

**Photoammonification and CDOM dynamics in aquatic environments.
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Photochemical degradation of chromophoric dissolved organic matter (CDOM) (loss of absorption coefficient at 350 nm (a_{350})) was observed in a series of irradiation experiments of filtered (0.1 μm) river, estuarine and coastal water samples covering a range of a_{350} (1-38 m^{-1}) and salinity (0-34). Simultaneously, increases in CDOM spectral slope ($S_{290-350}$) and the concentration of ammonium were observed. $S_{290-350}$ and a_{350} followed first order kinetics. Three separate phases were identified in the photochemical production of ammonium: a) lag phase ($\sim <1$ hour duration); b) production phase (~ 1 hours duration); c) consumption phase ($\sim >2$ hours duration). Ammonium photoproduction rates (mean rate: 113 $\text{nmol l}^{-1}\text{h}^{-1}$) were independent of initial a_{350} , $S_{290-350}$, NH_4^+ concentration and salinity suggesting that different pools of CDOM, found in natural waters, are responsible for photochemical ammonium production and uptake.

Fluorescent dissolved organic matter (FDOM), NO_3^- , NO_2^- , NH_4^+ , SiO_4^{2-} , PO_4^{3-} , a_{350} , and $S_{290-350}$ distributions in the Tyne and Tamar estuaries were typical of such environments. Estuarine a_{350} profiles versus salinity indicated consumption of $\sim 26\%$ and $\sim 36\%$ of riverine a_{350} input in the vicinity of the Estuarine Turbidity Maximum (ETM) for the Tyne and Tamar estuaries respectively, presumably mostly due to microbial remineralisation of CDOM. FDOM and $S_{290-350}$ data are consistent with photodegradation of CDOM in the lower Tyne and Tamar estuaries.

Oceanic, Atlantic Meridional Transect (AMT), cruise data showed subsurface a_{350} maxima and $S_{290-350}$ minima in the vicinity of the deep chlorophyll maximum (DCM) indicative of an autochthonous source. The values of $S_{290-350}$ from surface waters ($<7\text{m}$) were significantly higher than in deep waters (20-250m), presumably due to photodegradation of CDOM in the near surface layer. Compilation of all $S_{290-350}$ data (estuarine, coastal and oceanic) versus the light attenuation coefficient (K_d) show that higher $S_{290-350}$ values are found with decreasing light attenuation, suggesting that photodegradation regulates CDOM spectral slope. Nutrient (NO_3^- , NO_2^- , NH_4^+ , SiO_4^{2-} , PO_4^{3-}) distributions were typical for the environments encountered.

The estimated annual inputs of nitrogen in potentially photoproduced ammonium into coastal waters (PN) from the Tyne ($1.3 \times 10^{-6} \text{ Tg N a}^{-1}$) Rivers is $\sim <0.3\%$ of their estimated annual DIN inputs ($\sim 1.8 \times 10^{-3} \text{ Tg N a}^{-1}$ for each system). The global annual continental shelf ammonium photoproduction was estimated at $78 \pm 55 \text{ Tg N a}^{-1}$. The magnitude of such estimates demonstrates the role and importance of photoammonification in the aquatic N-cycle.