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Formation and reactivity of dissolved species from the photolysis of particulate organic matter

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In aquatic systems, the exposure of natural organic matter (NOM) to sunlight can initiate a number of pathways by which biologically recalcitrant fractions (*e.g.,* lignins or tannins) are chemically altered. Specific reactions include either the direct absorption of a photon or reaction with a second photolytically generated species (*e.g.,* the hydroxyl radical, singlet oxygen, excited triplet state NOM, etc.). Such reactions can also alter the the physical state of NOM by facilitating the cycling between the particulate (POM) and dissolved (DOM) pools, though we presently lack a chemically rigorous description of this process. Here, we examine such photodissolution processes directly by examining the chemical composition and reactivity of DOM produced via the photolysis of POM (100 mg/L, 40 – 100 micron particles) derived from the lignocellulose rich common reed *Phragmites austeralis*. DOM production from irradiated samples (~ 1.0 ppmC/week) was significantly greater than measured from dark controls (< 0.1 ppmC/week) indicating that slow dissolution or biodegradation of POM were minor processes relative to those induced by photolysis. The chemical composition of DOM following three weeks of continuous irradiation was measured using negative mode ESI with ultra-high resolution FT-ICR-MS. Ions were unambiguously assigned chemical formulae based on their measured exact masses and following 7 days of photoexposure ~65% were characterized as being compositionally similar to lignins and condensed hydrocarbons. Following an additional week of irradiation ion identities did not change dramatically, however, the relative abundances lignin-type ions decreased with a coincident increase in tannin- and condensed hydrocarbon-like ions. We discuss these results in the context of the specific photochemical mechanisms responsible while highlighting the implications for subsequent biological transformations of previously bio-recalcitrant material.