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Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea

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Abstract

The release of ammonium from the photochemical degradation of dissolved organic matter (DOM) has been proposed by earlier studies as a potentially important remineralisation pathway for refractory organic nitrogen. In this study the photochemical production of ammonium from Baltic Sea DOM was assessed in the laboratory. Filtered samples from the Bothnian Bay, the Gulf of Finland and the Arkona Sea were exposed to UVA light at environmentally relevant levels, and the developments in ammonium concentrations, light absorption, fluorescence and molecular size distribution were followed. The exposures resulted in a decrease in DOM absorption and loss of the larger sized fraction of DOM. Analysis of the fluorescence properties of DOM using parallel factor analysis (PARAFAC) identified 6 independent components. Five components decreased in intensity as a result of the UVA exposures. One component was produced as a result of the exposures and represents labile photoproducts derived from terrestrial DOM. The characteristics of DOM in samples from the Bothnian Bay and Gulf of Finland were similar and dominated by terrestrially derived material. The DOM from the Arkona Sea was more autochthonous in character. Photoammonification differed depending on the composition of DOM. Calculated photoammonification rates in surface waters varied between 121 and 382 μmol NH_4^+ L^{-1} d^{-1}. Estimated areal daily production rates ranged between 37 and 237 μmol NH_4^+ m^{-2} d^{-1}, which are comparable to atmospheric deposition rates and suggest that photochemical remineralisation of organic nitrogen may be a significant source of bioavailable nitrogen to surface waters during summer months with high irradiance and low inorganic nitrogen concentrations.

Keywords: Coloured dissolved organic matter; Ammonium; Photochemistry; Baltic Sea

1. Introduction

It is estimated that globally 70% of the nitrogen exported to coastal waters is bound within the pool of dissolved organic matter (DOM) (Meybeck, 1982). Free and combined amino acids, urea, nucleotides, moieties of fulvic and humic acids and other uncharacterised high molecular weight biomolecules all contribute to the pool of dissolved organic nitrogen (DON) (Bronk, 2002). The bulk of DON is present in the largely uncharacterised fraction (Bronk, 2002; Benner, 2002). As a result many aspects of the role of dissolved organic nitrogen as a nutrient source for marine production are not fully

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understood. One such process is photoammonification; the production of ammonium upon the exposure of DOM to UV light (Bushaw et al., 1996).

Over the last 10 years a series of studies on the occurrence and significance of photoammonification have been carried out. The results published appear to be contrasting (see brief review in Grzybowski (2003)). They can be classed into four categories; i) detectable ammonium production at environmentally relevant rates (e.g. Bushaw et al., 1996; Gao and Zepp, 1998; Vähätalo et al., 2003), ii) detectable ammonium production with questionable ecosystem relevance (Buffam and McGlathery, 2003), iii) no detectable production (e.g. Jørgensen et al., 1998; Bertilsson et al., 1999; Wiegner and Seitzinger, 2001) and iv) photochemically mediated incorporation of ammonium into DON (Kieber et al., 1997; Koopmans and Bronk, 2002; Vähätalo et al., 2003). These results likely reflect the fact that the process is specific to the original composition of the DOM pool, which can be expected to vary both geographically and seasonally. Additionally ambient concentrations of ammonium appear to influence the net result with high ammonium concentrations tending to result in a net loss of ammonium as a result of photodegradation (Kieber et al., 1997; Koopmans and Bronk, 2002).

Before comparing photochemical production rates or quantities between studies or samples it is important to normalise the production to the amount of light actually absorbed by the sample in the reaction vessel (Hu et al., 2002; Vähätalo and Zepp, 2005). The experimental conditions (e.g. intensity, spectral properties of the irradiation, path length and shape of incubation vessels, and exposure time) influence the result and make inter-study or even inter-sample comparison often difficult (Hu et al., 2002).

As with many coastal seas in densely populated regions, the Baltic Sea suffers from eutrophication. It has a limited water exchange with the Atlantic Ocean (via the North Sea) resulting in riverine inputs having considerable influence on its nutrient budgets. Riverine inputs are estimated to be responsible for 60% of the nitrogen supply to the Baltic (Stålnacke et al., 1999). Other important sources are atmospheric deposition and phytoplankton nitrogen fixation. Although about half of the freshwater total nitrogen supply is as dissolved inorganic nitrogen (DIN) (Stepanauskas et al., 2002), estuarine and near-shore biological productivity transforms a substantial amount DIN to DON (Stedmon et al., 2006) before it is transported offshore to the open Baltic Sea. This exported DON is a combination of terrestrially derived material and coastal/estuarine autochtonously produced material, and little is known about its susceptibility to photochemical degradation. Recently a study in the Gulf of Finland showed that DON can be photochemically mineralised to ammonium using simulated sunlight (Vähätalo and Zepp, 2005). Photoammonification was found to occur at rates which were similar to atmospheric deposition and thought to be an important source of bioavailable N, in offshore waters.

The aim of this work was to study the photochemical production of ammonium from samples from differing sites in the Baltic Sea and assess the its significance as a nitrogen source for offshore productivity. In conjunction changes in the optical characteristics (absorption and fluorescence properties) and molecular size distribution of the DOM were followed in order to detect the effects of photodegradation on DOM characteristics and take into account qualitative and quantitative differences between samples before and during the exposures.

2. Methods

2.1. Sampling and experimental set up

Water samples were collected during summer 2005 from three regional water quality monitoring stations in the Baltic Sea; Arkona Sea (St444, 55°00′N, 13°18′E, August), Kotka (St12370, 60°15′N, 27°15′E, August), and Oulu (St30372, 65°08′N, 24°36′E, September) (Fig. 1). Surface water samples were collected and placed in 5 L acid washed polyethylene containers and kept refrigerated (4 °C) and in the dark for 2–3 days before arriving at NERI, Denmark. In the laboratory each sample was first filtered through a pre-combusted GF/F filter, then subsequently filtered through 0.2 μm Millipore filter (pre-cleaned with 500 mL of Milli-Q) in order to remove the majority of bacteria. After filtration the water from each site was distributed into 24 quartz tubes (approximate volume of 200 mL). Twelve of the tubes were wrapped in aluminium foil and used as a dark control, whilst the remaining twelve were placed in front of a UV-A lamp (Q-panel, UVA340). The dark controls were incubated next to the exposed samples. There was no headspace in the tubes, and they were sealed with ground glass stoppers. Incubations were carried out at room temperature and the experimental set-up was black in order to limit internal reflection of light. Fig. 2 shows the spectral distribution and intensity of the lamp irradiance incident on the quartz tubes. The spectral properties of the lamp light and its intensity in the UV region of the spectrum was equivalent to that observed in summer at these latitudes (Fig. 2). Triplicate tubes from each treatment (UVA and dark) were harvested after 0, 6, 24 and 48 h. As an additional control for