Dynamics of chromophoric dissolved organic matter and dissolved organic carbon in experimental mesocosms

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Abstract. Since CDOM can significantly influence the optical characteristics of Case II waters, we investigated potential sources of CDOM and DOC during a month-long mesocosm experiment. Nutrient additions resulted in a large phytoplankton bloom, followed by a rapid decline. Despite this, DOC and CDOM increased slowly and linearly and were only weakly correlated with Chl\textsubscript{a}. However, there were stronger correlations between CDOM and bacteria, and sedimentary CDOM fluxes varied from 0 to a value large enough to explain the increase of CDOM in the tanks. These results suggest that bacteria and sediments may be more important in CDOM production than phytoplankton on this time scale.

1. Introduction

Chromophoric or coloured dissolved organic matter (CDOM) is the fraction of the dissolved organic matter that absorbs light in both the ultraviolet and visible ranges. The presence of CDOM in natural waters has been known since the late 1940s, when Kalle (1949) first noticed that seawater fluoresced when illuminated by ultraviolet light. Since then many studies have been conducted to determine the optical characteristics (e.g. Coble \textit{et al.} 1990, Green and Blough 1994) and spatial distribution of CDOM (e.g. Hoge \textit{et al.} 1993, Chen and Bada 1992). Also known as ‘gilvin’, ‘gelbstoff’, or ‘yellow stuff’, CDOM is ubiquitous to all water bodies. High concentrations are found in marshes, lakes, and rivers with lower concentrations in estuaries and coastal regions (Kirk 1994). The lowest concentrations of CDOM are found in open ocean regions, particularly mid-oceanic gyres such as the Sargasso Sea (Vodacek \textit{et al.} 1995).

Because CDOM absorbs both in the visible and ultraviolet ranges, it can represent a significant fraction of the total absorption of light in the water column. For example, in nearshore waters in August, DeGrandpre \textit{et al.} (1996) showed the absorption of CDOM at 442 nm easily exceeded that of particulates, which included absorption due to chlorophyll \textit{a} (Chl\textsubscript{a}). This is in contrast to the situation they observed in November, when the particulate fraction was dominant. At their furthest offshore station they observed a similar season reversal in dominance; however, the absorption by both components was much lower. This variability means that algorithms used to estimate Chl\textsubscript{a} concentration from ocean colour images have to take into account not only the presence of CDOM but must also consider the spatial...
and temporal variability in CDOM concentration. In coastal and estuarine systems, where CDOM is higher than in offshore regions, it is therefore particularly important to identify the sources and sinks of CDOM in order to assess the processes affecting the variability observed in CDOM concentrations.

Chromophoric dissolved organic matter is a part of the bulk pool of dissolved organic matter, usually measured as dissolved organic carbon (DOC). Until recently, DOC was thought to be a large pool with a long turnover time. However, recent developments in methodology have permitted the study of smaller scale dynamics of DOC cycling (Sugimura and Suzuki 1988, Sharp et al. 1993, 1995), and it has been shown that significant fractions of the DOC pool are consumed and produced at relatively short time scales (Kirchman et al. 1991, Carlson et al. 1994). Consequently, there has been a greater emphasis placed on the study of the importance of various sources and sinks of DOC.

Dissolved organic carbon is produced both autochthonously and allochthonously in natural waters. Within the water column, DOC is produced by cellular release during photosynthesis in the form of exudates (Sharp 1977), release of dissolved cellular contents as a consequence of viral lysis (Fuhrman and Suttle 1993) and from zooplankton sloppy feeding (Lampert 1978), release from zooplankton faecal matter and marine snow dissolution (Smith et al. 1992), and release during cell death and decay (Fukami et al. 1985). External sources of DOC include riverine inflows, wetland discharge, release from sediments (Burdige et al. 1992), and airborne inputs such as in precipitation and dry deposition (Velinsky et al. 1986). However, there has been very little research linking the in situ dynamics of DOC with those of CDOM.

There have been several studies of the external sources of CDOM. Concentrations are usually high in river waters, especially those with high humic and fulvic acid concentrations derived from soils. In black water rivers, very high CDOM concentrations from podzolic soils or peats are responsible for the tea-like colour of the water (Kirk 1994). Other identified sources of CDOM in estuaries includes sedimentary release (Skoog et al. 1996a) and inputs from wet deposition (Chen and Bada 1992).

In contrast, no direct biological sources of CDOM have been clearly identified. In recent work at the Bermuda Atlantic Time Series Station, Nelson et al. (1998) proposed that bacteria are a potential source of CDOM. They hypothesized that DOC from the spring phytoplankton bloom is processed into CDOM later in summer, resulting in a peak in fluorescence that is decoupled from the peak DOC concentration (Nelson et al. 1998). Moreover, Carder et al. (1989) also postulated that the increased CDOM concentrations that they observed in the Gulf of Mexico may have been due to the decline of a phytoplankton bloom that had been present in that region 11 days previously.

In contrast to our lack of information on biological sources of CDOM, a known removal mechanism for CDOM is photolysis (Skoog et al. 1996b). Chromophoric DOC is degraded by light into DOC compounds that do not absorb light in the ultraviolet and visible range (Keiber et al. 1989, Keiber et al. 1990; see also review by Moran and Zepp 1997). Photolysis of CDOM has also been shown as a source of inorganic nitrogen to coastal systems (Bushaw et al. 1996), and inorganic phosphate to fresh waters (Franko and Heath 1982).

The aim of this study was to investigate the dynamics of CDOM and DOC in a controlled mesocosm study. Production of DOC has been successfully studied in mesocosms, usually by observing the changes of DOC concentration following a
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phytoplankton bloom (e.g. Norrman et al. 1995, Smith et al. 1995). Here we extend this approach to examine the mechanisms by which CDOM may be biologically produced in such closed systems during an intense algal bloom initiated by experimental fertilization. This approach allowed us to estimate the time scales upon which CDOM may be produced in natural systems, which may have important implications for remote sensing of ocean colour. Mesocosms provide a mechanism by which studies of environmental ecosystems can be examined on smaller scales in controlled situations. They provide the investigator with the ability to control and even remove various factors from the experiment and therefore give the investigator the ability to isolate parts of the system. While useful for identifying potentially important mechanisms or processes, mesocosms may also provide information that must be carefully applied to natural systems that are much more complex.

2. Materials and methods

The data presented in this paper were collected during a 28-day experiment in October 1996. The mesocosms are part of the Multiscale Experimental Ecosystem Research Center (MEERC) at Horn Point Laboratory, which is funded by US EPA. The goals of MEERC are to understand the principles of scaling in the ecology of aquatic systems.

Three tanks of identical shape and size were used. The tanks are made of an inert plastic material, with dimensions of 1.13 m diameter and 1 m water depth. The exterior of each tank is surrounded with a silver foil covered bubble wrap insulation which effectively stops external radiation from entering the tanks from the side. The tanks are lit from above with fluorescent lights (Phillips Fluorescent Light F72T12/D/VHO) providing $200\mu\text{Em}^{-2}\text{s}^{-1}$ (or $8\text{Em}^{-2}\text{d}^{-1}$) of PAR (photosynthetically active radiation, 400–700 nm); the lights operate on a 12-hour light: 12-hour dark cycle, commencing at 0700. The daily irradiance totals are within the range expected for October in Maryland ($2–41\text{Em}^{-2}\text{d}^{-1}$) but are lower than the average monthly irradiance ($26\pm 9\text{Em}^{-2}\text{d}^{-1}$; Fisher et al. in press). Mixing within the tanks was obtained by mechanically controlled paddles operating at 3 rpm on a 4 hour on: 2 hour off cycle to achieve near-continuous vertical mixing and continuously oxidized sediment surfaces (Sanford 1997).

Prior to the start of the experiment, a 10 cm deep layer of homogenized sediment was placed in the bottom of each tank and allowed to settle for a week. The sediment had been initially collected in May 1995 from an adjacent cover in the Choptank River and had been stored in a holding tank except when it was in use in other experiments. The older mud was chosen instead of fresh mud for the experiment because of its low activity, which results in a small nutrient flux from the sediment (Cornwell, personal communication).

The tanks were filled with unfiltered estuarine water from the Choptank River, a sub-estuary of Chesapeake Bay. On Day 0 of the experiment 1.0 m$^3$ of water with a salinity of 9.3 PSU, was carefully added to each of the three tanks to prevent sediment disturbance. The water was distributed to the three experimental tanks simultaneously to ensure uniform water characteristics between the three tanks. For this experiment, river water had been initially collected and stored in a 10 m$^3$ holding tank for a month prior to filling the smaller (experimental) tanks. The water was stored in order to encourage the natural phytoplankton assemblages to deplete the nutrients present in the water, and the initial concentrations of dissolved nitrogen in each of the tanks were low ($\text{NO}_3^- = 0.89 \pm 0.13 \mu\text{M N}$, $\text{NO}_2^- = 1.03 \pm 0.07 \mu\text{M N}$,
NH₄ = 1.23 ± 0.15 μM N, urea = 0.09 ± 0.03 μM N). During this time, the holding tank was subject to both the same mixing and light regimes as the experiment in the smaller tanks.

The experiment reported here was part of another investigation, the goals of which were to examine the fate of nitrogen from different sources into various size ranges of the particulate fraction. To address this objective, three tanks and three nitrogen sources (nitrate, ammonium and urea) were used. This also provided the opportunity to investigate the effect of nitrogen source on the production of CDOM and DOC in these systems. Nitrate, ammonium, and urea can all be used by phytoplankton as their primary nitrogen source (McCarthy et al. 1977), and only one nitrogen source was added to each tank at the beginning of the experiment. On days 1, 2, and 3 at 0900, additions were made to each tank to increase concentrations by 5 μM N, and on day 4 a large pulse of nitrogen (25 μM N) was added to each tank in the respective nitrogen forms. On day 4, a pulse of phosphate (1 μM PO₄) was also added to relieve any phosphate limitation that might be occurring in the tanks with the large additions of nitrogen.

Water column samples were removed daily (0800) for the measurement of dissolved organic carbon (DOC), chromophoric dissolved organic matter (CDOM), chlorophyll a, nutrients, and bacterial number. On several days a more frequent sampling interval was adopted and samples were collected every four hours for a minimum of twenty four hours.

The water samples for all of the DOC/CDOM measurements were filtered through GF/F glass fibre filters in an all-glass, precleaned, filtration flask. Pre-cleaning of all glassware consisted of acid washing (10% HCL and copious rinses with deionized water), followed by combustion at 450°C for 1 hour; plastic was avoided whenever possible. Samples were stored in glass pre-cleaned bottles, sealed with Teflon lined caps, and frozen. The samples were kept frozen until the DOC and CDOM analyses were performed.

Prior to the DOC and CDOM measurements, the samples were defrosted at room temperature. Dissolved organic carbon concentrations were measured using an adaptation of the persulphate method (Sharp 1973, Sharp et al. 1995). For the analysis, 10 ml of sample was pipetted into an ampule, acidified with 100 μl 10% H₂SO₄ and gas stripped with oxygen for 10 mins. After initial CO₂ removal, 100 mg potassium persulphate were added as the oxidizing agent, and the ampules were gas stripped for a further 30 secs to remove any CO₂ introduced to the sample with the oxidizing agent. The ampules were then sealed under continuous flow of oxygen gas and immediately autoclaved for 55 minutes to convert organic carbon into CO₂ gas. During later analysis to measure the CO₂ derived from DOC oxidation, the ampules were broken in air and 7 ml of liquid was carefully removed into a 20 ml syringe. Then 0.25 ml of 10% H₂SO₄ was carefully added to the syringe without introducing air, followed by 7 ml of He gas. The syringe was shaken for 1 min to equilibrate the CO₂ between the gas and liquid phases, and the headspace gas was then injected into a gas chromatograph (Hach Carle Series 100 AGC) connected to a Hewlett-Packard 3393A Integrator. The CO₂ gas produced by DOC oxidation was calibrated against sucrose standards of known concentration ranging over 0–600 μM DOC. The sucrose standards were prepared in deionized water that had been previously autoclaved with potassium persulphate (10 g in 11 DI water) and ammulpted as outlined above for samples. The autoclaved DI water was also used as the experimental blank and was usually equivalent to 20–30 μM DOC.
The fluorescence of the chromophoric fraction was measured as soon as possible after the DOC analysis and always within 24 hrs. Prior to the analysis, the samples were stored in the dark in a refrigerator, and immediately prior to the optical measurements the samples were allowed to slowly warm to room temperature (20°C). The fluorescence of the samples was measured on an Aminco-Bowman Series 2 Luminescence Spectrofluorometer using a 1 cm quartz cell. An excitation wavelength of 355 nm was used, resulting in a water Raman response at 404 nm and a CDOM emission centered around 450 nm. Milli-Q water was used as a blank for the fluorescence measurements. All sample CDOM fluorescence intensities were normalized to the Raman and to an external standard, 10 μg l⁻¹ quinine sulphate in 10% H₂SO₄ (Green and Blough 1994), which is equivalent to ten normalized fluorescence units (NFIU, Hoge et al. 1993).

Concentration of Chl a of the samples was measured using the fluorometric method of Parsons et al. (1984) using excitation and emission wavelengths of 450 nm and 670 nm respectively. Briefly, duplicate volumes of water were filtered onto GF/F glass fibre filters, and the filters were frozen until analysis. The filter was ground and Chl a extracted in 90% acetone and the fluorescence was measured using a fluorometer (Turner Designs Fluorometer 10), calibrated with commercially available Chl a standard (Sigma Chemical Co.).

Water samples for the ambient nutrient concentrations were filtered through Whatman GF/F glass fibre filters. The filtrate was frozen for later determination of nitrate (NO₃), nitrite (NO₂), ammonium (NH₄), urea and total dissolved nitrogen (DON). Prior to analysis samples were defrosted at room temperature. Nitrate, nitrite and urea were measured colorimetrically using the methods of Parsons et al. (1984), ammonium was measured using the protocol of Solorzano (1969), and total dissolved nitrogen was measured on an Antek DON Analyzer.

The acridine orange direct count (AODC) procedure was used for bacteria counting. Water samples (5 mls) were preserved with glutaraldehyde, dyed with 80% acridine orange, then counted using epifluorescence microscopy (Hobbie et al. 1977).

Sediment cores were taken from the tanks at the end of the experiment to measure the fluxes of both DOC and CDOM from the sediments. Two cores were collected from each tank and were incubated in benthic flux chambers (Cowan and Boynton 1996). Each chamber had an internal diameter of 10 cm and contained a 10 cm deep sediment core overlaid with 20 cm of filtered Choptank River water. The benthic flux chambers were sealed and incubated for 48 hours. The chambers were subjected to a 12-hour light: 12-hour dark cycle for 48 hours and were constantly stirred by magnetic stirrers within the chambers. Water samples were collected for DOC and CDOM every 12 hours. A blank core of filtered river water was also run in parallel with the sediment cores.

We used both correlation and regression statistical tests to evaluate the statistical relationships in this research. We used both Pearsons’ Product Moment correlation for the variables that were normally distributed and Spearman’s Rank Order Correlation for the variables that failed a normality test (Sigma Stat, Jandel Scientific Software). Linear regressions were used to evaluate the time course data and the sediment flux data. All statistical relationships are reported as not significant (NS, \( p > 0.05 \)), significant (*, \( 0.05 > p > 0.01 \), or highly significant (**, \( 0.01 > p \)).

3. Results

A large phytoplankton bloom occurred in all three tanks following the nutrient additions (figure 1). The stepwise nutrient additions increased the original back-
ground concentration of 1 μM N NO₃, NH₄, or urea and resulted in a peak nutrient concentration of about 30–40 μM N in the tanks on days 3–5 (figure 1 (b)). Concentrations declined rapidly between days 5–10 and were relatively low thereafter. The highest phytoplankton biomass occurred on day 5 (70–110 μg Chl a l⁻¹; figure 1 (a)) and then fell quite rapidly through day 10, apparently in response to the removal of nitrogen from the water (figure 1 (b)). Thereafter, Chl a remained between 5–20 μg Chl a l⁻¹ for the duration of the experiment. Bacterial numbers (figure 1) increased exponentially from 0.67 to 3.57 × 10^6 ml⁻¹ towards the end of the experiment (r² = 0.60**). These data are similar to bacterial numbers obtained from similar experiments done previously in these tanks (e.g. Bryant 1995).

No significant differences were noted between the three tanks in the positive exponential rise to the peak in algal biomass, in the exponential fall to low biomass levels, nor in the relatively constant biomass during days 10–28 (ANOVA). Because there was no significant difference between the three tanks, we have treated the three tanks as replicate mesocosms with equal N enrichments in subsequent data analyses.

Both CDOM and DOC increased linearly over the course of the experiment...
As in figure 1, there were no significant differences in the CDOM or DOC production rate between the three different nitrogen sources, and all data were pooled to obtain single net rates of production for both CDOM and DOC. CDOM, measured as Normalized Fluorescence Units (NFIU), increased steadily over the course of the experiment at a rate of 0.30 NFIU d$^{-1}$. There was no peak in CDOM production that corresponded with the peak and crash of the phytoplankton bloom (figure 1). DOC concentration also increased steadily at a rate of 0.174 µmol C L$^{-1}$ d$^{-1}$, also with no clear relation to the phytoplankton bloom and crash.

There were weak but significant relations between CDOM and Chl$\alpha$ ($r^2 = 0.09^{**}$, figure 3(a)) and DOC and Chl$\alpha$ ($r^2 = 0.18^{**}$, figure 3(b)). However, it is likely that these weak statistical results are caused by the large number of data points at lower Chl$\alpha$ concentrations and reflects no functionally significant relations. Contrasting figures 1 and 2, there was no obvious connection between the bloom dynamics (figure 1(a)) and the steady increase in CDOM and DOC (figure 2).

Bacterial abundance was more strongly related to CDOM. There was a significant, positive correlation between CDOM and bacterial number ($r^2 = 0.40^{**}$, figure 2).
Figure 3. Relation between CDOM, DOC and Chl-a. CDOM and DOC are weakly inversely correlated with Chl-a concentrations ($r^2 = 0.09^{**}$, $r^2 = 0.18^{**}$, respectively). Legend as in figure 1.

figure 4(a)), again with no significant difference between N sources. However, there was no relation between DOC and bacterial number ($r^2 = 0.01$, NS, figure 4(b)), and there were no significant differences in the mean DOC values between N sources. Overall, DOC concentrations were quite high (mean = 362 $\mu$M C), increased slowly during the experiment (figure 2(b)) were unrelated to bacterial numbers (figure 4(b)), and were inversely related (possibly spuriously) to phytoplankton abundance (figure 3(b)).

In all but one sediment core there were no significant fluxes of CDOM or DOC either into or out of the sediment (figures 5 and 6). Blank cores (filtered water) showed no significant changes in DOC or CDOM over the course of the incubation and are omitted for clarity. One core from the nitrate tank exhibited a significant flux of CDOM ($r^2 = 0.90^*$) out of the sediment at a rate that increased concentration in the overlying water by $1.14 \pm 0.22$ (s.e.) NFIU d$^{-1}$.

4. Discussion

There is a paucity of information available on studies of the biological production of CDOM and the time scales over which this production occurs. Some studies have observed correlations between nutrient profiles and CDOM concentration in oceanic and coastal environments (Hayase et al. 1988, Momzikoff et al. 1992). For example,
there are strong correlations between apparent oxygen utilization (AOU), nutrient profiles, and CDOM fluorescence profiles in the deep waters of the Central Pacific (Hayase and Shinozuka 1995). The higher concentrations of CDOM in the deeper waters probably arise from the bacterially mediated regeneration of particulate matter in deeper waters combined with photolysis of CDOM in surface waters, resulting in a profile characteristic of nutrients such as phosphate or nitrate (e.g. low concentrations at the surface and higher concentrations in the aphotic zone). Therefore, it seems probable that deep water production of CDOM is at least partially bacterially mediated. In contrast to this, Momzikoff et al. (1992), working in the Ligurian Sea region of the Mediterranean, have hypothesized that the increases in CDOM they observed were of both phytoplanktonic and zooplanktonic origin. They observed strong correlations between the position of the peaks in Chl$\alpha$ and CDOM in their profiles. The correlation was strongest in the region farthest from shore, and was less well defined in the stations nearer shore. The position of the CDOM peaks and the position of a scattering layer caused by zooplankton, which were coincidental in many of their profiles, may indicate a zooplanktonic origin of CDOM (Momzikoff et al. 1992).

In this study, the relation between algal biomass and CDOM concentration was
Figure 5. Sediment core incubations for measurements of DOC fluxes. No significant fluxes were observed for any of the sediment cores, and there were no significant differences between the blank cores (filtered river water, data not shown) and the duplicate sediment cores from any of the tanks. Filled circles = sediment core a, open circles = sediment core b.

very weak. This is perhaps surprising as there was a large phytoplankton bloom (> 70 µg Chl a l⁻¹) followed by a rapid crash. Despite these large changes in phytoplankton abundance there was no clear, functional relation between algal biomass and CDOM concentration. While there were weak negative correlations between Chl a, CDOM, and DOC which were statistically significant, these relations are probably not functionally significant, and in any event suggest an inverse relation between these three parameters. This seems to indicate that phytoplankton, at least in this type of experiment, are not a direct source of CDOM during the relatively short time scale of the experiment (28 days). Similarly, there was no clear relation between the crash of the phytoplankton bloom and the appearance of DOC. This is in contrast to the results of Normman et al. (1995) who observed an increase in DOC in their mesocosm experiment following the crash of the phytoplankton bloom. In a culture experiment, Chen and Wangersky (1993) also observed increases in DOC concentration over the twelve days of their experiment. Using the data of Normman et al. (1995), we calculated a DOC increase of 3.16 µM C per unit change in Chl a (µg l⁻¹) during their experiment. If an equivalent release had occurred in
Figure 6. Sediment core incubations for measurements of CDOM fluxes. Only one core exhibited a significant flux of CDOM out of the sediment ($r^2 = 0.90^*$), in all other cores including the blanks (filtered river water, data not shown) no significant flux was observed in either direction. Legend as figure 5.

Our experimental tanks, we would have expected an increase in DOC of 245 $\mu$M C in each of the tanks. However, during the entire period, the increase in DOC over background that we observed in the tanks was 108 $\mu$M C. It is not clear why there were differences between the data presented here (no DOC increase directly related to the crash of the bloom) and those reported by others. There was considerable day to day variability in DOC concentration in the tanks, which, combined with a high background DOC concentration, may partially explain our lack of an observable to observe increase in DOC directly related to the crash of the bloom. However, our data do not support the concept of a DOC pulse resulting from the crash of a phytoplankton bloom under our conditions.

There was also an apparent lack of fluxes of both CDOM and DOC either into or out of the sediments, except in one core from the nitrate enriched tank. The mud surface and overlying water were oxic at all times throughout the experiment, as was also the case during the flux chamber experiments. This may be important because Skoog et al. (1996a) have reported that they failed to see fluxes of CDOM out of sediment cores from the Baltic until oxygen deficient conditions were present.
in the overlying water. This may mean that the sediment CDOM/DOC fluxes we observed may represent a lower flux than what would be observed in a natural system with seasonal anoxia.

However, for the one core that did have a positive flux of CDOM out of the sediment, we have calculated the impact of this on the increases of CDOM observed in the tanks. Remembering that 1 NFIU is equivalent to the fluorescence of 1 mg m$^{-3}$ quinine sulphate (in order to manipulate units), then we can estimate the flux of CDOM out of the core ($F$, mg quinine sulphate units m$^{-2}$ d$^{-1}$), using

$$F = (d \frac{[\text{CDOM}]}{dt})z$$  \hspace{1cm} (1)

where $t =$ time in days and $z =$ water depth in metres above the sediment (Fisher et al. 1982). The volumetric change in CDOM (1.14 NFIU d$^{-1}$) in the one core with a significant flux into the overlying water ($z = 20$ cm) was used to compute a flux of 0.23 mg quinine sulphate units m$^{-2}$ d$^{-1}$. We can similarly use the observed concentration change in CDOM in the mesocosm (0.30 NFIU d$^{-1}$) to compute a flux, assuming all CDOM originates from the sediments in the mesocosm. Given the average water depth of 0.75 m in the mesocosms, this rate of change of CDOM is equivalent to a flux of 0.22 mg quinine sulphate units m$^{-2}$ d$^{-1}$, essentially equivalent to the one observed flux from the nitrate mesocosm. Thus, unfortunately our sediment flux experiments gave results that ranged from 0 (5 of 6 cores) to a rate that can explain the observed rate of change of CDOM in the water column of the mesocosm (1 of 6 cores). It is likely that our core incubations did not have enough data points and/or sensitivity to resolve the CDOM fluxes from the sediments, and the role of CDOM fluxes from sediments remains unresolved by our data.

It is also interesting to note that there was no concomitant flux of DOC out of the sediment for any core, including the one with the significant flux of CDOM. It is likely that the CDOM measurements were able to detect smaller changes than the DOC measurements, as the precision of the fluorescence measurement is much better than that for the DOC measurements. The depth of water column overlying the sediment within the cores was also quite large, which may explain why we failed to see any other significant fluxes of DOC or CDOM from any of the other cores. Furthermore, the high background DOC and CDOM precludes highly sensitive measurements of CDOM and DOC fluxes.

The one statistically significant flux represents an upper limit of what could have occurred in the tank during the experiment. Spatial heterogeneity of sediments is to be expected, and it is possible that the one measurable flux did not exist all over the surface of the mud in the tanks. However, using the data presented here, we cannot rule out the possibility that the sediments have the potential to be a significant, and perhaps the dominant source of CDOM to the overlying water.

The bacterial biomass data is similar to that from previous experiments in these tanks (Bryant 1995). The increase in bacterial number towards a stable population size may have been a consequence of either resource or grazing limitation, as also noted by Bryant (1995), who observed an increase in heterotrophic nanoflagellates that are known to graze on bacteria. The relationship between the bacterial biomass and the increase in CDOM concentration is significant and positive (figure 4). The mechanisms by which CDOM is associated with bacteria are unclear from this experiment, but it is possible that the bacteria are a direct source of CDOM, either by direct release of CDOM, or as a by-product of some other process. It has been previously shown that bacteria may be integral in the production of CDOM (Nelson
et al. 1998). Such evidence as the increased concentrations of CDOM in deeper waters mirroring the nutrient profiles in the deep ocean supports this view.

The relative importance of sediments and bacteria as sources of CDOM is difficult to separate from this experiment. The shallow depth of the water column undoubtedly influences the outcome and increases the importance of sediment-derived inputs. However, in natural systems with a deeper water column, bacterially derived production of CDOM is likely to be more important. Moreover, if the relationship between bacterial biomass and CDOM concentration proves to be a functionally important one in natural systems, this will be evidence to support the importance of bacterial processes in the production of CDOM. It is clear from these data, however, that phytoplankton blooms do not appear to be a large source of CDOM on the time scale of approximately one month.

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References

Bryant, A. L., 1995, Effects of mesocosm dimension on the factors regulating heterotrophic bacterioplankton dynamics. MS. Thesis, University of Maryland, USA.


