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High-frequency sensor evidence for widespread, condition-dependent photodegradation and recharging of aromatic DOM

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Photochemical processing of riverine dissolved organic matter (DOM) strongly influences its composition, bioavailability, and downstream fate. Photobleaching and transformation of aromatic DOM can affect in-stream metabolism and shift DOM composition toward more microbially reactive forms. Despite its importance, photodegradation within natural waters remains poorly quantified. Most estimates are derived from lab experiments or a limited number of site-specific environmental case studies. Aromatic DOM is abundant in many freshwater systems and is highly susceptible to photodegradation. This aromatic DOM can be tracked using light absorbance of water at 254 nm (a254), a reliable estimate of aromatic and conjugated DOM. High frequency, in situ observations diel hysteresis of a254 levels can be used to estimate photodegradation rates at a scale not possible with other methods.

To quantify photodegradation dynamics, we analyzed high frequency sensor records from 23 NEON sites spanning diverse climatic and hydrologic regimes, complemented by NOAA buoy observations in Lake Erie. We estimated photodegradation rates using diel hysteresis between a254 and photosynthetically active radiation (PAR) across sites and interpreted these patterns alongside temperature, turbidity, and discharge.

Across all sites, we detected ~13,000 diel cycles, of which nearly 9,000 passed quality-control criteria and were retained as hysteresis events. We found both clockwise hysteresis loops, indicating net a254 photodegradation, and counterclockwise hysteresis loops that indicate “recharging” of aromatic DOM via in situ transformation or external inputs. Net decreases in a254 displayed strong seasonality, with the largest declines occurring during periods of greater PAR. The extent of photodegradation increased with lower latitudes, consistent with greater UV exposure. Lastly, many sites showed diel increases in a254, demonstrating that aromatic DOM can be replenished on short timescales by hydrologic connectivity or in stream processing.