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Recalcitrant dissolved organic matter in lakes: a critical but neglected carbon sink

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Abstract

Lakes are hotspots for the biogeochemical processing of carbon, including dissolved organic matter (DOM). A less degradable fraction of DOM, preserved for a long time, can be categorized as recalcitrant DOM (RDOM). Lake RDOM is an important but neglected carbon sink, and its characteristics and transformation processes remain largely unknown.

Highlights

- Recalcitrant dissolved organic matter (RDOM) is an important but neglected carbon sink in lakes.
- The heterogeneity of lake environments determines the diversity and complexity of RDOM.
- New techniques allow detailed studies of the mechanisms of RDOM formation and related processes.

Keywords Lake, Dissolved organic matter, Recalcitrant, Carbon sink

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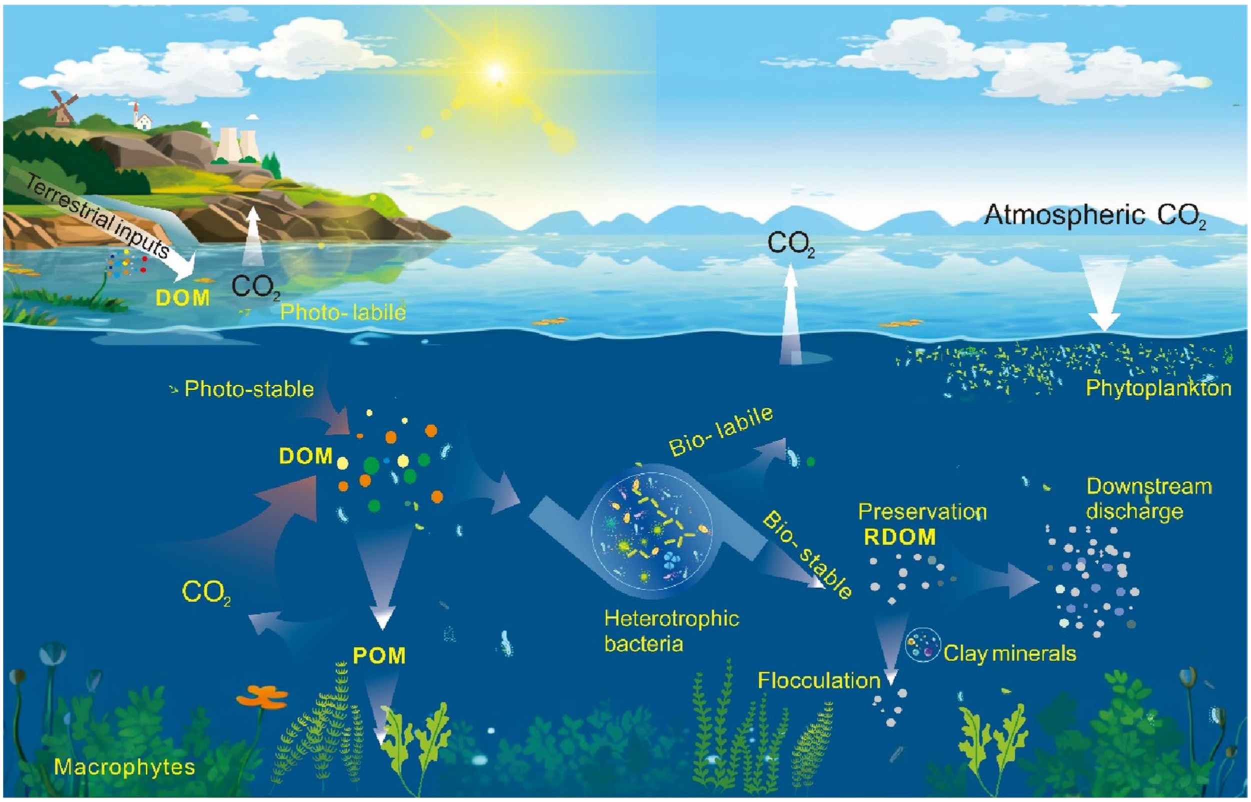
Graphical Abstract



1 Main text

The transport, transformation, production, degradation, and mineralization of organic carbon in inland ecosystems largely determine greenhouse gas emissions and the carbon balance, with implications for climate change (Battin et al. 2009). Despite that lakes cover < 2% of the Earth's surface area, they act as a fundamental link between the carbon cycles of terrestrial and inland water ecosystems. Globally, lakes and other wetland ecosystems fix organic carbon equivalent to ~ 50% of the organic carbon uptake by the oceans (Tranvik et al. 2009). Dissolved organic matter (DOM) typically constitutes the dominant pool of organic carbon in freshwaters (Drake et al. 2023; Zhou et al. 2023). Due to the differential degradation of DOM in lakes depending on bioavailability and photodegradability, the role of lakes in offsetting human CO_2 emissions is uncertain (Jia et al. 2023). DOM preserved for a long period of time is categorized as recalcitrant DOM (RDOM), considered as a carbon sink (Xia et al. 2022). RDOM in the ocean can have a mean turnover time of about 5,000 years (Jiao et al. 2010); however, so far, the turnover time of RDOM in lakes is largely unknown.

In lake ecosystems, DOM is classified according to its sources (autochthonous or allochthonous) and its lability (highly labile, semi-labile, and recalcitrant) (Jiao et al. 2010). Degradation of algae and aquatic plants in lakes contributes to the production of autochthonous DOM (Zhang et al. 2009). Allochthonous DOM inputs mainly comprise DOM derived from soil leachate, domestic sewage, and agricultural effluents and they are typically major contributors to the lake DOM pool. These DOM inputs can undergo significant bacterial and UV transformation after entering a lake, with terrestrial aromatic DOM being selectively photodegraded to low-molecular-weight compounds and CO_2 (Fig. 1; Cory et al. 2013). In pristine catchments, soil organic matter is the primary contributor to the allochthonous DOM pool and can be biologically stable (Drake et al. 2019). In comparison, autochthonous DOM derived from algal degradation produces most of the low-molecular-weight organic compounds, including amino acids, carbohydrates, and

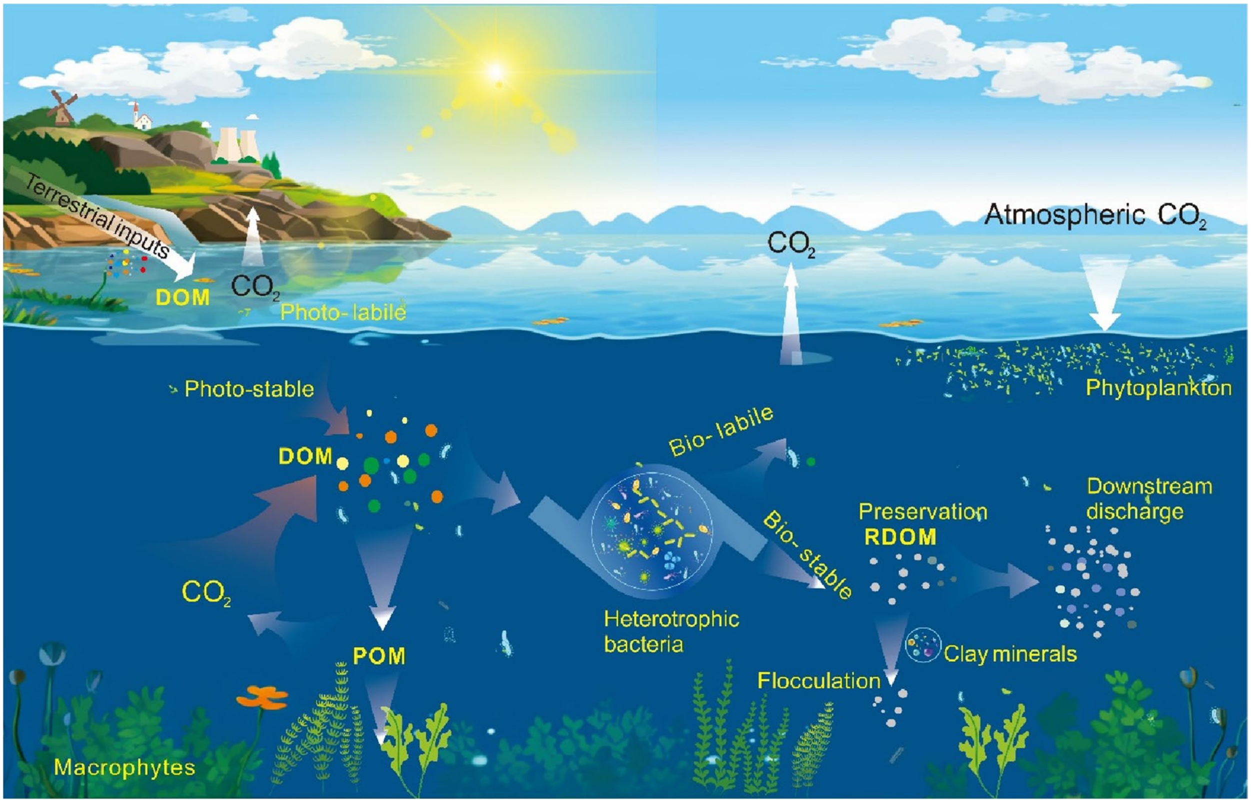


Fig. 1 Schematic diagram showing the formation processes of recalcitrant dissolved organic matter (RDOM) in lakes. RDOM in lakes is either retained in the water column, flocculated and precipitated to the sediment, or exported for downstream discharge. DOM: dissolved organic matter; POM: particulate organic matter

carboxylic acids, which can be readily utilized by microorganisms and degraded to dissolved inorganic matter and CO_2 (Fig. 1). Therefore, autochthonous DOM is considered to be more biologically labile than soil-derived allochthonous DOM (Salcher et al. 2013). Due to the variations in lake environments and the associated biological communities and activities, the chemical composition and molecular structural stability of different DOM sources vary widely (Guillemette et al. 2015). For example, submerged plants have cellulose that is more difficult to degrade, and diatoms have a higher proportion of nondegradable glycine compared to cyanobacteria. However, the dynamics of RDOM in lakes are so far not well studied (Xia et al. 2022).

The turnover time of DOM in rivers and lakes is much shorter than in the ocean but cannot be directly estimated using the $\Delta^{14}C$ dating technique (Xia et al. 2022). In streams, RDOM can contribute up to 62% of the total DOM pool (McLaughlin and Kaplan 2013). Microbial degradation experiments have shown that labile DOM in lake water accounts for up to > 50% of the DOM pool (Zhou et al. 2020) and that microorganisms would preferentially utilize freshly produced DOM, leaving RDOM for downstream discharge (Lu et al. 2013) or storage in the lakes (e.g., by flocculation followed by sedimentation). In addition to the imported allochthonous DOM, the metabolites, residues, and cell debris of primary production in lakes are relatively recalcitrant after utilization by microorganisms, and this RDOM fraction accounts, for example, for ~ 50% of the DOM pool in karst lakes (Xia et al. 2022). In closed catchments formed by impermeable bedrock in Antarctica fresh waters, autochthonous DOM forms ubiquitous and persistent in-water humus after photodegradation (Kida et al. 2019). Accordingly, it has been found that photooxidation of DOM constitutes 70%-95% of the total carbon processed in Arctic fresh waters (Cory et al. 2014). Photochemical processes have also been shown to enhance the cross-linking, humidification, and polymerization of unstable biomolecules into more recalcitrant compounds (Hassett 2006).

Most RDOM in lakes is the product of microbial metabolism. DOM serves as a major bacterial source of carbon and nutrients for metabolic activities. DOM aromaticity associating negatively with the bioavailability of organic matter can lead to differences in bacterial community structure, function, and mutualistic networks by affecting bacterial primary and secondary productivity, growth, and respiration rates (Guillemette et al. 2015; Hassett 2006; Zhou et al. 2021). Previous studies have shown that bacterial utilization of DOM is largely based on physiological needs but also influenced by environmental factors such as temperature, dissolved oxygen, and nutrient availability, which provide sufficient energy and materials for the synthesis of the necessary extracellular and transport enzymes (Xenopoulos et al. 2021). Environmental heterogeneity is a key factor in shaping the distribution patterns of planktonic bacteria in lakes and species richness (Zhou et al. 2021). Higher microbial diversity may provide more metabolic pathways to degrade and produce RDOM molecules (Zhou et al. 2021). Elucidating the chemical composition and quantifying the size of the RDOM pool are highly relevant to obtain carbon neutrality. Further disentangling the coupling linkages between environmental factors, bacterioplankton, and DOM is crucial for the understanding of the stability of carbon sources and sinks in lakes (Xia et al. 2022) and should be a future research priority.

There is a lack of hypotheses associated with the production and stability of RDOM in lake ecosystems. In comparison, reasons for the stability of RDOM in the oceans are currently summarized under the umbrella of three major hypotheses, the "environment hypothesis", the "intrinsic stability hypothesis", and the "molecular diversity hypothesis" (Dittmar 2015). The "environmental hypothesis" of RDOM production links DOM to the responsiveness of specific environmental conditions or to specific time periods (Dittmar 2015). These include the composition and activity of planktonic bacterial communities, redox state, mineral binding, and substrate accessibility by microorganisms and their enzymes. For example, limited availability of inorganic and organic nutrients may limit bacterial growth and DOM utilization through competition. Elucidating the key factors that influence the degradability and stability of DOM in lakes is an important area of future research. The "intrinsic stability hypothesis" links the reactivity of DOM to its molecular composition (Dittmar 2015). The molecular composition of RDOM may be synthesized by aquatic microbes, or it may be altered by abiotic modifications due to physicochemical perturbations. These abiotic modifications may result in the formation of a more stable fraction of DOM (Cory et al. 2014), thus contributing to the RDOM pool in lakes. The "molecular diversity hypothesis" suggests that bacteria in the deep ocean must maintain appropriate enzymes, transport systems, and metabolic pathways for DOM catabolism and anabolism (Dittmar 2015; Arrieta et al. 2015). However, such a strategy is difficult to have if the RDOM has a diverse chemical composition or the concentration is too low to be utilized by microbes. Due to the complexity of lake environments and the high biological activity in lakes, the composition of DOM and the stability of the molecular structure vary tremendously among different aquatic organisms in lakes. The "environmental hypothesis" mechanism may play an important role in the stability of DOM in lake ecosystems. Therefore, identifying the interactions between RDOM and planktonic bacteria across different environmental gradients (e.g., trophic status, catchment land use, sorption to metals and clay minerals) is key to understanding the dynamics of RDOM in lakes.

Fortunately, advances are made in metagenomic analysis and DOM identification, involving growing utilization of high- and ultrahigh-resolution mass spectrometry (e.g., FT-ICR MS and Orbitrap MS) (Hu et al. 2022). This provides unique opportunities to explore the link between microbial carbon pumps and the mechanisms of RDOM formation and to deepen our understanding of the interactions between the microbial community and the chemical composition of DOM as well as the outgassing of greenhouse gases from lakes (Li et al. 2022; McDonough et al. 2022). Big data and systems science approaches, including machine learning and numerical simulation, can further help to elucidate the role of RDOM in the lake carbon cycling and the role of lakes relative to the future climate change.

Abbreviations

CO_2	Carbon dioxide
DOM	Dissolved organic matter
FT-ICR MS	Fourier transform ion cyclotron resonance mass spectrometry
RDOM	Recalcitrant dissolved organic matter

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Authors' contributions
Yongqiang Zhou and Yunlin Zhang acquired funding. Erik Jeppesen conducted investigation. Yunlin Zhang and Erik Jeppesen supervised the study. Conceptualization was performed by Fan Xia and Yongqiang Zhou. Fan Xiao prepared visualization. The first draft of the manuscript was written by Fan Xiao, Yongqiang Zhou, and Lei Zhou. Yongqiang Zhou, Lei Zhou, Yunlin Zhang, and Erik Jeppesen reviewed and edited the manuscript.

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Availability of data and materials
Not applicable.

Declarations

Competing interests
The authors declare that they have no known competing financial interests or personal relationships that influence the work reported in this paper.

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