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Photodegradation of aquatic humic substances: An important factor for the Baltic carbon cycle?

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Although humic substances (HS) are often considered as chemically stable and non-biodegradable in a marine environment, it is well known that exposure to light will lead to a decomposition of these substances. Laboratory experiments of photodegradation by UV-irradiation of aquatic humic substances and natural water resulted in a rapid and quantitative degradation. Seasonal variations in the humic fraction of the total organic carbon (TOC) was indicated in field studies in humic-rich water in Sweden. The HS/TOC-ratio was considerably higher during the dark part of the year than during the light season. Both the laboratory results and the field studies indicate the potential importance of photodegradation of HS and formation of CO_2 for the global carbon cycle, though other mechanisms like microbial degradation are possible. Furthermore, the formation of biodegradable low-molecular weight organic acids from terrestrial humic substances may be essential for partly heterotrophic systems like the Bothnian Bay.

Introduction

Humic substances (HS) of terrestrial origin represent a large but not well characterized part of the total organic carbon (TOC) found in the sea (Meyers-Shulte and Hedges 1986). HS are still generally viewed as biologically inert and they are not supposed to take part in a significant way in the nutrient dynamics of the sea. Flocculation and deposition of the high molecular weight (HMW) organic fraction on the bottoms (Sholkovitz 1976, Fox 1983) or adsorption to mineral particles (Davis and Gloor 1981) and thereafter a decomposition are the accepted mechanisms of their sink. There is indications that a major part of the riverine dissolved organic matter (DOM) is mixed conservatively in some estuaries (Mantoura and Woodward 1983), suggesting that the above mentioned sinks are at most slow processes. Nevertheless, budget estimations (Elmgren 1984) from the subarctic Bothnian Bay in the northern part of the Baltic Sea show that the end products, probably CO_2 and low molecular weight (LMW) organic acids (Bertilsson and Allard 1996, Dahlén *et al.* 1996) will to a large extent be brought back into the water mass and possibly to the atmosphere. Only a small fraction of the supplied TOC is assumed to sequester in the sediments. Therefore the load of terrestrial HS to the ocean represents a potential source of both nutrients (LMW organic acids, inorganic nitrogen and phosphorus) and CO_2. Important questions are the decomposition rate and the fate of the end products. The present work is devoted to a possibly important mechanism in the global carbon cycle namely photodegradation studies of HS in the laboratory. Though the laboratory experiments are compared with field studies in the Baltic Sea, they have broader implications. The temperate or subarctic Baltic Sea is heavily loaded by HS from forests or wet lands. This combined with its slow turn over makes the Baltic an ideal testbench for the carbon dynamics of the Arctic.

Degradation by UV radiation

Laboratory studies

Light-induced degradation experiments of HMW organic fractions have been performed on isolated aquatic humic substances as well as on natural water from a lake with a fairly high TOC (10–15 mg l^{-1}). Some results from these laboratory studies are described here whereas experimental details are found in other publications.

A fulvic acid dissolved in water was irradiated with UV light (intensity of 16 W m^{-2} at 254 nm) for periods between 0 and 60 hrs (Allard *et al.* 1994). The intensity used can be compared with the intensity from the total skylight of 1 kW m^{-2} over the wavelength range 280 to 2 800 nm (Nowell and Hoigne 1992), although it comprises the most energetic parts of the spectrum. This highly energetic light resulted in a degradation of FA by up to 50% in about 5–6 hrs shown by both losses of TOC and a reduction of the UV absorbance within the range 220 to 500 nm (Allard *et al.* 1994). The average molecular weight of the FA decreased from above 1 800 (M_n) to below 1 000 after 1 hr of irradiation and further to around 500 after 8–10 hrs and to 300 or below after 24 hrs. The decrease in molecular weight was accompanied by a production of LMW organic acids detected using capillary zone electrophoresis (CZE). Up to 60% of the remaining TOC could be accounted for, the main product being acetic acid.

Similar irradiation experiments were also carried out with lake water (Lake Bjän, a shallow lake in southern Sweden with predominant coniferous forest and bogs in its catchment). It was performed at both 254 and 365 nm (light intensity 8 W m^{-2}). Parallel tests on irradiated and non-irradiated water samples are shown in Fig. 1. It is evident that TOC and absorbance (at 365 nm) decreased with time in the irradiated samples while only minor changes were observed in those kept in the dark. However, the decay rate is much slower for the samples irradiated at 365 nm than for those irradiated at 254 nm. A similar response was obtained for filtered samples (0.2 µm) indicating insignificant microbial degradation. Other studies show that exposure of sterile filtered water from Lake Bjän to low intensity UV-A radiation for 89 hrs resulted in a decrease in the concentration of dissolved organic carbon (DOC) and to qualitative changes in the composition of the organic matter (Dahlén *et al.* 1996). A production of LMW organic acids was observed. Oxalic, malonic, formic and acetic acids were identified and quantified with CZE.

Thus, a substantial degradation of humic substances, induced by UV radiation, is obvious. It confirms previous observations reported already in the 70-ies and 80-ies (Strome and Miller 1978, Conrad and Seiler 1980, Mopper and Stahovec 1986, Kieber and Mopper 1987, Kieber *et al.* 1987) and suggested already by Whipple (1914). The proposed formation of mainly low-molecular weight acids (Conrad and Seiler 1980, Mopper and Stahovec 1986, Kieber and Mopper 1987, Kieber *et al.* 1987) are confirmed, and the dominating ones quantified. HS have generally been considered by biologists as the refractory part of the DOC (Elmgren 1984, Fenchel and Blackburn 1979) and therefore of limited value for biological production. The humic fraction can be quantitatively photodegraded in a short time (hours - days), forming biologically labile compounds as shown above. HS have been found to have a positive influence on the productivity of phytoplankton (Granéli *et al.* 1985, Tranvik 1988) and of bacterial biomass (Bertilsson and Allard 1996). Further, microcosm experiments (Wikner and Hagström 1991) have shown that UV radiation of HS stimulates the bacterial growth. These experiments indicate that organically bound nitrogen in HS becomes available for primary production. Schnitzer (1985) reports a nitrogen content of 0.5–3% and up to 5–6% in FA and HA, respectively. The previously sug-

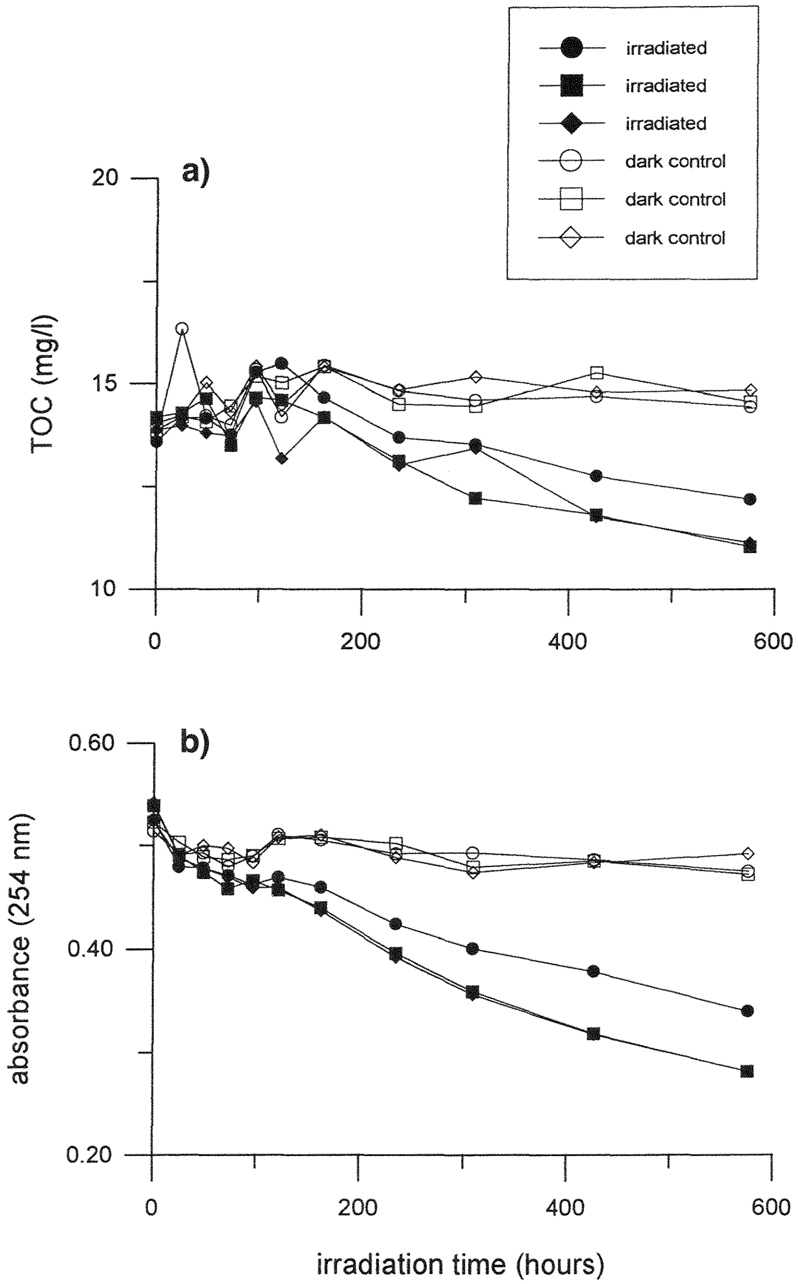

Fig. 1. Changes in TOC (a) and absorbance at 254 nm (b) after irradiation with UV light at 365 nm of water samples from Lake Bjän.

gested importance of photchemically produced bioavailable compounds and nutrients is clear.

Field studies

Photodegradation is obviously fast enough to cause diurnal variations of TOC in surface waters, which has also been reported (see e.g. Kieber *et al.* 1989). The HS fraction of TOC is expected to vary with the length of the day. An attempt to measure the HS fraction (spectrophotometric determination at 250 nm) have been done using samples from the Kalix River, Sweden, in the northern part of the subarctic oligotrophic Gulf of Bothnia. This river, which is unaffected by

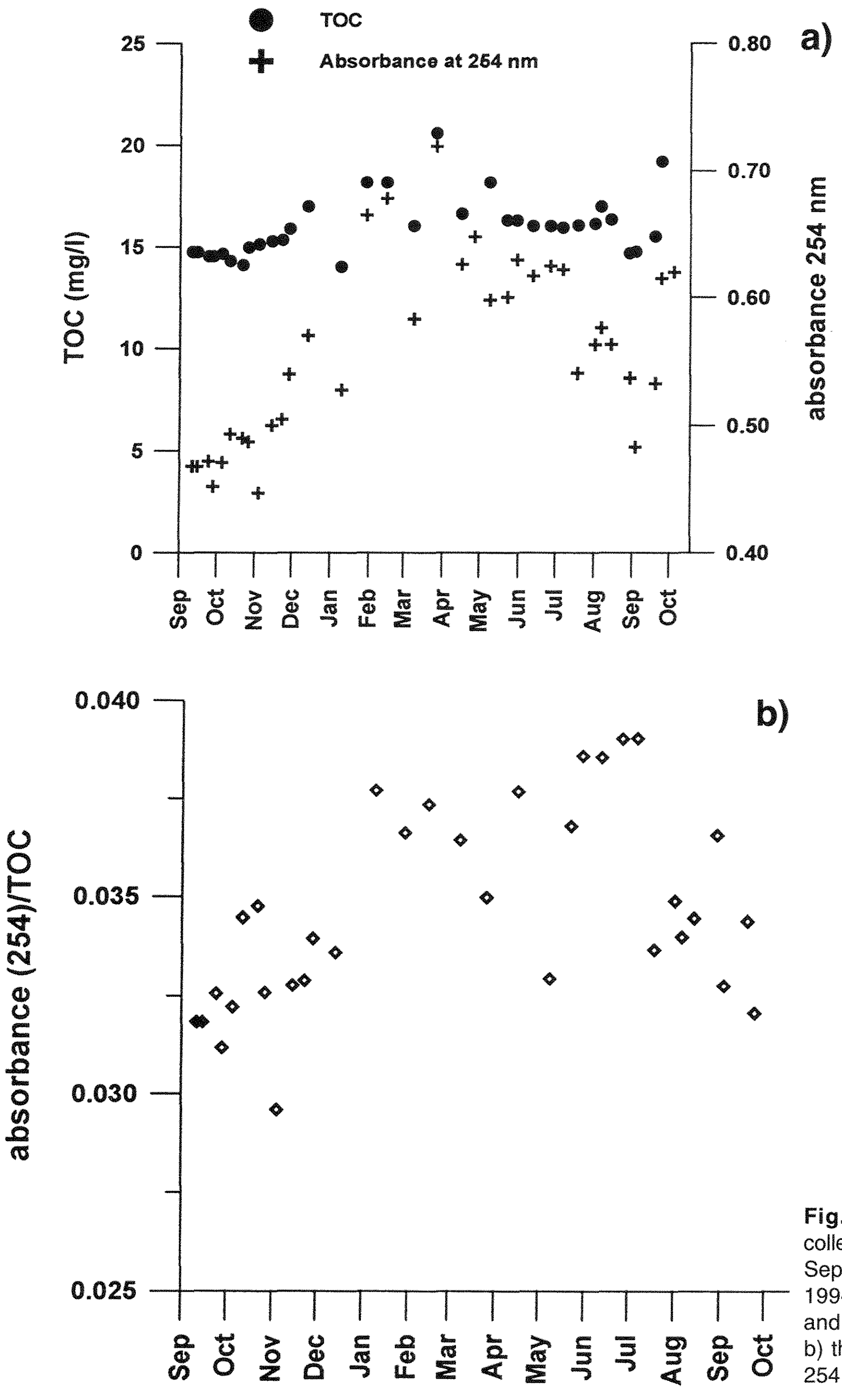

Fig. 2. Water samples collected in Lake Bjän during September 1993 to October 1994. Variation in a) TOC and absorbance at 254 nm; b) the ratio (absorbance at 254 nm)/TOC.

hydroelectric power plant installations, is close to the Arctic Circle, with daylight most of the summer and a corresponding darkness during winter. Time series (weekly samples over 13 months) show a higher abs$_{250}$/TOC-ratio during the dark period by a factor of 2–3 (Allard *et al.* 1994). However, the increase in the ratio is difficult to interpret. It might be an effect of an increased fraction of HS which, however, can be superimposed by a fairly high absorbance caused by suspended matter containing iron released during the winter. Microbial degradation and drainage from deeper soil strata are two other possibilities but the microbial activity is low during the winter season as is the specific leakage. If the leakage originates from the deeper parts of the soil, it is reasonable to expect a decreasing TOC in consort with the humic concentration contrary to what is observed in the Kalix River.

Analysis of water samples from Lake Bjän collected during one year showed a fairly constant TOC level but a large variation in the absorbance analysed at 254 nm (Fig. 2a). Thus, an increase in the ratio absorbance/TOC was obtained during the winter period (Fig. 2b). The increase of the humic fraction might in this case be explained by a slower degradation during the winter. No indications of influence from particulate iron have been observed in the lake but the effect of the ice and snow cover during the winter is not fully analysed.

Another experiment that shows the efficiency of photodecomposition is given by Wedborg *et al.* (1994). They exposed water samples from the Baltic proper placed in quartz beakers to daylight. A 50–70% decrease in fluorescence was obtained over five days exposure. Finally continuous daylight exposure of humic rich water samples from rivers and coastal water along the Siberian coast during the month of July (1994) further confirms the rapid light-induced degradation of the HMW organic matter (Rahm *et al.* 1994).

TOC and Bothnian Bay

Knowledge about kinetics and fate of riverborne TOC supplied to the sea is poor as is evident from above. Nevertheless, it has implications for both the marine ecosystem and the carbon cycle. Since the oceans contain about fifty times as much CO_2 (the ultimate end product in the TOC degradation) as the atmosphere and there is a regular exchange of CO_2 between them, the oceans play an important role in the global carbon cycle and in the global climate. In this perspective it is important to identify and, if possible, quantify the various mechanisms controlling this carbon cycle. The scale of the processes involved makes it productive to study a limited semi-enclosed sea such as the Bothnian Bay.

The primary production is phosphorus limited in the Bothnian Bay (Granéli *et al.* 1990). It receives fresh water from, among others, the Kalix River. It has a short growing season (4–5 months) and a low primary productivity of about 28 g $Cm^{-2}yr^{-1}$ (Elmgren 1984) compared to the eutrophic, nitrogen-limited Baltic proper (Granéli *et al.* 1990). The latter have some 7–10 months growing season and a substantial primary production of about 156 g $Cm^{-2}yr^{-1}$ (Elmgren 1984). This productivity should be compared to the corresponding terrestrial TOC input (80% of which are humic substances; Pettersson *et al.* 1996) of 21 and 5 g $Cm^{-2}yr^{-1}$ for the Bothnian Bay and the Baltic proper, respectively (Elmgren 1984). While the latter is dominated by autotrophic production there are strong indications that heterotrophic production dominates the Gulf of Bothnia (Wikner and Hagström 1991), i.e. the primary production is to a large extent based on the supply of terrestrial organic matter. It has been known for the last decade that the heterotrophic production is more important for the zooplankton population than phytoplankton in this region (Kankala *et al.* 1983). A mass budget (Wulff and Stigebrandt 1989) based on HS data by Nyquist (1979) gives an annual internal sink of roughly 9 g $Cm^{-2}yr^{-1}$ in the Bothnian Bay. Up to 90% of this is eventually remineralized, probably released as CO_2, and only about 2 g $Cm^{-2}yr^{-1}$ is assumed to be sequestered in the sediments (Elmgren 1984). These figures indicate a fairly rapid decomposition of terrestrial HS which would support the heterotrophic production.

Arctic Ocean

Tundra environment occupies some 7% of the Earth's land area and contains about 13% of its soil carbon (Post *et al.* 1982). The pathways of this carbon under potentially changing global climate is an important question. Some carbon leaves the tundra by river runoff and enters the oceans. A CO_2 budget of the Arctic Ocean based on total carbonate measurements (Andersson *et al.* 1990) states that half the total carbon supply from the tundra is as organic matter (40×10^{12} g C yr^{-1} from a total freshwater runoff of 3.5×10^{12} m^3 yr^{-1}, giving a TOC concentration of about 10 mg l^{-1}). This is about 20% of all carbon sequestered annually in northern ecosystems (Oechel and Strain 1985). It will also represent 5–13% of the global TOC river load (Longhurst 1991). TOC is supposed to be deposited and decomposed in the sediments, releasing CO_2 that in the end becomes a part of the total amount of carbonate of the Arctic Ocean. Our hypothesis is that UV degradation of TOC is a fast and efficient process leading to a partial decomposition of a large fraction of the TOC that is supplied with the freshwater to the stably stratified shelf and coastal regions during the summer season. The presence of this stable, low saline, surface layer would increase the possibility of exposure to UV radiation during the summer months as the mixing with deeper lying water masses are limited. Note that the transparency of UV radiation may be small due to the high concentrations of HS but intense mixing in the surface layer will anyhow result in an efficient exposure of the HS. A high degree of turbidity will, on the other hand, decrease the efficiency of the radiation. The result of the above mentioned process should be an increase of both the bioavailability of organic carbon and CO_2 release. The degraded TOC may also act as a nitrogen and phosphorus source for the coastal zone.

Discussion

Our laboratory experiments as well as the literature presented above indicate that UV radiation is an effective degradation mechanism for HS. The experiments also show that the decomposition rates are strongly dependent on the wavelength. Moreover, the field studies presented indicate that UV induced degradation might be an important mechanism in nature. There is a well-known risk of increasing UV radiation in the future due to a decline in ozone concentration. An intensive work is directed to monitor the changing conditions of ozone concentration and UV radiation (Frederick and Alberts 1991, Beaglehole and Carter 1992) as well as the impact of these alterations on the life in the sea (Smith *et al.* 1992). Consequently photodegradation of HS may increase in arctic and subarctic waters in the future for the reasons discussed above. This would increase the formation rate of both labile organic substances, CO_2, and the terrestrial load of nitrogen and phosphorus associated to the HS. This would have consequences for both the oceanic primary production and the climate change. In regions like the subarctic Bothnian Bay changes in the supply and availability of organic matter should be of importance for both the food web structure and the carbon sink. For comparison, enhanced levels of UV-B radiation (in the range 280–320 nm) were associated with a substantial decrease in primary productivity in the Antarctic waters (Smith *et al.* 1992) which, however, in contrast to the Bothnian Bay, are poor in terrestrial organic compounds but rich in nutrients.

Analysed time series of humus concentrations in Swedish rivers during 1971–1986 (Andersson *et al.* 1991) show an increase in humus content of more than 3% yr^{-1} due to changed land use, increased terrestrial production and perhaps climate change. This gives an increased load of organic matter to the Baltic. Sofar, the only recognized long-term sinks in the ecosystem of northern Scandinavia are peat and sediments in lakes and coastal waters (Eriksson 1991). The special hydrological conditions of the large catchment areas covering the northern parts of the Euroasian and North American continents combined with their high organic carbon content makes the decomposition kinetics and the strongly seasonal load of TOC important in any investigation of the carbon cycle in these areas. The mixing properties of the surface layers and possible pycnoclines are also of importance, since they control the degree of UV-exposure. Hence the prospect of a changing climate in combination with a decreasing ozone layer is thought provoking in the light of the feedback mechanisms suggested above. We have not only to understand the role of HS in the land-ocean interaction but we must also be aware of probable effects of changes in e.g. climate and ozone concentration.

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