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EDITED BY

Maurice Millet,
Université de Strasbourg, France

REVIEWED BY

Ni Maofei,
Guizhou Minzu University, China

*CORRESPONDENCE

Jianqing Du,
✉ jqdu@ucas.ac.cn
Kang Xiao,
✉ kxiao@ucas.ac.cn

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Methods for molecular characterization of dissolved organic matter in the alpine water environment: an overview

Yongbao Zhang, Jianqing Du* and Kang Xiao*

Beijing Yanshan Earth Critical Zone National Research Station, College of Resources and Environment, University of Chinese Academy of Sciences, Beijing, China

The alpine area has become a sensitive indicator and amplifier of global climate change and human activities because of its unique geographical and climatic conditions. Being an essential part of biochemical cycling, dissolved organic matter (DOM) could effectively help understand the process, structure, and function of alpine aquatic ecosystems. Due to the low content and sampling difficulties, the analysis of DOM in alpine water demands high sensitivity with low sample volume, which has not been comprehensively reviewed. This review summarizes the DOM sampling, pretreatment, and analysis methods involving the characterization of concentration, spectroscopy, and molecular structure. Overall, conventional parameters are the basis of advanced characterization methods. Spectroscopic tests can reveal the optical properties of DOM in response to lights from ultraviolet to infrared wavelengths, to distinguish the chemical composition. Molecular structure characterizations can provide microscopic information such as functional groups, element ratios, and molecular weights. The combination of multiple methods can depict DOM composition from multiple perspectives. In sum, optimized sampling and pretreatment, high-sensitivity molecular characterization, and method integration are crucial for effectively analyzing DOM components in alpine waters. These perspectives help to standardize the DOM characterization process and to understand the correlation between DOM composition and its properties, as well as the migration and transformation of DOM.

KEYWORDS

dissolved organic matter (DOM), alpine water, molecular characterization, analytical methods, spectroscopy

1 Introduction

Dissolved organic matter (DOM) is a complex mixture of aromatic and aliphatic hydrocarbon structures that have attached various functional groups (Leenheer and Croué, 2003). In practice, it generally refers to organic components in water that can pass through 0.22–0.7 μm pore-size membranes (Chen et al., 2019; Li YT. et al., 2021; Sun et al., 2021). In natural waters, DOM generally contains proteins, amino acids, polysaccharides, lipids, lignins, humus, other trace substances, and unknown substances (Singer et al., 2012; He C. et al., 2022).

DOM is the major reactant and product in biogeochemical processes, which is proven to be important in global carbon cycling and climate change (Singer et al., 2012; Mu et al., 2016). The special geographical conditions in alpine regions, i.e., high altitude, low

temperature, and remote geographical location, lead to slow biological processes (Zhou et al., 2019) and weak anthropogenic activities, resulting in low DOM content in alpine water. For example, dissolved organic carbon concentrations in alpine water samples (elevation >4,000 m) from the Qinghai-Tibet Plateau were commonly less than 1 mg L⁻¹ (Chen et al., 2019; Li YT. et al., 2021; Niu et al., 2022). Alpine water includes alpine runoff, snow/ice, rainwater, reservoir water, alpine lake, and spring/underground water (Huss and Hock, 2018; Li et al., 2020; Zabłocka et al., 2020; Chen et al., 2021; Guo et al., 2022; Zhou et al., 2023). Moreover, due to the low road network density and common altitude stress, researchers generally need to walk a long way to sample in valleys or on the glacier, which leads to a long sampling period and largely restricts the volume and amount of water samples (Mostofa et al., 2009; Gao et al., 2019; Li Z. et al., 2021). Meanwhile, the variation of DOM during this long sampling period may strongly affect the analysis of DOM concentration and composition. Although pretreatments of water samples such as filtration, low-temperature storage, or acidification (pH < 2) might help maintain the stability of DOM (He J. et al., 2022), there are still uncertainties. For instance, water samples in the transect survey were generally collected in chronological order; differences in the period of low-temperature storage may lead to variances in DOM content and components. On the other hand, the acidification process may also cause a DOM reaction and affect analysis results (Du et al., 2021). In summary, 1) an appropriate sampling protocol (sampling point and quantity settings), 2) a simple but effective pretreatment protocol, and 3) high sensitivity with low sample volume are crucial for DOM analysis in alpine regions. These are also a few principles for subsequent screening of DOM research methods suitable for alpine water.

Up to November 2023, using alpine (plateau, alpine, or highland), water quality, and dissolved organic matter as keywords, ~500 articles were found in the Web of Science (WOS) database. Further screening found that ~70 papers focused on the DOM analysis and characterization methods for alpine water, among which most papers (~2/3) focused on the Tibetan Plateau (e.g., Hayakawa et al., 2004; Li et al., 2020; Du et al., 2022). Other study areas include Europe (Laurion et al., 2000; Mladenov et al., 2008; Singer et al., 2012), North America (Belzile et al., 2002; Morris and Hargreaves, 2003; Miller et al., 2009), and Antarctica (Guo et al., 2022). Using the same keywords to search in Chinese on China National Knowledge Infrastructure, 11 papers were retrieved (all on the Qinghai-Tibet Plateau). Overall, many methods, such as the element analysis, ultraviolet-visible (UV-vis) spectroscopy, fluorescence spectroscopy, and high-resolution mass spectrometry, have been applied to investigate the DOM composition in alpine water. This paper comprehensively reviews the advantages and disadvantages of these various methods.

2 Determination of total concentration

2.1 TOC and COD

Total organic carbon (TOC) is a basic index indicating the total amount of organic matter in water by carbon content, while

chemical oxygen demand (COD) measures reducing matter in water samples by chemical method. Generally, the TOC is measured by a TOC analyzer. After removal of inorganic carbon by acidification (pH < 2), the organic carbon remained in the sample is converted to CO₂ via catalytic combustion and quantified by a non-dispersive infrared detector (Mu et al., 2016). COD measures the oxygen equivalent consumed by oxidizing organic matter to CO₂ with a strong oxidizing agent (potassium permanganate or dichromate) under acidic conditions. The average oxidation state of carbohydrate carbon in DOM is about 0. The average oxidation state of carbon in proteins and humic acids usually ranges from 0 to -2 (Stumm and Morgan, 1996). The average oxidation state calculated by TOC and COD can obtain information such as the occurrence and valence of organic matter in water samples (Eq. 1), which can be used in the study of DOM component migration and transformation in alpine water environment and regional carbon cycle (Stumm and Morgan, 1996; Mu et al., 2016; Rodriguez-Cardona et al., 2020).

$$\text{Oxidation State} = \frac{4 * (\text{TOC} - \text{COD})}{\text{TOC}} \quad (1)$$

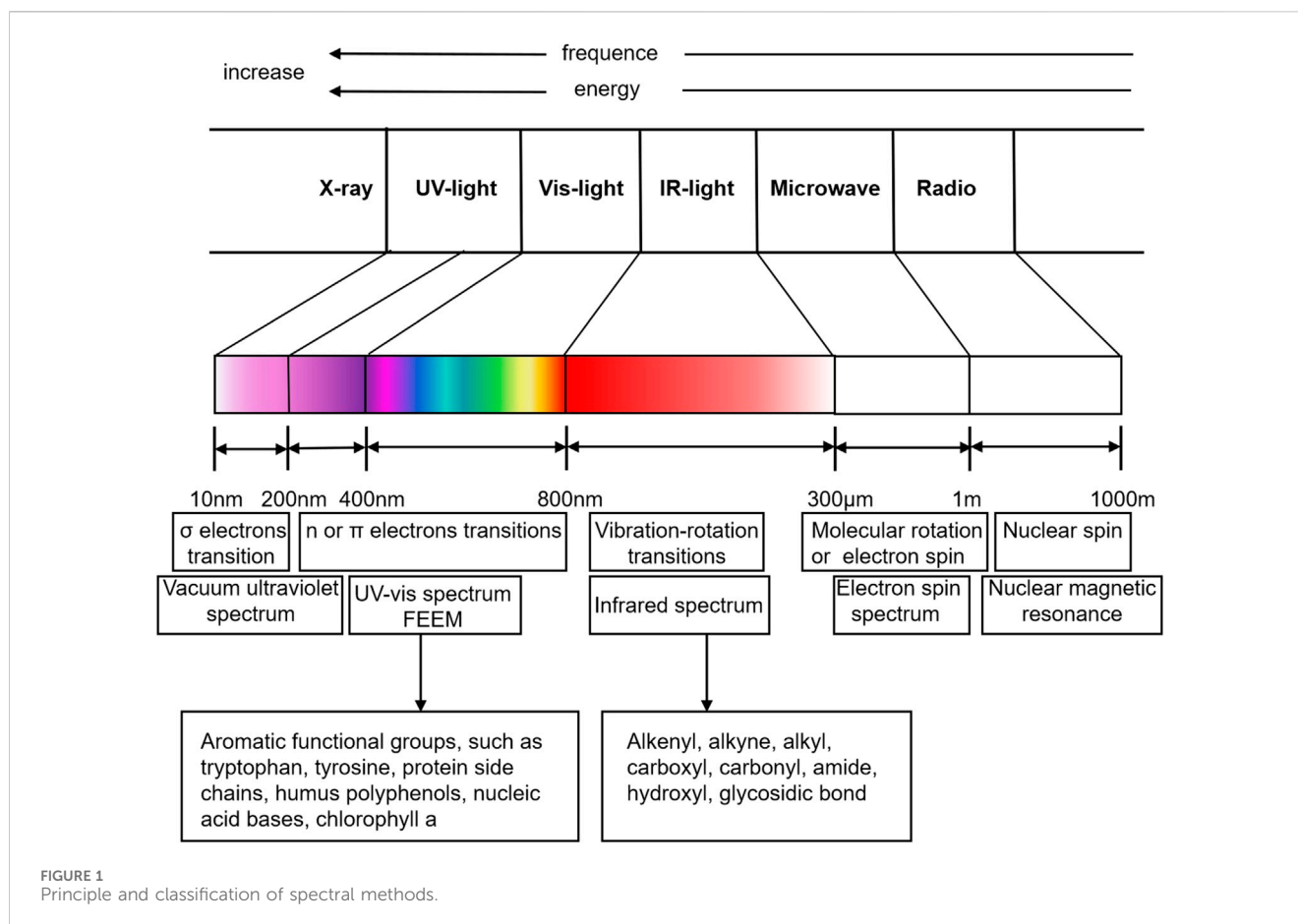
2.2 TON and TP

Total organic nitrogen (TON) is a basic index indicating the total amount of organic matter in water by nitrogen content, which is usually measured using a TON analyzer (combustion oxidation-chemiluminescence method). Total phosphorus (TP) is the sum of various chemical forms of granular and dissolved phosphorus in water, including orthophosphate, condensed phosphate, pyrophosphate, metaphosphate, and organic group combined phosphate. The water sample is usually dissolved with potassium persulfate or nitro-perchloric acid as an oxidant and then tested by spectrophotometry. N and P in water are derived from microbial metabolism, soil dissolution, anthropogenic sources, etc. (Qu et al., 2018). These processes are closely related to the formation and release of aquatic organic matter. The retention time of different molecular weight components in size-exclusion chromatography is different. Refining the molecular weight-related C and N composition by liquid chromatography combined with organic carbon and organic nitrogen detector (LC-OCD-OND) can potentially help explore the changing trend of DOM (Huber et al., 2011).

3 Spectral analysis

3.1 UV-vis spectrum

Figure 1 illustrates the principle and classification of spectral methods, ranging from ultraviolet and visible to infrared analysis. The UV-vis spectrum can detect the conjugated double bond structure, such as benzene ring and amide, generating n or π electron excitation. Different components in DOM have various molar absorption coefficients, and the absorbance follows Lambert-Beer's law. On the peptide bond backbone of protein-like



components, the carbonyl has $\pi \rightarrow \pi^*$ transition at 190 nm and the peptide bond has $n \rightarrow \pi^*$ transition at 210–220 nm. On the peptide side chain, the phenylalanine benzene ring, tyrosine phenolic group, and tryptophan indole group exhibit $\pi \rightarrow \pi^*$ transitions at 255–270 nm, 270–285 nm, and 285–305 nm, respectively. The nucleic acids absorb light at around 260 nm due to $\pi \rightarrow \pi^*$ transition of the bases (Rodger, 2013). Humic substances exhibit a broad spectrum of absorption from UV to visible range with relatively high absorbance at 250–300 nm, which could be attributed to the presence of multiple aromatic groups and complex interchromophore interactions (Del Vecchio and Blough, 2004).

Empirical secondary parameters (ratios of absorbance at different wavelengths) such as molecular weight index A_{365}/A_{250} , humification index A_{400}/A_{300} , hydrophobicity index A_{250}/A_{204} , aromaticity index A_{210}/A_{254} , and nonpolar index A_{220}/A_{254} can be obtained by calculating absorbance data (Peuravuori and Pihlaja, 1997; Erlandsson et al., 2012; Al-Juboori et al., 2016). The larger these indices, the stronger their corresponding properties. In addition, the absorbance ratio can be obtained by dividing the absorbance by the TOC concentration, such as the specific UV absorbance at 254 nm (SUV_{254}) (Weishaar et al., 2003), representing aromaticity. Compared with the total amount analysis method, the UV-vis spectroscopy has the advantages of fast detection speed (consuming a few to 10 minutes), low detection limit (mg L^{-1} level), and small sample volume (a few to 10 mL), which can meet

the needs of DOM characterization in alpine water (Yan et al., 2016; Song et al., 2019). In addition, the sensitivity of DOM detection in alpine water can be improved by sample concentration or by using appropriate cuvettes to enlarge optical path difference. The UV-vis spectral analysis based on characteristic absorbance and secondary parameters can offer a quick glance at the composition and content of DOM in alpine water, and the detailed properties of DOM components can be cross-examined by other methods.

3.2 Fluorescence excitation-emission matrix

Fluorescence excitation-emission matrix (FEEM) detects the fluorophoric portion of DOM by exciting the electrons through $n \rightarrow \pi$ or $\pi \rightarrow \pi^*$ transition, which then experience vibrational relaxation or internal conversion and emit fluorescence through $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition back to the ground state. Substances with high fluorescence intensity and fluorescence quantum yield often have structures of conjugated π bonds, rigid planes, heterocycles, and/or electron donating groups ($-\text{OH}$ or $-\text{CN}$ group). Substances with asymmetric structures, such as tryptophan/tyrosine in proteins and phenols in humus, have distinctive fluorescence properties (Peuravuori and Pihlaja, 1997; Mostofa et al., 2009). The quenching effect of halogen and metal ions in water samples may reduce the fluorescence intensity, and the pH and temperature

during the detection may also change the properties of organic matter and affect the fluorescence intensity.

In the FEEM test, fluorescence signals can be scanned in the excitation wavelength (Ex) range of 200–650 nm and the emission wavelength (Em) range of 200–800 nm. For DOM identification, the occurrence of fluorescence in different excitation/emission (Ex/Em) wavelength positions indicates the occurrence of different DOM components (Supplementary Table SA1). At a given wavelength position the fluorescence intensity indicates the relative abundance of the corresponding DOM component. Protein-like substances usually exhibit fluorescence at a relatively low Em (<380 nm), with aromatic proteins having a lower Ex (<250 nm) than microbial byproduct-related proteins (250–360 nm) (Chen et al., 2003; Yu et al., 2020). Humus-like substances usually have fluorescence at a medium Em (380–520 nm), with the fulvic acid-like and humic acid-like subset excited at low and medium Ex (<250 nm and 250–420 nm), respectively (Chen et al., 2003; Mladenov et al., 2007). In contrast, the fluorescence of biological pigments (such as chlorophyll a, phycocyanin and phycoerythrin) occurs in notably high Em (>550 nm) regions with varied Ex from 400 to 630 nm (Nebbioso and Piccolo, 2013).

Rich information can be obtained from FEEM by different data analysis methods, including fluorescence regional integration (FRI), parallel factor analysis (PARAFAC), and two-dimensional correlation spectroscopic analysis (2DCOS). FRI divides the scanning matrix into five wavelength regions and calculates the contribution rate of fluorescence intensity in each wavelength region to the total fluorescence, which can be used to distinguish humic acid-like and protein-like components in alpine waters (Li YT. et al., 2021). The derived parameters of FRI include the hydrophobicity parameter, humification parameter, wavelength parameter, and Stokes shift parameter related to fluorescence energy (Xiao et al., 2020). PARAFAC can extract principal components from complex DOM and trace their spatiotemporal variations accordingly (García et al., 2020). The 2DCOS can spread the spectral changes caused by external disturbances to two dimensions, and explore the sensitivity relationship between spectral signal changes and external factors such as altitude, location, time, and meteorological conditions (Noda and Ozaki, 2004; Chen et al., 2019; Li YT. et al., 2021). FEEM has the advantages of high sensitivity ($\mu\text{g L}^{-1}$ level), small sample amount (less than 2–5 mL), fast measurement speed (consuming a few to 10 minutes), and rich information. The characteristics of microsample but high sensitivity can well fit the needs of alpine water analysis. Therefore, FEEM has been widely used in exploring DOM components in alpine waters.

3.3 Infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy detects specific structures with dipole moments because their molecular vibrations and rotations are related to infrared light absorption. By analyzing the absorption wavenumber of the spectrum, information of chemical bonds (functional groups) corresponding to different molecules can be obtained. For example, characteristic wavenumbers useful for DOM analysis include 3,200–3,600 cm^{-1} (hydrogen bonds), 2,850–2,960 cm^{-1} (-CH), 1,690–1,760 cm^{-1} (carbonyls), 1,600–1,690/1,480–1,575/1,260–1,300 cm^{-1} (amide

I/II/III in proteins), $\sim 1,100 \text{ cm}^{-1}$ (C-O in polysaccharides), and $\sim 1,030 \text{ cm}^{-1}$ (C-O-C in polysaccharides or humus) (Krimm and Bandekar, 1986; Pretsch et al., 2011; Xiao et al., 2022). FT-IR is fast and non-destructive to the sample. FT-IR can obtain the molecular structure of DOM, but the characteristic peaks overlapping caused by the coexistence of multiple functional group absorption peaks often appear in the analysis of DOM samples. This method has not been frequently used for characterization of DOM in alpine waters.

4 Chemical structure analysis

4.1 Mass spectrometry

Charged ions with different charge-mass ratios can be detected by mass spectrometry (MS). The inorganic salts in alpine water samples greatly challenge the analysis of ultra-low DOM concentration (Pan et al., 2023). Generally, the desalting, separation, and concentration of DOM components are prerequisites for DOM characterization. DOM can usually be extracted by ultrafiltration, freeze-drying, reverse osmosis combined with electro dialysis, or solid phase extraction methods (Kim et al., 2022). Fourier transform ion cyclotron resonance (FT-ICR) MS can deeply analyze the chemical structure of DOM in natural environments and water treatment processes with ultra-high mass resolution (the $m/\Delta m$ ratio reaching 10^4 – 10^6) and sub-ppb level mass accuracy. It is suitable for accurately analyzing molecular weights and chemical compositions of various structural fragments in the complex DOM macromolecules in alpine water (He C. et al., 2022).

The full procedure for FT-ICR MS analysis is illustrated in Supplementary Figure SA1. Electrospray ionization can produce ions of various valence states and has high selectivity for polar acidic functional groups; however, it has seldom been used to study DOM (Persson et al., 2005). The FT-ICR MS results can be presented with a van Krevelen diagram to show the differences in DOM components from different sources, and the evolution of specific structures in DOM in different environmental processes can be found through molecular comparison (Pan et al., 2023). Each test requires an equivalent of 100–200 μg TOC mass. FT-ICR MS has high resolution and can provide a huge amount of information; however, its preprocessing is complex and the test is relatively expensive. Moreover, ionization of the complex DOM is often variable, likely to produce unrepeatable results. Quantitative analysis of DOM at molecular level based on FT-ICR MS is a significant but challenging task in future alpine water research.

4.2 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is a physical phenomenon of nuclear absorption and re-emission of electromagnetic radiation in the magnetic field. Before testing, the sample should be pretreated to ensure it does not contain paramagnetic substances and insoluble impurities to eliminate the resolution error (Emery et al., 2001; Hertkorn et al., 2016). NMR is highly selective and provides detailed picture information of the molecular structure of solid and liquid phase samples to distinguish the different connections of functional

TABLE 1 Molecular characterization methods of dissolved organic matter and their application in alpine waters.

Characterization methods	Targets	Advantages	Disadvantages	Spatial-scale and research type	Representative references
Basic analysis	TOC, COD, TN, TP	Simple pretreatment (usually only filtration) and common instrument	Non-discriminative for specific DOM components	Large spatial-scale and long-term monitoring	Mu et al. (2016); Qu et al. (2018); Rodriguez-Cardona et al. (2020)
UV-vis	Conjugated systems or chromophores	Fast detection speed (a few to 10 minutes), low detection limit (ppm level), small sample volume (a few to 10 mL) and nondestructive to the sample	Insignificant spectral characteristics	Large spatial-scale and <i>in-situ</i> monitoring	Yan et al. (2016); Song et al. (2019); Li et al. (2021a)
FEEM	Fluorescence characteristics	High sensitivity (ppb level), small sample volume (a few to 10 mL), fast measurement speed (a few to 10 minutes), rich information and nondestructive to the sample	Inaccuracy for quantitative analysis, relatively complex for data processing, and susceptible to inner filter, quenching and Raman scattering effects	Large spatial-scale and <i>in-situ</i> monitoring	Peuravuori and Pihlaja (1997); Mostofa et al. (2009); Li et al. (2021a)
FT-IR	Chemical bonds or functional groups	Fast detection speed (a few to 10 minutes) and nondestructive to the sample	Relatively large sample amount (100 mg freeze-dried sample), overlapping of characteristic peaks, and inaccuracy for quantitative analysis	Small spatial-scale and long-term monitoring	Rarely reported for alpine waters
FT-ICR MS	High-resolution mass-charge spectrum	Ultra-high mass resolution ($m/\Delta m$ reaching 10^4 – 10^6) and sub-ppb level mass accuracy	Relatively complex pretreatment, expensive test cost, and poor repeatability of the results	Small spatial-scale and long-term monitoring	He et al. (2022a); Pan et al. (2023)
NMR	Element-specific molecular structural characteristics	Rich structural information and nondestructive to the sample	Large quantity of samples and high sample preparation requirements	Small spatial-scale and long-term monitoring	Rarely reported for alpine waters
LC-OCD-OND	Molecular weight size distribution	Simple pretreatment (usually only filtration)	Large quantity of samples	Small spatial-scale and long-term monitoring	Rarely reported for alpine waters

groups within the DOM molecule (Mao and Schmidt-Rohr, 2003). Measurement of the ^1H spectrum in conventional continuous wave methods requires more than 50 mg of samples. When testing the ^{13}C spectrum, measuring the Fourier transform (FT) spectrum is necessary. The FT ^{13}C spectrum requires 50–100 mg samples and the FT ^1H spectrum requires 1–10 mg samples (Simpson et al., 2011). NMR can distinguish multiple atoms in a single molecule or collections of molecules of the same type. However, since DOM bears complex compositions, there could be considerable overlap of signals in the NMR spectrum. NMR has been rarely used in the alpine water DOM analysis.

4.3 Chromatographic separation

Chromatographic separation can achieve selective enrichment through the difference of charged properties. Combining chromatographic separation with optical detector and mass spectrometry can effectively characterize the DOM components in alpine water (Sandron et al., 2015; Maurischat et al., 2022). LC-OCD-OND requires no complex pretreatment, while DOM samples generally need to be filtered through a 0.22 μm mixed cellulose ester membrane. An LC-OCD-OND test often requires more than 50 mL of a sample with a TOC sample concentration of

less than 5 mg L^{-1} . LC-OCD-OND can be applied to characterize natural organic matter to indicate the properties and changes of substances through different molecular weights (Huber et al., 2011). Currently, the coupling of chromatography and detector based on molecular weight and hydrophobicity has been widely used in non-alpine water analysis, showing great potential in the DOM analyses of alpine water.

5 Method comparisons

Disentangling the DOM composition and structure, such as microscopic morphology, molecular weight distribution, and chemical bond composition, is essential for understanding its reaction processes and mechanisms and feedback to environmental change. Various DOM characterization methods have been applied to the alpine water quality assessment and the evaluation of anthropogenic effects on DOM-induced biogeochemical cycling (Zhang et al., 2007; Mu et al., 2016; Ma et al., 2018; Wang et al., 2018; Zhou et al., 2019; Li et al., 2020; Du et al., 2022). Different characterization methods have their own advantages and disadvantages for the case of alpine water analysis (Table 1). Basic analysis (TOC, COD, TN, and TP) can obtain the information of DOM based on total concentration, which is the basis

of advanced characterization methods. Spectral testing requires a small water volume and can reveal the optical properties of DOM in response to light from ultraviolet to infrared wavelengths to distinguish its chemical composition. In addition, further analysis of the spectral data can obtain more information on the properties and composition of DOM. Such advantages ensure its great potential in both *in-situ* monitoring and large spatial-scale DOM research (e.g., regional studies in the Tibetan Plateau or a large river basin), particularly in rural alpine areas. However, the spectral characterization methods (UV-vis and FEEM) could not achieve full quantification of the molecular composition, and thus, we need the molecular structure characterization to depict the microscopic information, such as functional groups, element ratios, and molecular weights. Nevertheless, the molecular structure characterization requires a large amount of water and is generally achievable in long-term observational studies with a fixed location or small spatial-scale studies (e.g., a small watershed or a lake).

6 Summary and prospect

The DOM components of alpine water are complex; therefore, using a single method is inadequate and may produce inaccurate results. The comprehensive use of spectroscopy, chromatography, and high-resolution mass spectrometry provides technical support for disentangling DOM's intricate environmental behaviors, such as adsorption, migration, binding, complexation, and photoinduction. In summary, future research should pay attention to the following issues.

1. Optimized sampling and pretreatment. Some structural characterization methods (e.g., NMR and MS) often require complex DOM extraction and separation processes. Many steps, such as sample collection, transport, storage and pretreatment, will lead to disturbance. Obtaining uncontaminated DOM samples with high repeatability is a challenge. Using portable instruments or simple equipment for on-site testing and optimizing the pretreatment method can improve the sample's representativeness.
2. High-sensitivity molecular characterization. The concentration of DOM in alpine water is often low. Adequate concentration of samples and choosing appropriate experimental conditions, such as appropriate cuvettes or light sources in spectral analysis, can improve the sensitivity of analysis.
3. Methods integration. Methods such as spectroscopy and MS contain rich information detailing the composition and molecular structure information of DOM. In *in-situ* monitoring, we could build up the statistical relationship between spectroscopy and mass spectrometry analysis through methods such as machine learning. On this

basis, it is possible to integrate high-frequency spectroscopy analysis and low-frequency mass spectrometry analysis via transfer learning and the relationship established by *in-situ* monitoring in large spatial-scale studies sharing similar environmental and hydrological conditions. Together with the improvement of portable spectral detection equipment, it would largely reduce the workload of field sampling and analysis in tracking DOM composition and changes in alpine waters, particularly in rural or glacial areas.

Author contributions

YZ: Investigation, Writing–original draft. JD: Methodology, Writing–review and editing. KX: Conceptualization, Supervision, Writing–review and editing, Funding acquisition.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvc.2024.1339628/full#supplementary-material>

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