

**Aspects of aquatic CO photoproduction from CDOM
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CO photoproduction and HS photobleaching were found to correlate to humic substance (HS) light-absorption (a_{350}) and aromatic carbon, but not to ketones, in 16 diverse HS isolates. Aquatic-HS had steeper spectral-slopes (S) with lower a_{350} and aromatic content than terrestrial-HS. Following irradiation, S steepened implying that spectral differences between aquatic and terrestrial-HS were due to photobleaching in surface waters. Photobleaching decreased, a_{350} increased and S steepened with increasing pH. CO photoproduction rates were lowest at neutral pH, increasing in acidic and alkaline samples. Riverine, estuarine and coastal water CO apparent quantum yield (AQY) are presented and were found to correlate significantly with CDOM concentration. CO and photobleaching AQYs also showed strong photon dose dependence.

A_{350} decreased and $S_{350-290}$ steepened with increasing salinity in estuarine waters. Modelled estuarine CDOM photobleaching indicated that steeper S values at higher salinities were due primarily to photobleaching, not mixing with steep S marine CDOM. Modelled CO photoproduction was 2.9 ± 1.3 and 968 ± 223 TgCO yr⁻¹, in the global estuary and ocean respectively. CO emission rates were calculated to be 6.8-13.4 and 0.56 ± 0.26 TgCO yr⁻¹ in the global ocean and estuary, respectively. Global ocean and estuary oxidation rates were estimated to be 915 ± 752 and 2.8 ± 1.0 TgCO yr⁻¹, respectively. Comparison of oceanic CO photoproduction with oxidation and emission rates indicates the oceanic CO cycle is approximately balanced. Oceanic CO photoproduction, CO₂ photoproduction and photo-induced DOC consumption by heterotrophs were calculated to account for the photodegradation 12.4 Gt DOC yr⁻¹, ~26% of annual oceanic primary production. Estimated mean global estuarine DOC photodegradation (87 Tg C yr⁻¹) represents ~34% of the annual global riverine DOC flux to the oceans. The magnitude of these rates demonstrates the importance of photochemistry in the marine and estuarine DOC cycles.