



Temperature sensitivity of CO₂, CH₄, CO, and H₂ release during photodegradation of organic material

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Recent studies suggest that photochemical breakdown (hereafter 'photodegradation') of plant material by ultraviolet (UV) radiation may circumvent biotic decomposition and account for as much as a third of decomposition in arid and semiarid ecosystems. Current knowledge of the mechanism by which UV breaks down plant-derived carbon compounds such as cellulose and lignin is limited. Previous studies suggest that photodegradation may not only release CO₂, but also CO and CH₄, and that gas production may be sensitive to temperature. We established a laboratory experiment to test the temperature sensitivity of greenhouse gases (CO₂ and CH₄) and indirect greenhouse gases (CO and H₂) during photodegradation of plant material. The photochemical reaction was induced using a 300 W xenon lamp solar simulator in a closed quartz chamber connected to a high resolution wavelength-scanned cavity ringdown spectrometer for CO₂-CH₄ and a reduced compound photometer gas chromatograph for CO and H₂. The temperature was controlled using a water bath connected to a chiller/heater below the chamber to control chamber temperatures at 15, 25, 35, 45, and 55°C. We compared emission rates from two artificial materials that were high in lignin (basswood sheet) and cellulose (filter paper) and leaves of four species of plant litter collected from their native habitats in the southwestern U.S.: dried leaflets of velvet mesquite, culms and leaves of Indian ricegrass (C4 grass) and little bluestem grass (C3 grass), and piñon pine needles. The rates of CO₂ and CO emissions from photodegradation ranged from 3-67 $\mu\text{mol CO}_2\text{-C m}^{-2}\text{ hr}^{-1}$ and 2-34 $\mu\text{mol CO-C m}^{-2}\text{ hr}^{-1}$ and were positively correlated to temperature for all materials (magnitude of fluxes: basswood > leaf materials > filter paper). In contrast, the rate of CH₄ and H₂ ranged from 0-0.5 $\mu\text{mol CH}_4\text{-C m}^{-2}\text{ hr}^{-1}$ and 0-4 $\mu\text{mol H}_2\text{ m}^{-2}\text{ hr}^{-1}$, but the temperature responses varied among materials. For instance, the rate of CH₄ and H₂ emissions were positively correlated with temperature during photodegradation of basswood, but they were not correlated with temperature for the filter paper. Our results suggest that complex compounds such as lignin may be more sensitive to increasing temperature than cellulose and that higher temperatures often observed in land surface of arid and semiarid ecosystems in summer may greatly enhance photodegradation of fallen plant litter. From the laboratory measurements, we estimate that the global abiotic production of trace gases from plant litter would be roughly 95-286 Tg CO₂ yr⁻¹, 32-96 Tg CO yr⁻¹, 0.30-0.90 Tg CH₄ yr⁻¹, and up to 3 Tg H₂ yr⁻¹. In conclusion, we suggest that the combined processes of thermal and photodegradation of organic matter may be a previously under-accounted source of C-based trace gases and H₂ from terrestrial systems and may need to be considered in large scale trace gas observation efforts and in global C and H budgets.