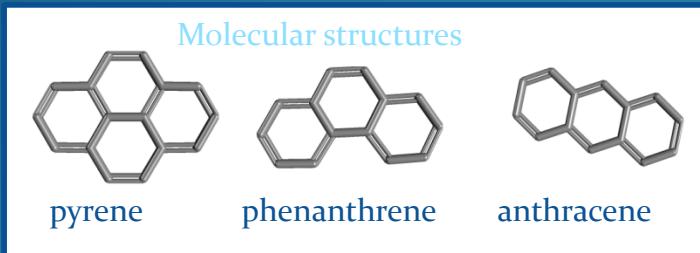


Solution medium effects on the photolysis of polycyclic aromatic hydrocarbons (PAHs) in aqueous medium

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Introduction

PAHs are carcinogenic compounds formed from fossil fuel combustion. They are degraded by sunlight in natural waters. Our study examines the effect of salts and humic acids (produced from degrading plants) on the rates, pathways and products of PAH photolysis in water.



Conclusions

These results contrast with those we previously obtained for pyrene, which exhibited: 1) a salt effect suggesting the role of charged species in a rate limiting step in the kinetic mechanism; and 2) DOM effects other than simple competitive absorption suggesting sensitization through binding. This suggests that these PAHs undergo different photodegradation pathways , possibly via a photoionization mechanism for pyrene vs. direct photolysis for phenanthrene and anthracene. They also likely have different binding constants to humic acid with pyrene being more strongly bound and its photolysis thus affected beyond simple light absorption effects.

Results

Phenanthrene photolysis followed first order kinetics, with an estimated photodegradation half-life in sunlight in pure water of 10.3 ± 0.7 hours, in the mid-range of previously published results. Photolysis rate constants decreased by a factor of 5 in solutions with humic acid concentrations from 0 to 10 mg C L⁻¹. This decrease could be modeled entirely based on competitive light absorption effects due to the added humics. No significant ionic strength or oxygen effects were observed, consistent with a direct photolysis mechanism. In the absence of significant solution medium effects, the photodegradation lifetime of phenanthrene will depend only on solar fluxes (i.e. temporal and seasonal changes in sunlight) and not vary with a freshwater to marine environment.

Similar results were observed for anthracene. , However the photolysis rate was significantly faster than phenanthrene. The anthracene half-life was estimated to be 1.5 minutes.

Solid phase micro-extraction GC/MS and fluorescence quenching approaches to measuring DOM-PAH binding coefficients were investigated. The fluorescence quenching approach was found to be more sensitive and suitable for undergraduate student capabilities. Binding coefficients of 0.0352 for chrysene and 0.056 L/mg humic acid for benzo(a) anthracene were measured in pure water.

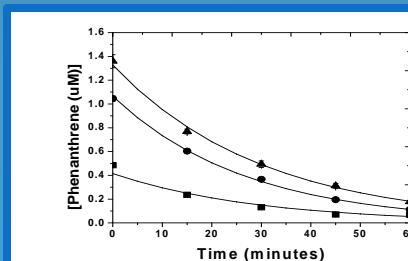


Fig. 1 Concentration vs. time
For irradiated phenanthrene in water

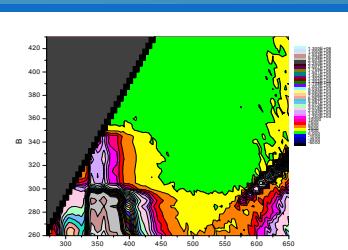


Fig. 2. 3D excitation-emission matrix
Fluorescence spectrum of phenanthrene .
Post-irradiation, peak intensities decrease