



Seasonal and diel relationships between the isotopic compositions of dissolved and particulate organic matter in freshwater ecosystems

SUSAN E. ZIEGLER^{1,2,*} and MARILYN L. FOGEL¹

¹*Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington, DC 20015, USA;* ²*Current address: Department of Biological Sciences, University of Arkansas, 622 Science Building, Fayetteville, AR 72701, USA;* **Author for correspondence (e-mail: susanz@uark.edu; phone: 479-575-6342; fax: 479-575-4010)*

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Abstract. A study of the isotopic composition of organic matter was conducted in a freshwater marsh over seasonal and diel time scales to determine the sources of dissolved organic matter (DOM) and the processes leading to its formation. Bulk C and N isotopic compositions of the bacterial fraction (0.2–0.7 μm) and particulate organic matter (POM; 0.7–10 μm) were compared on a seasonal basis with the change in $\delta^{13}\text{C}$ of DOM. The bulk isotopic data support the idea that DOM was, in part, derived from the breakdown of larger organic matter fractions. The bacterial fraction and POM were compositionally similar throughout the year, based on a comparison of the $\delta^{13}\text{C}$ of individual amino acids in each fraction. Annual variation in the $\delta^{13}\text{C}$ of amino acids in DOM was greater relative to the variation in larger fractions indicating that microbial reworking was an important factor determining the proteinaceous component of DOM. The ^{13}C enrichment of serine and leucine in each organic matter fraction suggested microbial reworking was an important factor determining organic matter composition during the most productive times of year. Changes in the bulk $\delta^{13}\text{C}$ of DOM were more significant over daily, relative to seasonal, time scales where values ranged by 6‰ and followed changes in chlorophyll *a* concentrations. Although bulk $\delta^{13}\text{C}$ values for POM ranged only from –29 to –28‰ during the same diel period, the $\delta^{13}\text{C}$ of alanine in POM ranged from –30 to –22‰. Alanine is directly synthesized from pyruvate and is therefore a good metabolic indicator. The $\delta^{13}\text{C}$ of individual amino acids in DOM revealed the diel change in the importance of autotrophic versus heterotrophic activity in influencing DOM composition. Diel changes in the $\delta^{13}\text{C}$ of phenylalanine, synthesized by common pathways in phytoplankton and bacteria, were similar in both DOM and POM. The diel change in $\delta^{13}\text{C}$ of isoleucine and valine, synthesized through different pathways in phytoplankton and bacteria, were distinctly different in DOM versus POM. This disparity indicated a decoupling of the POM and DOM pools, which suggests a greater source of bacterial-derived organic matter at night. The results of this study demonstrate the use of the isotopic composition of individual amino acids in determining the importance of microbial reworking and autotrophic versus heterotrophic contributions to DOM over both diel and seasonal time scales.