CHAPTER 5

• Chlorophyll a as a marker for bioturbation and carbon flux in southern and central North Sea sediments •

5.1. Introduction

To understand the activity of benthic communities, it is important to assess the amount and quality of the organic matter sedimenting to and buried in marine sediments. Clear relationships have been observed, especially in coastal shelf seas, but also in the deep-sea, between the input of fresh organic matter, such as algal detritus or faecal pellets, and the metabolic reaction of the benthic community (Kanneworff & Christensen 1986, Pfannkuche 1992). However, time-lags or quantitative discrepancies can occur between detritus sedimentation and benthic metabolism. Christensen & Kanneworff (1985) and Boon et al. (1998) showed the rapid reaction by benthic macrofauna to spring bloom sedimentation, while the maximum of bacterial production was attained in (late) summer (Van Duyl & Kop 1994). Furthermore, as Roden & Tuttle (1996) have pointed out, the seasonal discrepancies between organic matter input and the metabolic activity of benthic communities, are to a large extent explained by the temperature-dependent remineralisation activities of bacterial organisms, and by the seasonally varying input of fresh labile organic matter as compared to more refractory organic matter.

In this study, the seasonal variation of chlorophyll a input into the shallow sediments of the North Sea, a European shallow coastal shelf sea, and sediment oxygen demand (SOD) were combined to gain insight into the relation between bioturbation, community respiration and algal matter input to the sediments. Chlorophyll a is used in this study as an indicator for the input of metabolisable organic matter as a food source for benthic organisms (Kanneworff & Christensen 1986, Boon et al. 1998). The depth distribution of chlorophyll a was modelled with both a diffusive as well as a non-local mixing model (Soetaert et al. 1996), from which particle mixing activity in, and fluxes of chlorophyll to the sediments were calculated. These chlorophyll a fluxes as well as the sediment oxygen demand were converted into carbon units. This gives an estimate of a benthic carbon budget for three locations in the southern and central North Sea. Part of the data on chlorophyll a concentrations in the sediments and sediment oxygen consumption have been published in Boon et al. (1998). The latter paper also contains information on the seasonally changes in phytopigment composition and hence algal succession in water and sediment from the stations mentioned here.

5.2. Methods

Description of study sites

Three stations in the southern and central North Sea were visited at 23 to 25 February, 20 to 22 March, 10 to 12 May, 14 to 16 June, 2 to 4 August and 15 to 17 November 1993 with the RV Pelagia (Fig. 5.1). Some characteristics of sampling locations are presented in Table 5.1. Station BF (depth 28 m) is situated at ca. 30 nautical miles west of

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the Dutch coast in an area called Broad Fourteens. Tidal currents near the bottom vary between ca. 10 and 45 cm.s\(^{-1}\), causing extensive resuspension of surficial detritus and sand (Boon unpubl. res.). This suspended material is transported northwards, due to the typical counter-clockwise residual water movement in the southern North Sea (Otto et al. 1990). As a consequence, the sediments at station BF contain low amounts of fine silt particles (size<63 \(\mu\)m) and organic carbon (Creutzberg et al. 1984). However, periodic input of fresh algal detritus is substantial (Boon et al. 1998), probably because of deposition of the bed-load during slack periods in the tidal cycle (Jenness & Duineveld 1985, Boon unpubl. res.).

Station FF (depth 39 m) is located on a gentle slope about 60 nautical miles north of station BF, in an area referred to as the Frisian Front (Creutzberg et al. 1984). Water masses entering the North Sea with the tide via the English Channel in the south and around the north of Scotland, form a convergence zone stretching from Anglia (UK) to the German Bight and the Danish west coast (Otto et al. 1990). As a result, this creates a tidal front at this convergence zone, the Frisian Front. This area is characterised by an higher sedimentation of detritus compared to stn BF, due to slowing down of currents when the water mass from the south enters deeper water. Furthermore, the primary production at the front is often prolonged after the spring bloom. This is likely due to the reflux of mineralisation products to the photic zone, thus enhancing algal production. It has been postulated that these characteristics are responsible for the increased benthic biomass and oxygen consumption at the Frisian Front, compared to areas north and south of it (Creutzberg 1985).

Station OG (depth 49 m) is situated at the Oyster Ground, some 60 nautical miles north of the station FF. The Oyster Ground is a somewhat isolated deeper basin (~ 50 m), bordered by relatively shallow areas, like the Dogger Bank to the north and the Southern Bight to the south, and England to the west. Residual water input is mainly from the west, but with prolonged southern winds, frontal and southern water masses can reach this area (Otto et al 1990). The near-bottom water current velocity (max. ~ 15 cm.s\(^{-1}\)) at this location is less than that at stn FF (Van Raaphorst et al. 1998). The presence of subfossil bivalves (~ 9000 y) at or near the sediment surface illustrates the lack of net-deposition in this area (Cadée 1984), despite the relatively low water current velocity.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Depth (m)</th>
<th>Water column mixing</th>
<th>Sediment type</th>
<th>C(_{org}) (% in sed.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broad Fourteens (stn BF)</td>
<td>53°00'</td>
<td>3°52'</td>
<td>28</td>
<td>mixed</td>
<td>medium</td>
<td>0.05 - 0.1</td>
</tr>
<tr>
<td>Frisian Front (stn FF)</td>
<td>53°42'</td>
<td>4°30'</td>
<td>39</td>
<td>transitional</td>
<td>silt and fine sand</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>Oyster Ground (stn OG)</td>
<td>54°31'</td>
<td>4°28'</td>
<td>49</td>
<td>summer stratified</td>
<td>fine sand and silt</td>
<td>0.1 - 0.5</td>
</tr>
</tbody>
</table>

The sediment type contains less silt and organic carbon than is found at stn FF, but more than at stn BF. Zoobenthic biomass levels are also intermediate at this site (Duineveld et al. 1991).

**Sampling and analytical procedures**

Duplicate sediment samples were taken for pigment analyses, each from a different box core using acrylic linings (Ø 5 cm). Sediment cores were collected with a cylindrical box.
corer (∅ 31 cm) developed at the Netherlands Institute for Sea Research (NIOZ), after a modification of Reineck’s box corer (Reineck 1963). Our box corer encloses a 30 to 50 cm long sediment column together with 15 to 25 l of overlying bottom water. Any disturbance of the sediment-water interface and contamination by water from the upper water column was prevented by a closing lid on the upper end of the box corer. Taking the amount of samples to be analysed into account, only two sediment cores were taken. Maximum sample depth (25 cm) could only be reached in the soft sediments at stn FF. At the other stations, sample depth varied between 10 and 20 cm, due to the compactness of the sediment. The cores were stored at -80°C until analysis in the laboratory. Prior to analysis, sediment samples were vertically sliced into segments from 0 to 1, 1 to 2, 2 to 3, 3 to 4, 4 to 5, 5 to 7, 8 to 10, 13 to 15, 18 to 20 and 23 to 25 cm depth and freeze-dried. Lyophilisation of the sediment samples did not result in a loss of pigments compared to direct extraction of the wet sediment samples.

Phytopigment analyses on the samples were performed by reverse-phase high performance liquid chromatography (RP-HPLC), using a Waters Associate liquid chromatograph equipped with a Bio-Sil C18 HL 90-5 S (Bio-Rad) column and a Model 991 Waters photo diode array spectrophotometer. Pigments were extracted in methanol containing 2% ammonium acetate-buffer and 5% double-distilled water. The solvent and gradient system was similar to that described by Kraay et al. (1992). Calibration of the spectrophotometer was done similar to that described by Kraay et al. (1992). Calibration of the spectrophotometer was done using pigment standards from Fluka Chemie A.G., Buchs, Switzerland. Storage of sediment samples at -80°C showed no significant decline in chlorophyll a concentrations over a 2 year period (unpubl. res.). Furthermore, replicate analyses of similar, homogenated samples showed a variation well below 10% of the average value. Identification of chlorophyll a was done by spectral analysis and retention time. Quantity was calculated according to an extension of Beer’s Law, as described by Mantoura & Llewellyn (1983). Porosity data were used to express the chlorophyll a concentrations per volume of sediment (data supplied by dr. Wim van Raaphorst, Netherlands Institute for Sea Research).

Sediment Oxygen Demand (SOD), which covers the aerobic respiration of the sediment community and partly the oxidation of reduced substances as well (Canfield et al. 1993), was determined at stn BF and stn FF in replicates (3 to 4) by shipboard incubations of sediment cores. The cores were taken with the cylindrical box corer described above, in which a detachable polyester core tube (∅ 30 cm) was inserted. The core tubes were placed into a water bath on-deck with an opaque lid to prevent light from entering. The water was cooled to in-situ temperature. A height-adjustable lid was sealed to each core tube by means of an inflatable ring in the outer edge. The lid contained a stirring device and an oxygen electrode (Yellow Spring Instruments 620) to monitor the oxygen concentration in the head space. The electrode was calibrated in aerated, oxygen-saturated water (100% O2), and in oxygen-depleted (sodium sulphite) water (0% O2). SOD was estimated from the linear part of the first 2 to 3 hours of the concentration-time series. The sediment oxygen demand was corrected for the oxygen use by the electrode. Sediment oxygen consumption data at stn OG were derived from literature (De Wilde et al. 1984, Cramer 1990).

Modelling and budget calculations

Assuming steady-state conditions, random diffusive mixing and simple first-order decomposition kinetics, the following diagenetic equation was used to fit down-core distributions of organic matter in sediments (Berner 1980, Sun et al. 1994):

\[
dC/\partial t = 0 = D_b(\partial^2 C/ \partial x^2) - w(\partial C/\partial x) - \lambda C (1)
\]

with \(C\) = concentration compound in sediments, \(t =\) time, \(D_b =\) particle mixing coefficient or bioturbation rate, \(x =\) depth in
sediments, $\omega = \text{sedimentation rate and } \lambda = \text{first-order decay constant of the organic material.}$

A recent study by De Haas et al. (1997), who measured $^{210}\text{Pb}$ profiles in North Sea sediments, showed that at the stations BF and FF no net sedimentation or insignificant sedimentation could be determined. The absence of net sedimentation at station OG is indicated by the presence of subfossil (~9000 y BP) bivalve remains at the sediment surface (Cadée 1984).

The insignificance or absence of sedimentation rates at our stations results in a negligible effect of the factor $\omega(\partial C/\partial x)$ in equation (1). Hence, to our purpose we omitted this factor, which simplifies the diagenetic equation to

$$\frac{\partial C}{\partial t} = D_b \left( \frac{\partial^2 C}{\partial x^2} \right) - \lambda C$$

(2)

The solution with the following boundary conditions: at $x = 0$, $C = C_0$ and at $x = \infty$, $C = C_e$, is:

$$C_x = C_0 \exp \left(-x \sqrt{\lambda / D_b}\right) + C_e$$

(3)

where $t = \text{time (d)}, x = \text{depth (cm)}, C_e = \text{concentration of chlorophyll } a \text{ at depth } x \text{ in sediment (} \mu g \text{.cm}^{-3}\text{)}, C_0 = \text{concentration of chlorophyll } a \text{ at the sediment-water interface (} \mu g \text{.cm}^{-3}\text{)}, C_b = \text{background concentration of chlorophyll } a \text{ at large } x \text{ (} \mu g \text{.cm}^{-3}\text{)}, D_b = \text{mixing coefficient (} \text{cm}^2 \cdot \text{d}^{-1}\text{)} \text{ and } \lambda = \text{first order degradation constant of chlorophyll } a \text{ (d}^{-1}\text{)}$.

Soetaert et al. (1996) developed fitting routines to model the down-core distribution of $^{210}\text{Pb}$ in ocean sediments. They described models for steady-state diffusive mixing as well as non-local mixing situations. We modified their routines to model the depth-distribution of chlorophyll $a$ in North Sea sediments. In our routines, the variables mentioned in equation (2) relate to days in stead of years, and $\omega$ and $Sp$ (production term for $^{210}\text{Pb}$) were set to zero.

Six different models were developed by Soetaert et al. (1996). The first model, model 1, describes the situation in which no bioturbation occurs, and the depth-distribution of the studied compound is dominated by sedimentation. Since we omitted this term from our diagenetic equations, this model was not used in our study. The second model, model 2, describes the steady-state diffusive mixing, calculated by solving our equation (2) for the whole profile of chlorophyll $a$. In their paper, Soetaert et al. (1996) have developed 4 different non-local mixing models, with increasing complexity. Here, only their model 3, the simplest non-local mixing model, is applied. The other, more sophisticated models did not give a better description of the down-core distribution of chlorophyll $a$ in our study. These models are not mentioned further here, and the reader should consult Soetaert et al. (1996) for further information.

In Fig. 5.2, a schematic representation of the two models used here is given, with the diagenetic equations and their boundary conditions. Model 2 (the same term as in Soetaert et al. 1996) consists of only one layer, with a flux boundary at the sediment-water interface. The depth distribution of chlorophyll $a$ is described by equation (2). Model 3 is a modification of model 2, by injecting non-locally part of the flux at depth $L$. Hence, two layers are considered, one from the sediment-water interface to $L$ and the other from $L$ to infinite depth. Equation (2) is applied on both layers, assuming equal bioturbation in both layers.

The fitting routines also calculated fluxes of chlorophyll $a$ to the sediment. In the case of model 2, this is the flux to the sediment-water interface, in case of model 3, the injected flux to depth $L$ is also calculated (see also Fig. 5.2). These fluxes ($J$) were calculated according to Fick’s law (Berner 1980), assuming steady-state conditions:

$$J = -D_b (\frac{\partial C}{\partial x}) \big|_{x=0}$$

(4)

which has the solved form:

$$J = C_0 \sqrt{D_b \lambda}$$

(5)
In case of model 2, this equation was applied on the whole sediment layer. In the case of model 3, this equation was also applied on the second layer, from L to infinity, and calculated as follows:

\[ J_2 = -D_b \left( \frac{dC_2}{dx} \right)_L + D_b \left( \frac{dC_1}{dx} \right)_L \]  

(6)

Here, \( J_2 \) is the flux to the second layer in model 3, from L to infinity, \( C_1 \) is the concentration of chlorophyll \( a \) in the layer from 0 to L and \( C_2 \) in the layer from L to infinity. The flux calculated with the models will here be referred to as the model-approach.

Another way of calculating the chlorophyll \( a \) flux is simply to balance supply and breakdown (Sun et al. 1994):

\[ J = \lambda I \]  

(7)

where \( I \) is the inventory of chlorophyll \( a \) in the sediment (summed over maximum depth; \( \mu g.cm^{-2} \)). The flux calculated with equation (7) will here be referred to as the inventory-approach.

To test whether model 2 or model 3 gave best fit on the depth-distribution of chlorophyll \( a \), a one-tailed \( F \)-test was used (Sokal & Rohlf 1995). This test calculated the difference in the residual variance between modelled and observed data in the two models. The null hypothesis was that there was no difference in residual variance between the two models. In this case, model 2 gave the best fit. If the residual variance in model 3 was smaller than in model 2 (\( p<0.01 \)), then the null hypothesis was rejected, and model 3 gave the best fit. Differences between bioturbation rates and fluxes from the different stations or months were tested with ANOVA and Tukey HSD tests, using Systat for Windows.

### 5.3. Results

#### Chlorophyll \( a \) profiles

Most chlorophyll \( a \) profiles exhibited an exponential decrease with depth, which was best described with model 2, the diffusive mixing model. An example is given in Fig. 5.3, in June at station BF. Certain profiles, however, showed a subsurface maximum of chlorophyll \( a \), of which an example is given in Fig. 5.3, in November at station BF. These depth-distributions of chlorophyll \( a \) were best described by model 3, the non-local mixing model. From the difference between the diffusive and non-local mixing curves in Fig. 5.3, it is clear to see why fitting a diffusive model on a non-local mixed situation gives an over-estimate of the bioturbation rate. In Table 5.2, it is indicated in which cases the non-local mixing model 3 gave a better description of chlorophyll profiles than the diffusive model 2.

#### Bioturbation rates

In Table 5.2, the bioturbation rates or particle mixing coefficients \( D_b \) are given for the three stations under study. The first-order degradation constant \( \lambda \) for chlorophyll \( a \) was derived from literature, and a value of 0.03 d\(^{-1}\) was assumed (e.g. Bianchi & Findlay 1991, Sun et al. 1993).

At stn BF, a seasonal cycle is noticeable: bioturbation is relatively low in February and March, and highest in May and June (\( p<0.05 \)). In August, a decrease in mixing was apparent (\( p<0.1 \)). At stn FF, the highest mixing rate was found in February (\( p<0.1 \)). Apart from this exceptional value, a seasonal trend can be inferred with increased mixing in May and August, although this was not significant. Also at stn OG, the February

<table>
<thead>
<tr>
<th>Station/Month</th>
<th>February</th>
<th>March</th>
<th>May</th>
<th>June</th>
<th>August</th>
<th>November</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>average</td>
<td>0.0037</td>
<td>0.0029(^{b)}| 0.240</td>
<td>0.064</td>
<td>0.021</td>
<td>0.048(^{c)}|</td>
</tr>
<tr>
<td></td>
<td>C.V.</td>
<td>11</td>
<td>38</td>
<td>34</td>
<td>17</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 5.2: Bioturbation rates (cm\(^2\).d\(^{-1}\)) at stations BF, FF and OG. C.V. is coefficient of variation.
Benthic carbon budget southern North Sea

<table>
<thead>
<tr>
<th></th>
<th>FF</th>
<th>OG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>average</td>
</tr>
<tr>
<td></td>
<td>5.41</td>
<td>0.285</td>
</tr>
<tr>
<td>C.V.</td>
<td>0.022&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.91&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.063</td>
<td>0.243&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.676&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.097&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.105&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.412&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>112</td>
</tr>
</tbody>
</table>

<sup>1</sup> model 3 gave best fit on one of the duplicate cores; <sup>2</sup> model 3 gave best fit on both duplicate cores.

mixing rate was (insignificantly) higher than in March. The highest average bioturbation rate was found in May, but due to high variation it was not significantly higher than in March. However, mixing in June was significantly higher than in March (p<0.05), and in August it decreased again (p<0.05). No consistent differences in bioturbation rate could be detected among the stations. Mixing was lower at stn BF than at stn FF in February (p<0.05) and November (p<0.1). Furthermore, in February, mixing was higher at stn FF than at stn OG, but in June the reverse was found (p<0.1).

**Chlorophyll a fluxes**

The fluxes of chlorophyll a into the sediment (Table 5.3a and 5.3b) were calculated in two ways, first using the model-approach and second using the inventory-approach. A graphical presentation of these data is given in Fig. 5.4, where they have been converted to carbon units, using a carbon to chlorophyll a ratio of 50 (w/w). Although fluxes are given as values per day, they should not be viewed as daily fluxes. Due to the decay rate of chlorophyll a in terms of weeks, the fluxes in Table 5.3 should also be regarded as more time-averaged values.

The two models gave similar seasonal patterns (r>0.7, p<0.05), with maximum average fluxes of chlorophyll a in May at stns BF and FF and in March at stn OG. More specifically, at stn BF, an increase in flux from February to May was noted (p<0.05 inventory), with thereafter a decrease in August and November (p<0.05 inventory). At stn FF, the differences between the two approaches were more distinct: the model-approach resulted in a higher flux (p<0.05) in February than in March, then again a higher flux in May (p<0.1), and (non-significant) lower fluxes in later months. The inventory-approach gave a higher flux in May than in February and March (p<0.05), with (non-significant) lower values in June and August, and a lower flux in November (p<0.05). At stn OG, the two approaches gave comparable results. In March, an increase in flux was found compared to February, but in May this did become significant (p<0.05). The model-approach showed a decrease again in June (p<0.1).

A general trend is observed when the chlorophyll a fluxes into the sediment are compared among the stations. The lowest fluxes occurred at stn BF, intermediate fluxes at stn OG and highest fluxes at stn FF. According to the model-approach, these differences were significant between stns BF, FF and OG in February and November (p<0.05) and between stns OG and FF in May (p<0.1). The inventory-approach gave more significant differences, except for June and August, when no significant differences were found among the three stations, and for March when no significant differences were observed between stns FF and OG.

**Sediment oxygen demand**

The values of the sediment oxygen demand (SOD) at stns BF and FF are the results of measurements from this study. Data from the months during which we had no cruises and thus no samples (January, April, July, September, October and December) originate from cruises undertaken in earlier years. The SOD values at stn OG are from studies by De...
Chapter 5

\[\text{Section 5.4. Discussion}\]

### Models

Most profiles were best described with model 2, and the other profiles with model 3, which is comparable to the results found by Soetaert et al. (1996) for \(^{210}\text{Pb}\) in margin sediments of the east Atlantic Ocean. It is interesting to note that in our as well as in their study, none of the more sophisticated non-local mixing models gave a better fit than model 3.

In the cases where we found a subsurface maximum of chlorophyll \(a\), the diffusive mixing model (model 2) gave considerable higher mixing coefficients and fluxes into the sediment. Other studies where down-core concentrations of short-lived radionuclides or biogenic compounds were measured, demonstrated that such non-local particle mixing is a fairly common phenomenon (Sun et al. 1994, Wheatcroft et al. 1994). However, in these studies only diffusive mixing models have been applied, suggesting that part of the mixing rates calculated in those studies have been overestimated.

\[\text{Seasonal and geographical variation of chlorophyll a flux}\]

Some differences in standard deviation were observed between the two methods to calculate chlorophyll \(a\) fluxes to the sediment. In the model-approach, the bioturbation rate played an important role. Hence, the large variation in the modelled bioturbation rates was reflected in the fluxes. The variation of the fluxes calculated with the inventory-approach depended solely on the variation in the inventory of chlorophyll

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### Table

<table>
<thead>
<tr>
<th>Station/Month</th>
<th>February</th>
<th>March</th>
<th>May</th>
<th>June</th>
<th>August</th>
<th>November</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF average</td>
<td>86</td>
<td>673</td>
<td>2307</td>
<td>997</td>
<td>774</td>
<td>231</td>
</tr>
<tr>
<td>C.V.</td>
<td>63</td>
<td>53</td>
<td>54</td>
<td>99</td>
<td>111</td>
<td>96</td>
</tr>
<tr>
<td>FF average</td>
<td>5680</td>
<td>972</td>
<td>7255</td>
<td>2519</td>
<td>5010</td>
<td>3655</td>
</tr>
<tr>
<td>C.V.</td>
<td>16</td>
<td>36</td>
<td>47</td>
<td>139</td>
<td>65</td>
<td>16</td>
</tr>
<tr>
<td>OG average</td>
<td>860</td>
<td>2357</td>
<td>2113</td>
<td>1929</td>
<td>1831</td>
<td>1832</td>
</tr>
<tr>
<td>C.V.</td>
<td>28</td>
<td>115</td>
<td>20</td>
<td>26</td>
<td>96</td>
<td>31</td>
</tr>
</tbody>
</table>

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Wilde et al. (1984) and from a nearby station (Cramer 1990).

The SOD results (Table 5.4, Fig. 5.4) clearly reflect a seasonal cycle. At stn BF, oxygen consumption was relatively low in winter, and increased until June \((p<0.05)\), whereafter it decreased \((p<0.1)\). The seasonal variation of SOD at stn FF also showed lowest values in winter, increasing levels in spring and summer, but with peaks in August and September, followed by a decrease towards winter values again in October. A comparable pattern was found at stn OG, with SOD values lower than at stn FF \((p<0.05)\), and not significantly higher than at stn BF. Furthermore, the annually averaged SOD was highest at stn FF, intermediate at stn OG and lowest at stn BF, although the differences between stns BF and OG were not significant.
alpha in the sediments (Boon et al. 1998), which was considerably lower than the variation in fluxes calculated according to the model. The fluxes as calculated by both methods gave comparable seasonal patterns (r>0.74), and differences between stations. The maximum flux in March and/or May at the three stations reflects the spring bloom sedimentation. In February, a relatively high input of chlorophyll alpha was found at station FF according to the model. The fluxes calculated with the model depend on the mixing rate, which was also quite high in February at this station (see also the discussion on mixing below). When the inventory of chlorophyll alpha at this station in February is taken into account, this flux seems too high, especially when the relatively low bottom water temperature and thus low degradation rates are considered. The inventory-approach gave a flux more similar to that in March and considerably lower than the autumn values and probably is more realistic. However, in other years relatively high inputs of algal detritus have been recorded this early in the year. Joint & Pomroy (1993) found a late winter increase in chlorophyll alpha in the water column by the end of February 1989 at the latitude of the Frisian Front and a month later (end March) at the Oyster Ground, a pattern comparable to our results. Although in 1993 (the year of our study) no early bloom was noted at the Broad Fourteens, this was the case in 1994 (Boon & Duineveld 1996). However, there exist notable annual differences in spatial onset and timing of early spring blooms; in May 1994, the typical spring bloom of Phaeocystis sp., as found in 1993 (Boon et al. 1998), was absent at stations BF and FF (Boon & Duineveld 1996; station OG not studied). The chlorophyll alpha flux was highest at station FF in all months (p<0.05) except in March. These relatively high values support the earlier findings of Creutzberg (1985), Cramer (1990) and Baars et al. (1991) that in a relatively narrow zone at the Frisian Front, often increased primary production and benthic metabolism occur, compared to closely adjacent areas north and south of it.

### Table 5.4: Sediment oxygen consumption (mmol O_2/m^2/d); c.v. is coefficient of variation.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>BF</td>
<td>1.8</td>
<td>4.3</td>
<td>6.6</td>
<td>9.8</td>
<td>17.7</td>
<td>18.0</td>
<td>11.3</td>
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<td>1.6</td>
<td>1.2</td>
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<td>7</td>
<td>24</td>
<td>36</td>
<td>1</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
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<tr>
<td>FF</td>
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<td>7.5</td>
<td>29.5</td>
<td>27.8</td>
<td>32.8</td>
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<td>49.7</td>
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<td>14.9</td>
<td>17.2</td>
<td>15.5</td>
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<tr>
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<td>2</td>
<td>9</td>
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<td>56</td>
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<tr>
<td>OG</td>
<td>4.8</td>
<td>6.6</td>
<td>11.5</td>
<td>16.2</td>
<td>13.5</td>
<td>2.4</td>
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<tr>
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1) values from De Wilde et al. (1984); 2) values from Cramer (1990)

### Mixing

The bioturbation or particle mixing rate (D_b) is a measure for the physical activity of macrobenthos. Although subsurface deposit-feeders like conveyor-belt feeding species are the main contributors to mixing, also other benthic animals (e.g. predatory polychaetes, suspension-feeding Ophiuroides) conduce to bioturbation. The optimal foraging theory predicts higher ingestion rates when more or fresher food is available (Taghon & Jumars 1984). In the case of deposit-feeders, this means higher intake rates of sediment when more chlorophyll alpha is present. This is likely to be positively related to the physical activity (foraging) of the animals in the sediment. Thus, it was hypothesised that the mixing rates would be dependent on the input of chlorophyll alpha to the sediment. At station BF, a significant positive correlation between bioturbation and the chlorophyll alpha flux (inventory-approach) was indeed found (p<0.01); there is an increase in mixing and flux in May, with a decrease thereafter. At station FF no significant relation was found, although mixing and flux tended to follow the same pattern. Station OG demonstrated no
relation between these variables at all. A comparison between the bioturbation and the flux calculated with the model-approach is not valid, since these values were not determined independently. Mixing rates in Long Island Sound sediments, calculated by Sun et al. (1994) with chlorophyll a and 234Th, are in the same range and display a comparable seasonal range as our data. However, their data lack a correlation between bioturbation rate and chlorophyll a input into the sediments. Clearly, the relation between organic matter input and bioturbation rate is not straightforward. Furthermore, as can be seen in Table 5.2, there is a large variation in mixing rates between duplicate cores in our study; in many cases, the coefficient of variation is over 100. This could be an effect of a patchy distribution of the benthic fauna in the North Sea. An unexpected high mixing rate was observed at stn FF in February. Modelling the down-core distribution of chlorophyll a in the sediments here gave a relatively steep profile, although the concentrations of chlorophyll were relatively low. Such a distribution gives a high mixing rate, even when the actual amount of chlorophyll is low. If we consider the possibility that a small part of chlorophyll a is not directly available for degradation, through adsorption to or through other means of physical or chemical protection by fine sediment particles, such depth-distributions could develop without intense mixing. As a result, one would find high bioturbation rates when a model is applied and the total chlorophyll a pool is considered. The alternative is to subtract this refractory chlorophyll from the total pool, analogous to the subtraction of the background production in the case of modelling profiles of radionuclides. However, as yet there is no means by which such a less available fraction can be estimated or analysed. As a result, we consider the mixing rate at stn FF in February to be an overestimate.

An important factor influencing the calculation of the particle mixing rate, is the first-order decay constant λ for chlorophyll a. The average first-order degradation rate for chlorophyll a has been estimated to a value of 0.03 d⁻¹ in various studies (Graf 1989, Sun et al. 1993). Sun et al. (1994) calculated that this degradation rate varies along with the temperature, from 0.017 d⁻¹ at 2°C in the winter to 0.079 d⁻¹ at 22°C in the late summer. Taking this seasonal variation of λ into account, a twofold decrease and increase in mixing during the late summer and the winter and early spring respectively is predicted from the values presented here.

Another important factor influencing mixing rate could be the biomass and/or abundance of macrrobenthic organisms at the locations. Since bioturbation is the sum of all physical activities of such organisms, one might expect this factor to exert some influence. Although stn FF contains at least a twofold higher benthic biomass and abundance (Holtmann & Groenewold 1994), compared to stn BF the mixing rate was only higher at this station in two months (February, November). Thus, our results show that two important factors thought to determine the bioturbation rate (chlorophyll a input and macrrobenthic biomass/abundance) only show a limited influence. Another possibility is the limited validity of the steady-state model to describe

<table>
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<th>Station</th>
<th>Chlorophyll a flux</th>
<th>SOD</th>
<th>Primary Production</th>
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<tr>
<td></td>
<td>a</td>
<td>b</td>
<td></td>
</tr>
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<td>16</td>
<td>14</td>
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<td>76</td>
<td>82</td>
<td>89, 95²</td>
</tr>
<tr>
<td>OG</td>
<td>33</td>
<td>35</td>
<td>35³</td>
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</tbody>
</table>

¹ value calculated from Cramer (1990) and De Wilde et al. (1984); ² values from Cramer (1990); ³ values from Baars et al. (1991); ⁹ values from Joint & Pomroy (1993)

short-term, pulse-like events like the sedimentation and subsequent burial and breakdown of compounds with a relatively high turnover rate.

In conclusion, our data reveal a significant positive correlation between mixing and algal matter input at one station (BF), but no relation at the other two stations. Whether the values we found and especially the high variation herein, are typical, and which factors are of major importance remains speculative as such.

**Benthic carbon budget**

In order to compare the fluxes of chlorophyll $a$ with the sediment oxygen consumption, certain conversion factors were used to express all values in terms of carbon. The conversion of chlorophyll $a$ to carbon was done using a $(w/w)$ C to chlorophyll ratio of 50. It is acknowledged that this ratio can vary considerably, from 20 to 500, the latter being winter values, which are not associated to phytoplankton production (Baker et al. 1985). Fresh phytoplankton C to chlorophyll $a$ values normally vary in the range from 20 to 80 (Antia et al. 1963). According to the Redfield ratio, 77% of the consumed oxygen is involved, directly or indirectly, in the breakdown of organic carbon. Partly, this oxygen is used to oxidise reduced compounds (Mn, Fe, sulphides) from the anoxic zone (Canfield et al. 1993). The other 23% of the oxygen is used for nitrification. Hence, to convert the SOD values to carbon units, a factor of 0.77 was used.

Our data (Tables 5.3, 5.4 and Fig. 5.4) show an accumulation of chlorophyll $a$-carbon in spring, as indicated by the sediment inventory, due to increased fluxes in March and May. This spring input possibly fuelled the late summer SOD maximum, when fluxes of chlorophyll decreased relative to the spring values. Our results agree with those of Roden & Tuttle (1996), who modelled a build-up of metabolisable particulate organic matter (MPOC) in spring in the sediments due the increased sedimentation of labile organic matter. They showed that two factors contribute to the accumulation of organic matter in shallow shelf sediments early in the year: the increased sedimentation of algal detritus due to the spring bloom on the one hand and on the other hand the low water temperatures in spring inhibiting degradation.

Although this pattern of carbon accumulation in spring and mineralisation in late summer was also demonstrated at stn BF, it is evident from Fig. 5.4 that here the spring chlorophyll $a$ flux was just sufficient to fuel the actual SOD, when both were expressed in terms of carbon. The summer maximum in SOD was not balanced by the chlorophyll-carbon flux into the sediment. The reasons for the lack of balance at stn BF are not clear. Hüttel et al. (1996) found increased flux of particles to and exchange of nutrients from the sediment due to relatively high current velocities near the sea-bed. The resulting stimulation of bacterial activity could be responsible for an increased turnover of organic matter, resulting in an elevated SOD. Furthermore, a higher organic matter (and thus chlorophyll) turnover results in lower inventories of chlorophyll in the sediment, seriously affecting the fluxes calculated with our equations. Such effects underline the problems with applying a steady-state model on short-term dynamic systems.

An important factor influencing the somewhat simplified view of the benthic carbon budget we present here is the carbon to chlorophyll $a$ (C:chl) ratio. In a study on near-bottom seston at stns BF and FF (Boon & Duineveld 1996), we found this ratio to vary from 30 to $>1000$. Since both these locations are exposed to relatively high tidal near-bottom water currents (maxima of 45 and 25 cm.s$^{-1}$ respectively), a large proportion of the carbon originates from sedimentary resuspended organic matter which is
admixed with the fresh algal matter settling in the near-bottom realm. It is generally accepted that the majority of sedimentary carbon is refractory, and does not contribute much to benthic metabolism. Taking the limited depth of the study sites into account, newly settled algal matter is likely to be only slightly degraded, with a C:chl ratio between 30 and 100, when it becomes incorporated in the sediment. It is conceivable that, even though the total pool of carbon has a high C:chl ratio, especially fresh particles get entrapped by means of selective feeding. The reasonable balance in the carbon budgets here seems to justify the assumed C:chl ratio of 50. Furthermore, it indicates that for the purpose of this study, chlorophyll a is a good marker for the metabolisable pool of organic matter sedimenting to the sea-floor. Lastly, the possibility of benthic primary production in these shallow waters should be considered. Joint & Pomroy (1993) mentioned that during winter and spring 1993, the base of the euphotic zone was at or very close to the bottom in parts of the coastal regions of the Netherlands (near our station BF). Hence, according to this finding some of the sedimentary pigments could originate from benthic algae. However, since the sediment top layer of this area is subject to high near-bottom water current velocities (up to 45 cm.s\(^{-1}\)) leading to extensive resuspension (Jago et al. 1993, Boon & Duineveld 1996), it is unlikely that any benthic algal community would survive these harsh circumstances. Hence, we consider the contribution of benthic algal chlorophyll to the total sedimentary chlorophyll pool to be negligible.

According to the data in Table 5.5, 10-20 % of the annual primary production was mineralised in the sediments at stn BF, as compared to 20 to 25 % at stn FF and 15 to 41 % at stn OG. The primary production (PP) values of stn FF, derived from literature, vary considerably. Joint & Pomroy (1993) gave an annual PP of 150-200 g C.m\(^{-2}\), while Baars et al. (1991) estimated an annual PP of 420 g C.m\(^{-2}\). We assume the latter value to be a better estimate, since this value was measured at stn FF itself, while Joint & Pomroy's value was interpolated from measurements around this station. Baars et al. (1991) showed the PP at this station to be twice as high as stations 10 nautical miles north and south of it. Clearly, there is no decline in the proportion of primary production being mineralised in the sediments with depth among the three stations. Other factors, like hydrography may play an important role in this matter. However, a considerable proportion of the primary production at stn BF gets buried and mineralised in the sediments, despite the relatively high tidal current velocities here, which cause extensive resuspension in this area (Jago et al. 1993, Boon unpubl. res.).

The station with the highest macrobenthic biomass, stn FF, shows the highest sediment oxygen demand. However, the station with the lowest macrobenthic biomass, stn BF shows an annual SOD comparable to that of stn OG, which has a higher benthic biomass (Holtmann et al. 1995) It could be that such a difference is caused by the stimulated bacterial activity as a result of the coarser sediment type at stn BF, in combination with the higher tidal current velocities (Hütte et al. 1996). This would mean that the macrobenthos, and possibly also meiobenthos, have a higher share in the SOD at stns FF and OG than at stn BF.

Despite the relatively extended data set on organic matter sedimentation and the subsequent burial in sediments, knowledge on the degradation of organic matter in sediments is still lacking. Only few studies have attempted to calculate degradation rates for molecular organic compounds, or studied the effects of hydrographical circumstances and sediment types on such rates. This information is highly needed when using molecular markers like phytopigments for the processing of organic matter in the benthic realm. Moreover, the dynamical character of coastal ecosystems, and their intrinsic spatial and temporal heterogeneity, although acknowledged theoretically, still is an undervalued research topic. Future ecosystems studies on the
North Sea should certainly focus on these aspects, while degradation experiments on pigments and other organic molecules would significantly contribute to their use as biomarkers.