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Dark recovery of photodegraded chromophoric dissolved organic matter



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ABSTRACT

Aged samples of natural waters filtered with Whatman GFF filters had been irradiated with UVA radiation then stored in darkness and checked for changes in absorbance of chromophoric dissolved organic matter (CDOM). The recovery of absorbance (integrated within 250–600 nm wavelength range) of irradiated river water, lake water and seawater during 72 h dark storage at room temperature was 17, 34 and 25% respectively. The highest relative increase in absorbance was in the long wavelength part of the optical spectrum. The recovery was smaller in the samples kept at lower temperature.

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1. Introduction

Chromophoric dissolved organic matter (CDOM) is a light-absorbing component of organic matter dissolved in natural water. The ability to absorb sunlight results in the destruction of chromophores and the loss of water absorbance. This phenomenon, known as photobleaching, has been the subject of numerous investigations [24,6,17,23,20,22,11,26]. CDOM degradation via direct photoreactions stops with termination of irradiation and efficiency of the dark reactions seems to be limited due to fast decay of reactive photoproducts [14]. It is generally assumed that organic products of irradiation are chemically stable and very few reports on post-irradiation changes of phototransformed organics can be found in the scientific literature. Wheeler [25] showed that the absorbance of seawater/lipid solution increased after irradiation with UV. Kieber et al. [13] reported similar effects in irradiated seawater enriched with trinoleine that had been stored in the dark. The authors concluded that "It is unclear from these data whether new humic-type material was formed from the spiked trinolein, or if there is a reversal of the photobleaching of the ambient DOM". The present study suggests the possibility of the latter phenomenon.

2. Materials and methods

The samples of lake and river water were collected from Wdzydze Lake and the lower Vistula River (Poland) in summer

2015. In October 2015, the surface seawater was sampled from the deck of a sailing yacht located in the North Sea, five miles west from Stavanger (Norway). The samples were filtered onto Whatman GFF filters (47 mm diameter, $\sim 0.7 \mu\text{m}$ pore size) and aged in glass, half-filled carboys at room temperature, in the dark. In addition to the samples of natural water, a representative sample of commercially available humic substances, i.e. Aldrich humic acid sodium salt (technical grade, Sigma-Aldrich) was used. In this case, the solution was prepared and filtered one week prior to irradiation treatments that took place in December 2015. Immediately before irradiation, the samples were filtered again using Whatman GFF filters, then poured into pre-cleaned glass vessels and vigorously shaken in order to obtain oxygen saturation. All the glassware was cleaned by soaking it in 0.1 M HCl, rinsing with Milli-Q water, and baking at 450 °C for 12 h. Whatman GFF filters were baked first and then rinsed. Irradiation was performed in quartz tubes (in triplicate per one water type) of 8 mm inner diameter and 60 mL volume. Prior to irradiation, the tubes filled with sampled water were left for 8 h and then emptied and refilled. The water samples were exposed to UV radiation emitted by Cleo Advantage fluorescent tubes for 20 h. The dark controls were additionally wrapped in aluminum foil. The tubes were placed horizontally in a shallow water bath, the temperature was kept below 30 °C using tap water cooling. The distance between the tubes and the lamp was 4 cm. Radiation was measured with broadband sensors. The readouts of the UVB (280–315 nm) and UVA (315–380 nm) sensors were 6.3 W m^{-2} and 79.8 W m^{-2} , respectively. These values were approx. 3 fold higher than those recorded at midday hours in June in Gdynia, Poland (54 °N).

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The concentration of Dissolved Organic Carbon (DOC) was determined using a Vario Cube TOC analyzer by the non-purgeable organic carbon method. Twenty-milliliter aliquots of sampled water were poured into glass vials, acidified with 50 μl HCl (10 M) and then sparged with ultrapure oxygen for 10 min prior to combustion (it should be noted that this method does not include volatile organic compounds). The water samples (but not replicates) in the autosampler holder were interspaced with the vials containing acidified Milli-Q water. The limit of detection (LOD) was 0.05 mg l^{-1} . All samples were analyzed in triplicate.

The irradiated samples and dark controls were stored in the quartz tubes at room temperature (19–22 °C) in the dark. The replicates of lake water were kept in a refrigerator at 6 °C to be later warmed up before the measurement by placing them in a bucket filled with water at room temperature. Absorption spectra were recorded using a Jasco 630 V dual-beam spectrophotometer in 100-mm quartz cuvettes with Milli-Q water used as a reference. The spectrophotometer was warmed up 2–3 h prior to use. The quartz cuvette was filled to 2/3 of its volume (the level was marked on the side of the cuvette). Each measurement was commenced 20–30 s after placing the cuvette in the sample compartment with a 400 nm min^{-1} scan speed and a data interval of 1 nm. The cuvette was sequentially rinsed with Milli-Q water and the sampled water, however, it was not rinsed between the replicates of the same sample. The spectrum of Milli-Q water, recorded at the beginning of the measurements, was used for checking the apparatus stability. The absorption values (A) were converted to Napierian absorption coefficients (a) according to the equation $a = 2.303 \cdot A/l$, where l is the optical path length expressed in meters. The limit of

detection for the absorbance measurements (defined as triple standard deviation of the blank) was obtained by measuring the absorbance of Milli-Q water kept in separate quartz tubes. LOD increased from 0.01 to 0.02 m^{-1} between the long and short wavelengths parts of the spectrum.

3. Results

As illustrated in Fig. 1, irradiation caused a significant decrease in CDOM absorption. The losses, in terms of “total” absorbance (absorption coefficient integrated within the range of 250–600 nm), ranged from 48% in seawater to 53% in lake and river water. It should be noted that the most effective photobleaching occurred in the spectral range below 300 nm, which is outside the range of applied irradiation source.

The additional immediate effect of irradiation was a small but statistically significant ($p < 0.01$; two-tailed, paired t -test) increase in absorbance observed in the samples of lake and river water at the long wavelength end of optical spectrum (see Supplementary information for lake water raw data). The values of seawater absorbance within this part of the spectrum were below the limit of detection.

DOC concentrations did not significantly change during the irradiation treatment, except for the river water sample. For both non-irradiated and irradiated samples, no measurable changes in DOC concentration were detected during the post-irradiation storage.

The preliminary part of the experiment consisted of monitoring the changes in the irradiated separate replicates stored in the dark

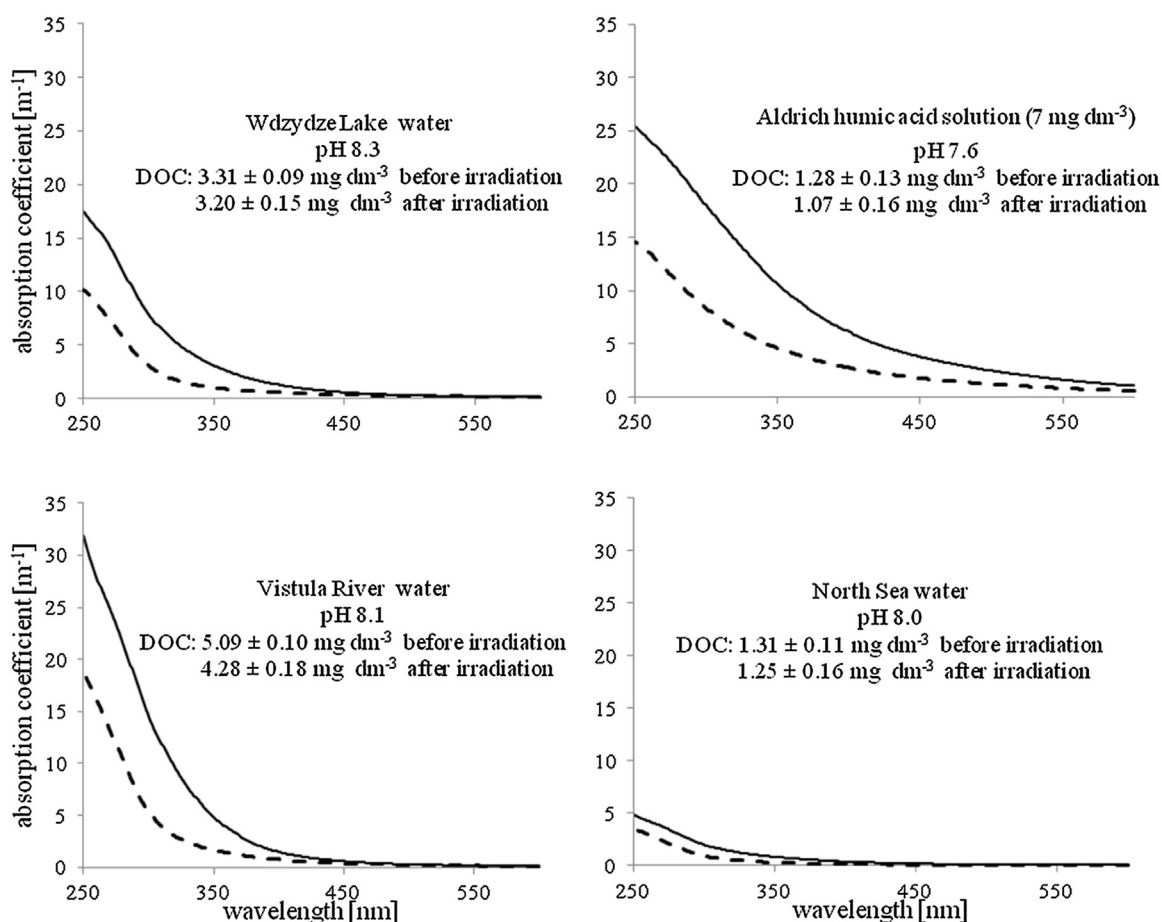


Fig. 1. Basic characteristics of the analyzed water samples.

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