4 MUD FLOC SIZE VARIATIONS ON A SEASONAL TIME SCALE. THE IMPACT OF A PHYTOPLANKTON BLOOM IN THE DOLLARD ESTUARY, THE NETHERLANDS


4.1 Introduction

Aggregation of mud particles into flocs is essential for the sedimentation of mud. Mud flocs exhibit a larger settling velocity than the individual particles, which increases sedimentation or even creates the possibility of mud sedimentation. Floc size and settling velocity are determined by the balance between flocculation and breakup. Breakup is primarily caused by turbulent shear (Dyer, 1989; Eisma, 1986; Hunt, 1986; Luettich et al., 1993; Van Leussen, 1994). Flocculation depends on the floc collision frequency and the floc collision efficiency. The collision frequency is mainly determined by the suspended sediment concentration (SSC) and the turbulence intensity. The collision efficiency mainly depends on mud and water properties like salinity, organic coatings and the presence of biopolymers that may ‘glue’ flocs together. Dyer (1989) used the SSC and turbulence intensity in his conceptual model describing the floc diameter, presented as figure 1.7 in chapter 1. Both factors show a strong variation on the time scale of a semi-diurnal tide. On this time scale Dyer’s conceptual model can be reasonably applied since the factors that determine the collision efficiency remain relatively constant on this tidal time scale. On a seasonal time scale however, the collision efficiency may play an important role.

On a seasonal time scale mud and water properties may show a larger variation which affects the collision efficiency of flocs and therefore also floc sizes and settling velocities. The collision efficiency of flocs is determined by the physico-chemical properties of the floc surface. An electrical charge causes repulsion of flocs thereby preventing floc collisions. When however flocs are close enough to each other, Van der Waals or hydrogen bonds will bind the flocs together. These bindings can be intensified by polymeric substances on the floc surface or by separate organic flocs that act as glue. The biological production of polymeric substances mainly varies on a larger time scale than the 13 hours of a semi-diurnal tide. The impact of biological processes on floc sizes and settling velocities can therefore only be studied on a larger time scale. Therefore floc sizes were measured every season from fall 1995 until December 1996. This chapter will show the seasonal floc size variations that occurred in the Dollard estuary during that period. A few of these measurements were taken during a plankton bloom. Especially at the end of this bloom there was a significant biological impact on the floc sizes in the Dollard. The frequency of these measurements was too limited for an extensive assessment of the flocculation processes occurring during the bloom. Still the few measurements that
were taken, do give an indication of the impact plankton blooms may have on the flocculation dynamics in an estuary.

4.2 Theory

Changes of floc sizes and settling velocities on a seasonal time scale are largely determined by changes in the collision efficiency. The binding processes that take place between particles determine this efficiency. The two main binding processes, salt flocculation and biological cohesion of mud flocs, and their possible impact on floc size will be dealt with.

4.2.1 Salt flocculation

Most fine-grained suspended particles in natural waters exhibit a negative surface charge (Neihof & Loeb, 1972; Loder & Liss, 1985). This negative charge of the suspended particles is balanced by a cloud of positively charged ions around it. Together they form the so-called electrical double-layer. When two particles approach each other and the positive ion clouds overlap, electrostatic repulsion between the particles prevents a particle collision. Increasing salinity, however, decreases the thickness of the double layer, due to the lesser gradient between the positive ion concentration around the particle and the ion concentration in the surrounding water. Particles may then approach so close to each other that the Van der Waals forces are stronger than the electrostatic repulsion, and this leads to flocculation.

In the past this classical concept of salt flocculation was thought to cause flocculation of suspended matter in estuaries at the interface between fresh and salt water. The floc sizes and settling velocities should then increase at the transition from fresh to saline water. The concept of salt flocculation at the limnic-brackish boundary is however disputed by several authors:

Puls & Kuehl (1986) found decreasing settling velocities at the transition from fresh to saline water in the Elbe estuary. They state that physico-chemical flocculation (salt flocculation) can not become effective due to organic coatings around the particles.

Eisma et al. (1991a) measured particle sizes in five Northwest European estuaries in situ and by Coulter Counter and pipette analysis. Sizes measured by Coulter Counter or pipette analysis became finer at the saltwater contact. The in situ floc sizes measured with the camera, however, did not become finer but remained the same. There was however no relation between the changes in salinity and the in situ floc size. Therefore Eisma et al. (1991a) concluded that the particle sizes measured by the Coulter Counter and pipette analysis were the fragments of flocs broken during sampling and size analysis. The decrease in these sizes with increasing salinity indicated an increase in fragility of the suspended flocs, possibly
due to mobilization of organic matter in the saline water which weakened the floc structure.

Neihof & Loeb (1972); Hunter & Liss (1979); Hunter & Liss (1982); Loder & Liss (1985) all showed that particles in natural waters have a highly uniform negative surface charge due to organic and/or metallic coatings. The surface charge is therefore independent of the type of suspended material (e.g. clay minerals). Hence, organic coatings can have a considerable effect on the degree of salt flocculation in natural waters. Hunter & Liss (1982) also showed that the surface charge decreases with salinity.

Gibbs (1983) measured the effect of organic coatings on the collision efficiency factor of flocs. Figure 4.1 shows the collision efficiency factor plotted against the salinity. It demonstrates that increasing salinity causes increasing collision efficiency due to the decrease in double layer thickness and maybe also due to the decrease in surface charge. Besides that, the collision efficiency of coated particles is much less than that of uncoated particles. Coatings therefore slow down the flocculation process. Since particles in natural waters are coated, this may explain why several authors do not observe flocculation at the limnic-brackish boundary.

Eisma et al. (1991b) state that flocculation does not take place primarily by Van der Waals forces but by organic matter, whereby long-chain organic molecules, such as natural polymers, play an important role. These molecules extend through the water mantle around the particle and stick together when particles approach each other. Salinity has little effect on this.

Figure 4.1  Effect of organic coatings on the flocculation process of natural sediment particles in blade type reactor tests (Gibbs, 1983). Reprinted with permission from Environmental Science & Technology 1983, 17,237-240. Copyright 1983 American Chemical Society
The classical concept of salt flocculation at the limnic-brackish boundary is therefore superseded. Van Leussen (1994) however measured the largest macroflocs at the seaward end of the estuary. This indicates an increase in flocculation ability (i.e. collision efficiency) with increasing salinity. Therefore, he states that salinity remains an important parameter in the flocculation of estuarine sediments, but not at the upper estuary with a few ‰ salinity. There organic coatings may retard the flocculation rate. At higher salinities however the double layer thickness may be sufficiently reduced for bridging between particles by polymers to become effective (Van Leussen, 1994).

It seems that the impact of salinity may differ along the estuary with its salinity gradient. Salinity changes may also occur on a specific location due to the tidal excursion and due to seasonal changes in freshwater input. It remains uncertain whether salinity will have an effect on the flocculation of the suspended sediments.

4.2.2 Biological cohesion of mud flocs

Wilkinson et al. (1997) studied the role of natural organic matter (NOM) for the coagulation of colloidal material in freshwater. They found that the chemical nature and structure of NOM is very important for the flocculation behaviour. NOM mainly produced in soils tended to form coatings around particles whose negative charge diminishes coagulation. NOM of aquatic origin appeared to accelerate the rate of coagulation by a polymer bridging process. Therefore the organic matter content alone is not likely to be a good parameter for defining biological cohesion of flocs. A more specific parameter like the biopolymer concentration in the suspended mud seems a better parameter, especially for defining the amount of sticky polymers present that may glue flocs together.

As was already stated above, natural polymeric substances can increase the collision efficiency which causes increased aggregation and therefore increased floc sizes (Decho, 1990; Eisma, 1986; Ten Brinke, 1993). These polymeric substances are mainly polysaccharides produced by plankton, benthos and bacteria (Harris & Mitchell, 1973; Avnimelech et al., 1982). Polymer bridging is thought to be an important biological flocculation mechanism. Polymer chains that are on one side attached to a particle and with the other side extending into the surrounding water can become attached to another particle (La Mer & Healy, 1963 in: Harris & Mitchell, 1973).

Another form of biological flocculation could be the flocculation by transparent exopolymeric particles (TEP). TEP are discrete transparent particles, rather than cell surface coatings (Alldredge et al., 1993). Discrete particles (TEP) are probably generated abiotically from the extracellular polysaccharides produced by diatoms (Passow et al. 1994). Passow & Alldredge (1995) observed that TEP are an important factor for the flocculation of diatoms during a bloom in a mesocosm. It seems that phytoplankton aggregation and the occurrence of organic flocs may be highly influenced by TEP. Whether TEP will be produced and how large the stickiness of it will be, depends on phytoplankton species composition, abundance and physiological state. In a natural
environment as the Dollard estuary TEP are of course not only capable of flocculating diatoms but also other organic or inorganic particles may be captured by TEP. In this way TEP could very well be responsible for the formation of large mud flocs.

It seems that biological cohesion of flocs is strongly related with phytoplankton (e.g. diatoms) and possibly also with bacteria. The growth of these organisms obviously depends on seasonal variations, which explains why changes in biological cohesion of flocs mainly take place on a seasonal time scale.

4.3 Field experiment and methodology

The research was carried out in the ‘Groote Gat’ tidal channel with the Video In Situ (VIS) as described in chapter 2 and figure 2.1. Simultaneously current velocities and suspended sediment concentrations over the vertical were also measured. Other collected parameters were the water level, wave height, water temperature, salinity and chlorophyll a. The amount of biopolymers present in the suspended sediment could not be directly determined. As a measure of these biopolymers, the EDTA extracted carbohydrates content of the suspended sediment was used. A more extensive description of the measurements and methodologies is given in chapter 2.

4.4 Results

The results of the first VIS measurement are shown in figure 4.2. (This figure was already shown in chapter 3 as figure 3.1, but is repeated here for an easy comparison with figure 4.3) Figure 4.2a shows an example of the water level variation throughout the tidal cycle with the corresponding bed level referenced to Dutch ordnance datum (N.A.P.) on 11 October 1995. This bed level changes in time because the measurement ship was floating with the current. During flood tide the ship was floating up to the estuary head where the channel is shallower. During ebb tide, the ship was floating back towards the estuary mouth where the channel is deeper again. The tidal excursion along which the measurements took place is shown in figure 2.1. Figure 4.2b shows the measured floc size distribution expressed as a volume percentage. That means that at about 12:00 h 76% of the volume of suspended sediment consists of flocs smaller than 300 µm and 24% of the suspended sediment volume consists of flocs larger than 300 µm. When the lines in figure 4.2b go down the floc sizes are actually increasing and vice versa. Figure 4.2b shows that the floc sizes vary quite strong during the tidal cycle. Figure 4.2c shows the depth averaged current velocity and the suspended sediment concentration (SSC) at the depth of the size measurements, at 2.9 m below the water surface. The SSC strongly correlates with the floc sizes, which may be explained by the increased floc collision frequency due to a larger abundance of flocs at higher SSC. Another factor that could influence the floc sizes on this tidal time scale is the turbulence intensity that causes increasing collision frequency with increasing current velocity. This may results in larger flocs, but it may also
cause floc breakup when the turbulence level is too high. Floc sizes may also increase due to resuspension of larger flocs from the bed.

Figure 4.2 VIS measurements 11 October 1995
Figure 4.3 VIS measurements 19 October 1995
There are two possible origins of the large flocs observed at high SSC. They are either formed by aggregation in the water column, or the large flocs were eroded from the bed. Observations on 29 May 1996 (discussed later in fig. 4.5) showed increasing floc sizes while sediment was settling out of the water column due to a decelerating current velocity. This suggests that at that time flocs were formed by aggregation in the water column, since it is very unlikely that large flocs were eroded from the bed and dispersed into the water column during a period of sediment settling.

The measurements of 11 October 1995 took place about two days after spring tide. Figure 4.3 shows the measurements on 19 October 1995, which was about two days after neap tide. These neap tide measurements are quite comparable to the spring tide measurements. There is still quite a large tidal variation of the floc size and a good correlation with the SSC. There are some differences. The range of current velocity, SSC as well as the range of the floc size distribution is a bit smaller during neap tide. The smaller range of the floc size distribution during neap tide seems coincidental since this was not observed in all measurements.

Not all measurements are shown in detail here, but the daily averaged floc size, the daily averaged range of the floc size and the SSC of all measurements are shown in figure 4.4. The presented averages are based on the floc volumes. That means that the average floc volume was calculated and then the equivalent diameter for a sphere of this volume was determined, as was explained in chapter 2. It is a volume based average diameter. In this way, the calculated floc sizes are representative of the larger flocs. It is these larger flocs that make up most of the suspended volume and therefore they are the most important for mud transport and sedimentation.

However, the use of a mass weighted average floc diameter would represent the suspended sediment mass. For mud transport and sedimentation the mass fluxes are important, not the volume fluxes. Therefore floc sizes and settling velocities were determined from a limited number of Video In Situ measurements. The Stokes density of the flocs was calculated and subsequently the mass weighted average diameter was determined. A comparison between this mass based diameter and the volume based diameter showed that the volume based diameter is only about 3% larger than the mass based diameter. This difference is small enough to justify the use of the volume based floc diameter as representative for most of the suspended sediment volume and mass.

Figure 4.4a shows that the average floc size is approximately the same for all measurements. There is one measurement however on 29 May 1996, where the average floc size as well as the range of floc sizes is significantly larger than during the rest of the year. Figure 4.5 shows this measurement.
Figure 4.4  a) Seasonal variation of mud floc size b) Seasonal variation of suspended sediment concentration c) Wave height, EPS, LOI, Chlorophyll-a’ and water temperature’ (* data from the National Institute for Coastal and Marine Management (RIKZ), The Netherlands)
Figure 4.5  VIS measurements 29 May 1996
The following can be concluded from figure 4.4 and 4.5:

1. **Tidal variation in floc size and SSC.**
   Figure 4.5b shows an abundance of flocs larger than 1000 µm during this day. As in the other VIS measurements the floc sizes show a tidal variation. Figure 4.5c shows that there is a correspondence with the SSC. The increase in floc size during ebb and flood corresponds with increases in SSC. However, during the ebb tide, floc sizes kept increasing until slack tide, while the SSC was already decreasing. Only after slack tide, when the flood current increased the floc size decreased again.

2. **Flocculation occurs in the water column.**
   The measurement of 29 May 1996 also shows that flocculation in the water column at least partly determines the floc size and that floc size is not entirely dependent on erosion of large flocs from the bed. This can be seen from the observed floc sizes during the ebb tide. At that time maximum floc sizes did not coincide with the maximum SSC. Maximum floc size occurred about two hours after maximum SSC while the current was decelerating and sediment was settling. Lower turbulence levels may have decreased floc breakup at that time, which allowed the growth of large flocs. This suggests that flocs were formed by aggregation in the water column, either by settling induced collisions or by collisions due to the remaining turbulence. An increase of the floc size due to erosion of large flocs from the bed and dispersion into the water column is very unlikely during this period of sediment settling.

3. **Large flocs are not caused by a large SSC.**
   When the measurement of 29 May 1996 is compared to the other measurements, the SSC on 29 May is too low to explain the observed large floc sizes. This can also be seen in figure 4.4b that shows the seasonal variation of the SSC. From figure 4.4a and 4.4b, it is clear that the SSC did not determine the floc size variations on this yearly time scale as it did on the tidal time scale. There can still be an influence of the SSC, but clearly also some other factors must have determined these floc size variations throughout the year. There may be a relation with a plankton bloom in April and May of 1996 that will be dealt with in the discussion.

4.5 **Discussion**

There are several other factors than SSC that may influence the seasonal variation of floc size. Changes in the collision efficiency seem to play an important role. This may depend on salinity and biological cohesion of flocs, but water temperature, organic content and turbulence in the water due to wind waves may also play a role in the seasonal variation of floc sizes.

These factors are plotted in figure 4.4c. The possible impact of biological cohesion of flocs is expressed in the chlorophyll-a content and the amount of EDTA extracted carbohydrates from the suspended sediment.
Figure 4.4c shows the following typical results:

- The wave height does not seem to have a large influence on the floc sizes in the tidal channel. On 11 and 19 October 1995, 11 and 18 April 1996 and on 14 and 21 October 1996 the wave height varied considerably between the measurements in the same week. However there was hardly any variation in average floc size (figure 4.4a). The range of floc sizes was lower on 19 October 1995 and 11 April 1996 when the waves were high, but the range was also lower on 14 October 1996 when the waves were low. There is no correlation between the range of floc sizes and wave height. There is also no clear relation between range of floc size and neap/spring tide.

- In April and May 1996 there was a large phytoplankton bloom in the Dollard estuary as can be seen from the Chlorophyll-a content of the water. At the end of this bloom the much larger floc sizes of 29 May 1996 were measured. Earlier in the bloom however on 11 and 18 April the floc sizes were still in the same range as in the other measurements. So there could be a relation between the large flocs and the bloom termination.

- The effect of the plankton bloom is not visible in the organic content of the suspended sediment. The organic content is expressed by the loss on ignition (LOI%), which is the percentage of combustible organic material. The percentage of organic material in the suspended sediment varies between 17% and 27%, with the highest values in autumn. During the bloom the suspended flocs were still mainly composed of inorganic material. There is no relation visible between LOI% and floc size.

- The water temperature does not seem to have a direct influence on the floc sizes. The large average floc size on 29 May 1996 coincided with a high water temperature, but on 1 and 8 August 1996 water temperatures were also high but no large flocs were observed. In addition, the low water temperature on 12 December 1996 is not associated with smaller flocs. The increase in water temperature in spring however may have been a starting factor for the plankton bloom in May and June.

- A low salinity occurred on 12 December 1996 and a high salinity on 1 August 1996. On these days the average SSC was quite high and comparable. The floc sizes were of the same order. This indicates that salinity is not a steering parameter for the floc size. That corresponds with the findings of Eisma et al. (1991a) who also found no relation between salinity and in situ floc size. The lower salinity in winter however is consistent with winter run-off and nutrient fluxes necessary for the onset of the spring plankton bloom.

Summarising, waves, water temperature, organic content and salinity do not seem to explain the seasonal variation in floc sizes. But there may be a relation between the plankton bloom in April and May 1996 and the large flocs at the end of this bloom on 29 May 1996.

Diatom blooms are often terminated by mass sedimentation of the diatoms. Flocculation of the phytoplankton cells into large flocs (marine snow) enhances the settling velocity of the diatoms (Smetacek, 1985). Diatoms are also known to form more sticky flocs during later
stages of a bloom (Decho, 1990; Kiørboe et al., 1990). Decho (1990) suggests that exopolymeric substances excreted by diatoms cause this aggregation. These biopolymers may act as some sort of glue and increase floc sizes.

Mass flocculation of diatoms into macroflocs (marine snow) has regularly been observed by several authors in the field (Alldredge & Silver, 1988; Kranck & Milligan, 1988; Alldredge & Gottschalk, 1989; Riebesell, 1991) and in mesocosms (Riebesell, 1989; Passow & Alldredge, 1995). The occurrence of large flocs only at the end of the phytoplankton bloom in the Dollard is therefore consistent with the observations of mass flocculation at the end of blooms found in literature. The large flocs observed on 29 May 1996 are suggested to be caused by biopolymers excreted by phytoplankton or bacteria. Ten Brinke (1993; 1994) also found significantly larger floc sizes during a period with high algal biomass in the Eastern Scheldt and suggested that these larger flocs were caused by sticky biopolymers.

As a measure for biopolymers, the EDTA-extracted carbohydrates content of the suspended sediment was used. During the plankton bloom this carbohydrate content was higher than during the rest of the year, but the highest amount of biopolymers was measured on 18 April. This is not at the end but more at about one-third of the plankton bloom duration. Large flocs occurred only at the end of the bloom. Therefore the quantitative amount of EDTA-extracted carbohydrate is probably not a good parameter to describe the stickiness of the suspended particles. The plankton bloom and accompanying biopolymers also do not cause an absolute increase in the amount of organic material in the suspended flocs, as can be seen from the LOI% in figure 4.4c.

Figure 4.6 shows the plankton species composition in the tidal channel Groote Gat in the Dollard estuary. In the beginning of the bloom the diatom *Skeletonema costatum* dominated. Then the diatoms almost disappeared and dinoflagellates, mainly *Heterocapsa rotundata*, and micro-flagellates dominated. Subsequently in May the diatom *Thalassiosira nordenskioeldii* was most abundant. Kiørboe & Hansen (1993) investigated the production of particulate mucus or transparent exopolymeric particles (TEP) by phytoplankton cells and its role in aggregate formation. They found that *Skeletonema costatum* cells are sticky in themselves, and coagulation depends on cell-cell sticking and does not involve mucus. This suggests that *Skeletonema costatum* will not contribute to mud floc aggregation. Kiørboe & Hansen (1993) even found that *Skeletonema costatum* at times excretes a solute substance that reduces enhanced flocculation. This seems in accordance with the observed “normal” floc sizes on 11 and 18 April 1996 during the *Skeletonema costatum* bloom (fig. 4.6).

Other investigated diatoms, however, produced TEP and coagulation depended on TEP-cell, rather than cell-cell sticking. *Thalassiosira nordenskioeldii* was not investigated by Kiørboe and Hansen (1993) but *Thalassiosira pseudonana* was among the investigated diatoms and it produced TEP. Such production of TEP may have contributed to the growth of the mud flocs at the end of the plankton bloom in the Dollard estuary. Bacterial activity may also favour the formation of large aggregates during the decline of a bloom.

![Graph showing observed phytoplankton](image)

**Figure 4.6** Observed Phytoplankton in the Dollard estuary. (Source: National Institute for Coastal and Marine Management (RIKZ), The Netherlands)

It seems clear that the quantity of biopolymers present in the mud flocs is not a good measure for the stickiness of these mud flocs. The particulate mucus produced by different species of diatoms differs in chemical composition (Decho, 1990) and appears also to differ in its surface properties (Kørboe & Hansen, 1993). That means that the ‘glue’ quality of biopolymers present in the water is more important than the absolute quantity. Therefore biological cohesion of flocs may depend on phytoplankton composition, phytoplankton concentration, the physiological state of phytoplankton and bacterial production or degradation of biopolymers during cell lysis at the decline of a bloom.

It is still not clear how the large flocs observed on 29 May 1996 were formed. The absolute quantity of EDTA-extracted carbohydrates could not explain it. The large floc sizes did however occur during the decline of the bloom, which is a commonly observed phenomenon in the ocean and coastal seas. Probably the biopolymers present on 29 May 1996 had a large impact on the overall stickiness of the suspended sediment, even though the absolute quantity was less than on 18 April 1996 when large flocs did not appear. Although the exact cause of the intensive flocculation on 29 May 1996 can not be
determined, it is likely that there is a relation with the plankton bloom. It seems that the mortality associated with the end of the bloom enhances the average size of the visualized flocs.

4.6 Conclusions

Many parameters that could affect mud floc size in the Dollard estuary were measured on 10 measurement days throughout the period of one year. This is a relatively short observation period for establishing seasonal fluctuations in floc sizes. Furthermore it is difficult to establish cause and effect relationships from correlations between observations. Despite these flaws the following conclusions can be drawn:

On a tidal time scale, floc sizes in the Dollard estuary were correlated with the SSC. The average floc size was about 140 µm.

On a seasonal time scale the observations of floc size and phytoplankton showed that during the decline of a spring plankton bloom floc sizes in the Dollard substantially increased. An average floc size of about 250 µm was observed. Factors like salinity, water temperature and wave height did not seem to have a direct influence on the seasonal fluctuation of floc sizes.

Large flocs can form in the water column from smaller aggregates or they are eroded from the bed. The observation of growing flocs while the SSC was already decreasing on 29 May 1996 shows that at least part of the suspended flocs were formed from smaller flocs or particles in the water column.

Biological cohesion of flocs is probably more dependent on the ‘glue’ quality of the biopolymers than on the absolute quantity. The quantity as well as the quality of the biopolymers may depend on the species composition, concentration and physiological state of phytoplankton and bacteria.

Biological processes seem more important than physical processes for the flocculation of fine sediment during the decline of a plankton bloom. This may have impact on the seasonal variation in fine-grained sediment dynamics.