey) represent the density profiles for spring, summer, and fall seasons, respectively. Density data were calculated on the basis of in situ measurements of salinity and temperature at the time of sampling, which are publicly available from the US Geological Survey data repository (https://catalog.data.gov/dataset/a-two-year-water-column-time-series-of-geochemical-data-during-a-limnological-shift-i-2017)

Highest DOC concentrations were observed in spring and summer of 2017, a time usually characterized by maximal abundance of phytoplankton and high snowmelt runoff from the Sierra Nevada (Melack et al. 2017). Snow water content in the Mono Lake Basin was substantially higher in 2017 compared with 2018 (Supplementary Fig. S4). Compared with samples collected in 2018, DOC concentrations at mid-depth were twofold higher in spring and summer of 2017. Phillips et al. (2021) hypothesized that differences in DOC concentration between 2017 and 2018 could be associated with increased grazing pressure from *Artemia* (brine shrimp) on the phytoplankton community during spring 2018, resulting in less DOC production through algae lysis. In 2018, DOC concentrations changed little between sampling, and slightly increased DOC concentrations were found immediately below the pycnocline (Fig. 3d–f). This vertical distribution is consistent with previous studies, which have found peaks in DOC concentrations around the same depth (~ 15 m) during meromictic conditions (Domagalski et al. 1989). In the water column, these high concentrations of DOC reported by Domagalski et al. (1989) (> 7000 mM) were attributed to hydrolysis of algal debris, potentially associated with high-pH waters. Increased chlorophyll-*a* concentrations were also observed at and below the pycnocline in 2018 (LADWP 2018, 2019; Phillips et al. 2021).

Patterns of variability in DOM composition were assessed via principal component analysis. We also pursued principal coordinate analysis (PCoA) based on Bray–Curtis dissimilarity matrices, and results were quantitatively similar to those shown here (Supplementary Fig. S5). Patterns were compared with multiple indices indicative of biogeochemical processes, including bio-formation and transformation of DOM, photodegradation, and relative contributions of sulfur-containing, creek-derived, *Picocystis* sp.-derived, and very stable compounds. Although the comparison is not independent, since those indices were developed using the FT-ICR MS data, they allowed for assessing processes that may have contributed to the observed variability (as in Lechtenfeld et al. 2014).

Our analyses revealed that significant changes in DOM composition occurred between seasons in 2017. Most spring and some summer DOM samples were characterized by higher contributions of *Picocystis* sp. DOM compared with fall, especially at depth (Fig. 5a). Additionally, most of the formulae enriched in samples from spring and several summer samples contained N and were categorized as highly unsaturated (HUCs) or unsaturated aliphatic compounds (UAs and NUAs), which have been shown to be a major fraction of phytoplankton exudates (e.g., Bittar et al. 2015). These are consistent with phytoplankton blooms playing a key role shaping the DOM composition during spring and summer, a time when maximum abundance of phytoplankton and highest snowmelt runoff from the Sierra Nevada are generally observed (Melack et al. 2017). Compared with samples collected in spring, fall samples were generally characterized by lower contributions of *Picocystis* sp. compounds (Fig. 5a), possibly indicating a decrease in phytoplankton-derived DOM. At the same time, an increase in creek-derived compounds was observed from spring to fall 2017 (Figs. 4a, 5b), suggesting a larger relative contribution of terrestrial DOM at the time of our fall sampling. A clear terrestrial signature was also imprinted in the particulate fraction during fall 2017, with the presence of long-chain terrestrially sourced saturated fatty acids (C_{21}–C_{30}; Phillips et al. 2021). The increase in the relative contribution of creek-derived DOM during fall can be related to increased terrestrial input, but also to the relative reduction in the contribution of *Picocystis* sp. DOM.

In addition to variations in *Picocystis* sp. and terrestrial inputs, other processes also likely contributed to changes in the composition of the DOM pool in the lake in 2017. Many fall and some summer samples had high contributions of S-containing compounds (Fig. 4a). High relative intensity of S-containing formulae has been associated with anaerobic sulfate reduction and abiotic sulfurization of DOM in freshwater systems and saline lakes (Poulin et al. 2017; Butturini et al. 2020; Jiang et al. 2022; Xu et al. 2022). Contribution of both sulfate reduction and sulfurization processes to the DOM pool is consistent with depletion of O_2 and presence of putative sulfate-reducing microorganisms observed at the same sampling time (Phillips et al. 2021). Many samples collected in spring and summer 2017 presented lower I_{photo} values (Fig. 4a), suggesting the presence of more photodegraded DOM (Bercovici et al. 2023). Fall samples were characterized by a higher contribution of very stable compounds (IoS) compared with samples collected earlier in the year. The time scale associated with the accumulation of IoS compounds is much longer than that of our sampling (Lechtenfeld et al. 2014; Kellerman et al. 2018), and thus variability in its relative contribution here is likely related to variability in inputs or in the relative abundance of other fractions of the DOM pool. For example, the relative contribution of *Picocystis* sp. DOM was larger during spring (Fig. 5a). As the relative abundance of that fraction decreased toward fall, the relative abundance of other fractions would increase, including that of IoS compounds.

Microbial processing is expected to play an important role shaping DOM composition in Mono Lake (Hollibaugh et al. 2001; Humayoun et al. 2003; Jørgensen et al. 2008). Samples collected during fall 2017 generally had higher I_{bio} values, suggesting a higher contribution of bio-formation and transformation. A possible explanation for that increase is that DOM is transformed throughout the seasons by microbial degradation resulting in the accumulation of bio-transformed material later in the year. The temporal resolution of our sampling did not allow for documenting the details

of such progression. Also, we note that the I_{bio} index was developed using a microbial inoculum with coastal water from the North Sea, which has very different microbial communities compared with Mono Lake (e.g., Humayoun et al. 2003; Osterholz et al. 2015; Phillips et al. 2021). Thus, it is also likely that the direct influence of *Picocystis* sp.-derived inputs on DOM composition was not captured by the index. Indeed, none of the formulae identified here as indicative of *Picocystis* sp.-derived DOM (Supplementary Fig. S2b) match the formulae identified by Bercovici et al. (2023) as indicative of bio-formation and transformation. Thus, the index almost certainly underestimates bio-formation early in the season, when the influence of *Picocystis* sp. DOM was larger. Despite this, we chose to report I_{bio} values here because they are significantly correlated with PC2 scores, suggesting that the index does provide useful information about changes in DOM composition in the system. It is possible that, as the organic material is processed by microbes over the seasons and transformed into other compounds, the microbial signal in the resulting DOM may become detectable by the index. Future studies pursuing biodegradation experiments in the dark could test this idea, identifying if compounds targeted by Bercovici et al. (2023) are indeed produced as a result of biodegradation of *Picocystis* sp.-derived DOM. If so, then the index can be used to provide information about microbial processing of DOM in Mono Lake. Using a similar approach to that used by Bercovici et al. (2023), the index could also be modified (or an alternative index could be developed) to include other formulae that better capture the influence of *Picocystis* sp.-derived DOM in Mono Lake.

Similar to 2017, the dominant mode of variability in DOM composition during meromictic conditions in 2018 also seems to be influenced by gradients of DOM sources from terrestrial (creeks) versus phytoplankton-derived (*Picocystis* sp.). However, this mode of variability captured changes in DOM composition with depth, instead of between sampling periods. For all seasons, samples collected at or immediately below the pycnocline (17 m in spring, 15 m in summer and fall), where O_2 was depleted (Supplementary Fig. S1b), were characterized by higher proportions of S-containing formulae and high S_{index} values (Fig. 6a, c; Supplementary Table S3). Phillips et al. (2021) reported increased concentrations of sulfide from spring to fall 2018 below the pycnocline, indicating occurrence of sulfate reduction presumably due to oxygen depletion. This is consistent with previous studies that have reported sulfide accumulation during prolonged anoxia (e.g., Oremland et al. 2004; Hollibaugh et al. 2005). As previously mentioned, anoxic conditions favor anaerobic metabolism of microbial communities and DOM sulfurization, resulting in higher proportions of S-containing molecular formulae (Gomez-Saez et al. 2021). PC1 was significantly correlated positively with I_{bio} (Fig. 6a). This is surprising, because the mode was also positively correlated with the contribution of *Picocystis* sp. DOM which, as discussed previously, most likely is not entirely captured by I_{bio}.

During meromictic conditions in 2018, DOM composition during spring and fall tended to group together in the PC decomposition (second component) and were separated from samples from summer (Fig. 6a). Interestingly, samples collected in summer 2018 were enriched in N-containing formulae, N-containing unsaturated aliphatic, and protein-like compounds (Fig. 6g–i), resembling phytoplankton-derived DOM (Landa et al. 2014; Bittar et al. 2015). Although the pattern of variability captured by PC2 was not significantly correlated to the contribution of *Picocystis* sp. DOM, the DOM composition in summer 2018 could still be associated with primary producers. Like most saline lakes, Mono Lake experiences cyanobacteria blooms, which are usually observed during summer and fall as a response to nutrient depletion following prolonged stratification (Budinoff and Hollibaugh 2007; Phillips et al. 2021). It has been reported that cyanobacteria DOM is mainly composed of N-containing molecular formulae, with substantial amounts of protein-like compounds being produced under N-limitation conditions (Bittar et al. 2015). An increase in the abundance of cyanobacteria was reported by Phillips et al. (2021) from spring to fall 2018; thus, summer DOM might have been influenced by cyanobacteria inputs. Unfortunately, no culture of cyanobacteria was available for analysis to identify their potential contribution to DOM composition.

It is useful to compare DOM composition in Mono Lake with the composition of DOM from other aquatic environments. Butturini et al. (2020, 2022) compared the degree of aromaticity (as quantified by an aromaticity index, AImod; Koch and Dittmar 2016) and the nominal oxidation state of carbon (NOSC; LaRowe and Van Cappellen 2011) of individual samples from freshwater ecosystems and from a few hypersaline endorheic lakes, and showed that the saline lakes tended to be much less aromatic on average. Adding Mono Lake observations to the comparison reveal that this is also true for Mono Lake, with the DOM being even less aromatic than in other saline lakes and in the ocean (Fig. 8), independently of the season or mixing/thermal state. Mono Lake DOM was also found to be quite reduced in comparison with some other saline lakes (Butturini et al. 2020).

Lastly, using samples collected at the same location and time as those analyzed here, Phillips et al. (2021) showed that POC concentrations in Mono Lake generally increased with depth. Stable isotopic signature (δ^{13}C-POC) and fatty acids composition of POC revealed a depleted δ^{13}C-signature (−32.2‰ to −30.2‰) accompanied by high relative contributions of short-chain saturated ($C_{14:0}$–$C_{20:0}$) and unsaturated ($C_{16:1}$–$C_{18:1}$) fatty acids, indicating that POC in Mono lake was strongly influenced by *Picocystis* sp. biomass

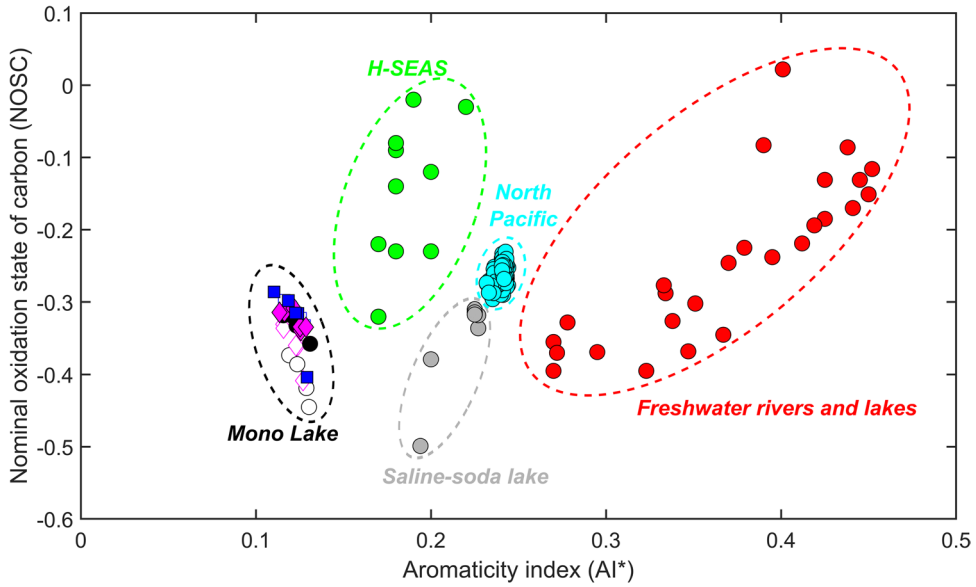

Fig. 8 Relationship between the aromaticity index and the nominal oxidation state of carbon in the northern North Pacific Ocean (cyan; profiles spanning the entire water column; Medeiros et al. 2015a), freshwater rivers and lakes (red; Kellerman et al. 2018), a tropical saline soda lake (gray; Butturini et al. 2020), La Salineta (green; a hypersaline shallow lake in northeast Spain; Butturini et al. 2022), and Mono Lake (black, magenta and blue represent spring, summer and fall, respectively; open symbols are data from 2017, while filled symbols are data from 2018). Samples from Medeiros et al. (2015a) and Butturini et al. (2020, 2022) were extracted using PPL cartridges

(Phillips et al. 2021). That is consistent with our analysis of the dissolved fraction, with many samples enriched in N-containing formulae, unsaturated aliphatics and protein-like compounds, suggesting a DOM pool likely associated with *Picocystis* sp. and possibly cyanobacteria inputs. Phillips et al. (2021) also reported evidence of terrestrial inputs (e.g., C_{21}–C_{30} saturated fatty acids) especially in the fall of 2017. This is again consistent with our observations, suggesting the influence of similar processes affecting both the particulate and the dissolved fractions.

Conclusions

Mono Lake experiences extreme oscillations in limnological conditions due to large variations in freshwater inputs, mainly derived from interannual variation in snowmelt runoff. These episodic changes in limnological conditions have triggered changes in microbial community composition (Humayoun et al. 2003; Phillips et al. 2021), which are important mediators of geochemical cycles. Our study tracked changes in the DOM pool that occurred during one of these shifts in limnological conditions in Mono Lake. Our results suggest that variations in DOM composition in 2017 were influenced by variability in DOM sources, including phytoplankton (*Picocystis* sp.) and terrestrial inputs, as well as changes in redox conditions and photodegradation. Microbial processing is also likely to have played an important role shaping DOM composition in the lake. In 2018, after the shift to meromictic conditions, S-containing compounds were more abundance below the pycnocline. Changes in DOM composition between seasons were less dominant and had a different pattern compared with its pattern during a typical mixing regimen. In all seasons, Mono Lake DOM was found to be less aromatic and more reduced in comparison with other saline endorheic lakes. Together, our findings suggest that the composition of DOM in Mono Lake is affected by episodic shifts in limnological conditions, adding valuable information on organic carbon cycling in a hypersaline lake.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00027-026-01283-6.

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Author contributions PM and JH conceived and designed the study. GU, PM, RC, and AM conducted lab and data analyses. JH coordinated sample collections in 2017 and 2018. GU wrote the manuscript. All authors provided revisions and feedback.

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Data availability Data used in this study are publicly available at PANGAEA (https://doi.org/10.1594/PANGAEA.983110).

Declarations

Conflict of interest The authors declare no competing interests.

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