Photochemical CDOM transformations & inorganic nitrogen production

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Overview of PhD Research

- Ammonium photoproduction
- Nutrients (nitrate, nitrite, phosphate), optical properties of chromophoric DOM
- We take regular measurements of photoammonification at monthly intervals offshore
- Seasonal and temporal photoammonification rates have never been investigated.
- Likely to be influenced by nitrogen inputs from photoammonification (e.g. nitrogen limited, stratified surface waters).

Absorbance measurements provide details of DOM levels and chromophores involved in degradation.
- To investigate the composition, concentration, distribution and dynamics of DOM cycling in the natural environment, we use 3D fluorescence excitation emission matrices combined with parallel factor analysis (PARAFAC) (see case study opposite).
- Advantages of this method include its sensitivity, negating the need to use extracted DOM samples. Measurements are rapid and require minimal sample volumes and preparation.

(1) Degradation of DOM - photobleaching

Irradiation of DOM causes absorbance and fluorescence loss, often called "photobleaching".

- Differential spectra (dark – light) of seawater absorbance during irradiation (~26hr)

(2) Ammonium photoproduction

Coverage of measurements
- Ammonium photoproduction measurements are biased towards fresh inland and river waters with few marine measurements. Our research focuses on marine areas likely to be influenced by nitrogen inputs from photoammonification (e.g. nitrogen limited, stratified surface waters).

Seasonal variations
- Seasonal and temporal photoammonification rates have never been investigated. We take regular measurements of photoammonification at monthly intervals offshore the Northumberland coast, NE, UK. We also measure temperature & salinity (CTD), nutrients (nitrate, nitrite, phosphate), optical properties of chromophoric DOM, dissolved organic carbon (DOC) and chlorophyll a.

Ammonium photoproduction from dissolved organic nitrogen on exposure of seawater samples to light (May 2007).

NH₄⁺ production and optical properties
- Large scale estimates of the influence of ammonification on nitrogen cycling require a proxy for production of ammonia. We investigate relationships between optical properties and ammonification rate. We also measure the apparent quantum yields of NH₄⁺ production.

(3) Impact of labile/volatile photoproducts

Photochemical DOM degradation produces biologically labile (e.g. NH₄⁺, amino acids) and gaseous (e.g. CO₂, DMS) photoproducts.

Increased microbial and plankton production has been observed in irradiated waters suggesting DOM photodegradation has significant effects on C & N cycling. We will study the effect of photodissociation on N budgets and investigate the combined photochemical and biological processes on DOM degradation. Estimates, and if possible measurements of associated gaseous photoproducts will be determined.

Summary of research
- Ammonification rates and kinetics of ammonium release from previously ignored, oceanic areas
- Increased understanding of link between DOM degradation and ammonium release
- Effect of DOM degradation on productivity
- Determination of proxies for ammonification rates from easily measurable optical properties

Tyne Estuary Case Study

Aims: To investigate if surface microlayer (ML) DOM has different composition & photochemical degradation rates compared to underlying bulk waters.

Why? The ML controls the air-sea exchange of substances between the hydrosphere and atmosphere. ML composition and degradation processes may influence this transfer of substances and alter the spectral irradiance in surface shallow waters.

ML and bulk water samples were collected along an estuarine transect (left), and analysed for absorbance & 3D fluorescence (0.2µm filtered). Samples from three sites (1, 3 & 5) were irradiated for 4 hours in a solar simulator.

3D Fluorescence scans of dissolved organic matter (DOM) were decomposed using PARAFAC to determine independent DOM fractions. Degradation rates were determined by calculating the half life of the component, assuming first order decay kinetics.

Absorbance
- An enrichment of ML DOM absorbance in relation to the underlying waters occurred at increasing salinities.

ML: Humic fraction from Howden sewage treatment plant, Bulk: Humic fraction from bulk seawater.

Summary of results
- More refractory DOM in ML compared to bulk waters is observed: ML may reduce bulk DOM degradation
- Humic-like fluorophores degrade at a faster rate than protein-like fluorophores
- Protein-like compounds may be photochemically produced
- ML and bulk humics display decreasing half lives with increasing salinity

Sample sites along the Tyne Estuary, North East England. Sites 1-6 spanned a salinity gradient of 0 - 32.

Absorbance coefficient (a₃₅₀) ratio (ML:bulk).
- Ratio >1 = ML enrichment
- Ratio <1 = ML depletion
- The peak (site 3) is likely to be the result of human-derived DOM from the Howden treatment plant.

Fluorescence

Preliminary modelling results identified 3 components that explained >90% of the fluorescence variability. Irradiation experiments identified differences in the degradation properties of each component (site 1 results below).

Humic-like fluorophores degrade at a faster rate than protein-like fluorophores

"Protein-like" components were produced, & possibly subsequently removed, during irradiations.

"Humic-like" components were removed during irradiations at differing rates.

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