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# SUSPENDED-MATTER PARTICLE SIZE IN SOME WEST-EUROPEAN ESTUARIES; PART I: PARTICLE-SIZE DISTRIBUTION

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## ABSTRACT

**Particle size of suspended matter was measured in five Northwest-European estuaries by Coulter counter and pipette analysis, and *in situ* with a suspension camera. Particle sizes measured by Coulter counter and pipette analysis became finer at the saltwater contact, but the *in situ* particle (floc) sizes did not show this. It is concluded that the particle size measured by Coulter counter and pipette analysis indicates the fragility (or firmness) of the flocs. The *in situ* particle size is variable, and is not related to changes in salinity, the content of organic matter in the flocs or the bulk composition of the organic matter. There is no consistent evidence that salt flocculation is an important factor in river mouths.**

## 1. INTRODUCTION

Particle-size distributions obtained in the estuaries of the Ems and Rhine rivers in 1980-1983 and in the Gironde in 1983-1984 indicated that at very low salinities the particle size of suspended matter measured by Coulter counter and/or pipette analysis became finer. It was most clearly seen in the Gironde where at low salinities (between 0 and 3) the fraction $< 4\ \mu m$ reached almost 100%. When the first measurements were made in the Rhine mouth, the presence of fine-grained suspended matter at low salinities was attributed partly to the formation of fine-grained gypsum particles of 1-3 $\mu$m diameter (EISMA *et al.*, 1980). During the subsequent work, it became clear that such particles were not present in sufficient numbers to have much influence on the particle-size distributions of the suspended matter. Therefore, the increase in the relative amounts of fine particles can be caused either by the formation of small flocs out of even smaller particles (flocculation), or by break-up of larger flocs. From a comparison with *in situ* size measurements based on *in situ* photography of the particles in the water, and comparison with large, carefully sampled, undisturbed flocs, it was concluded that the particles measured by Coulter counter or pipette analysis were mainly fragments of flocs broken up during sampling and size analysis (EISMA *et al.*, 1983). The presence of small floc fragments at low salinities was found to coincide in the Ems and Rhine estuaries (during the winter), with a maximum in the concentration of dissolved carbohydrates (EISMA *et al.*, 1982, 1983; EISMA, 1986). It was assumed that mobilization of polysaccharides at low salinities resulted in weakening the floc structure. After 1983 measurements were also carried out at the mouth of the Rhône river (in 1984-1985) and in the Scheldt estuary (in December 1986). The locations of the estuaries studied are shown in Fig. 1. These estuaries are of different character: the Ems, Rhine, Scheldt and Gironde estuaries are partially mixed tidal estuaries, while the Rhône river mouth is of the saltwedge type without tides. The Rhine and the Scheldt estuaries are very polluted; a salinity of S $\sim$0.6 is regularly observed in the Rhine river because of salt discharges from the mining industry. Very low salinities (S $\sim$0.1 or less) as observed in the other four estuaries hardly occur in the Rhine river mouth. The Gironde is a very long estuary (about 100 km), whereas the other estuaries have a length of about 25 km or less. The Gironde is also exceptional in that it receives the water from two rivers, the Garonne and the Dordogne.

In this paper (a) additional results of pipette and Coulter counter particle-size measurements are presented, and (b) a comparison of particle-size results obtained by pipette analysis and Coulter counter with *in situ* results obtained with a Benthos plankton camera is made. The particle-size measurements were usually part of a larger programme whereby data on organic matter, plankton, nutrients and/or biological activity were also collected. This made a better interpretation of the particle size data possible.

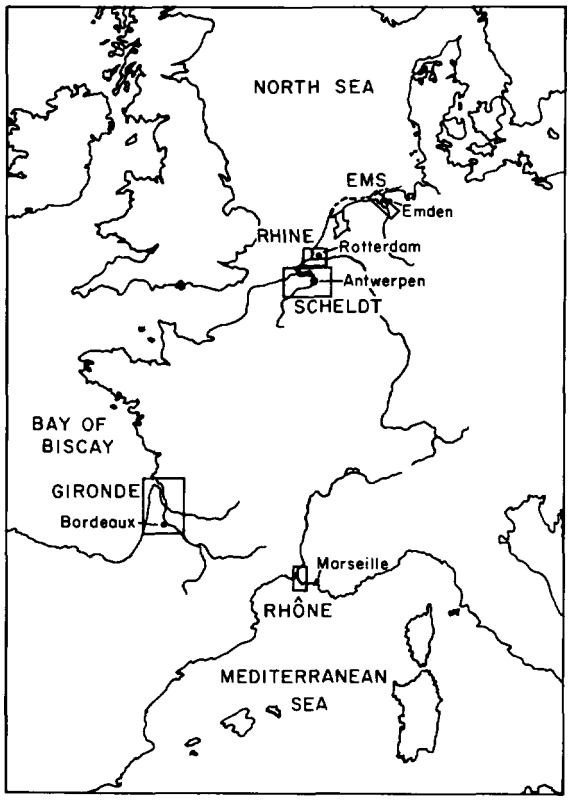



Fig. 1. Location of the estuaries of the rivers Ems, Rhine, Scheldt, Rhône and Gironde.

Acknowledgements.—We are much indebted to the MAFF Fisheries Laboratory, Lowestoft, U.K., for the loan of a Benthos plankton camera and to the captain and crews of the 'Navicula' (NIOZ, Texel), 'Luctor' and 'Jan Verwey' (DIHO, Yerseke), 'George Petit' (CNRS, Banyuls), 'Aquitaine' (CNRS, Bordeaux) and 'Ebalia' (IABA, Bordeaux) for a pleasant stay on their ships and for their help during sampling in the estuaries discussed in this paper. To J.H. Vosjan and E. Pauptit we are indebted for ETS data and to G.W. Berger, D. Waaiers and J. Visser for their help on board and in the laboratory. The sampling in the Gironde and in the Rhône mouth was part of the GRECO-ICO programme of the CNRS, France; the sampling in the Scheldt river and estuary was part of the CEC Project on Transfer Processes and Modelling in the Scheldt estuary (contract no. B 16-B-191-NL).

## 2. ANALYTICAL METHODS

Particle size was measured either by pipette analysis, a Coulter counter or *in situ* photography of the particles suspended in the water with a Benthos plankton camera. Sampling was achieved with a 5-$dm^3$ Niskin bottle or 1-$dm^3$ glass bottles mounted on a Postma sampler. Positioning was done with the help of buoys and beacons along the shore (Ems, Rhine, Scheldt, Gironde) and with radar or Loran (Rhône mouth).

### 2.1. PARTICLE-SIZE ANALYSIS

Pipette analysis was carried out in 1-$dm^3$ samples with a 25-$cm^3$ pipette. The depth to which the pipette was inserted into the sample and the time interval between shaking the sample and inserting the pipette were calculated on the basis of Stokes' Law, assuming the particles to be quartz spheres. The results therefore gave an equivalent size: microscope and camera analyses indicated that the particles were not spherical (at best only approximately so) and were flocs consisting of a mixture of mineral grains, organic matter and enclosed water.

The suspended matter concentrations of the samples measured ranged from approximately 2 $mg \cdot dm^{-3}$ to several hundred $mg \cdot dm^{-3}$, and were occasionally greater. The water sampled with the pipette was filtered over a pre-weighed 0.4 $\mu$m pore size 47-mm diameter Nuclepore filter by suction filtration. Weighing was done after drying at 70°C on a Cahn microbalance, which has an accuracy of 0.0001 mg. In this way, fractions containing only a few percent of the total amount of suspended material in a sample could also be accurately weighed at total concentrations as low as 2 $mg \cdot dm^{-3}$. Nuclepore filters were used because of their low weight ($\sim$15 mg), well-defined pore size, and low adsorption of air moisture after drying.

Because the pipette method is sensitive to mechanical disturbances (shock waves, vibration) and to temperature gradients in the room or laboratory, the samples for pipette analysis were either quickly brought to a 'quiet' room on land or analysed several hours later when the ship was at anchor with the engines off. When the ship was quiet on stream, the coarsest size fractions were pipetted off directly on board, which took less than 30 min, and the fine fractions were done later. No wall effects were observed using a 7-cm diameter tube. Shock waves and vibrations were avoided, and when they occurred, the analysis was repeated. Temperature effects were very difficult to eliminate in the absence of a constant-temperature room. Thus temperature effects may have influenced the results, particularly for the fine fractions and for samples with low suspended-matter concentrations. Multiple analyses of the same water sample showed that 10 to 20% of the results differed significantly from the other 80 to 90%, particularly for the finest size fractions ($<1$ $\mu$m, 1 to 2 $\mu$m), but in some cases even for the largest size fractions. This indicates that in general, within the

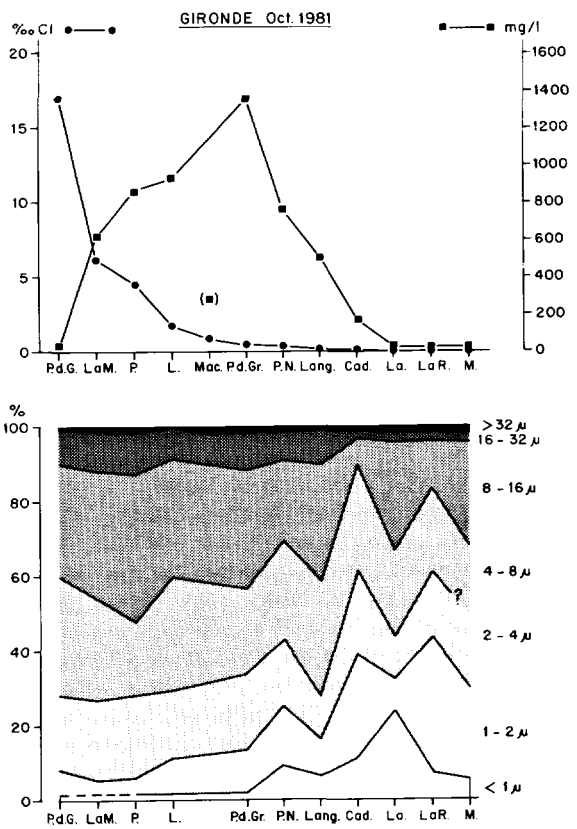
same estuary under more or less similar conditions, reproducible results are obtained but that pipette analysis only gives the general trends: samples showing an exceptional distribution should be discarded, although they may reflect real exceptional conditions.

Standard TAII equipment was used for Coultercounter analysis . Because the water must be conductive for making any sort of measurement, natural water samples with a salinity of less than S ~5 could not be reliably measured without adding salts. To avoid inducing artificial flocculation, pipette analysis was employed at low salinities, usually with some overlap with the Coulter counter. The Coulter counter distributions generally agreed well with those of the pipette analysis, as found before (EISMA *et al.*, 1983), but had less variability, which is evident in Fig. 6 for the river Scheldt and estuary. This is considered to reflect the larger susceptibility to error of the pipette method. Note that both for pipette and Coulter counter analyses, samples were obtained using sampling bottles so that the particles (flocs) were partly broken.

*In situ* photography with a Benthos plankton camera (EDGERTON *et al.*, 1981) produced pictures (silhouettes) of the particles in the water at a 1:2.51 magnification. Particles smaller than 90 to 100 $\mu$m became less sharp and seemed to disappear when out of focus. The negatives were analysed in an image analysis system, which was developed by DIFA Measuring Systems and NIOZ (EISMA *et al.*, 1990). Using the negatives for analysis had the advantage that particles in the water showed up white, while dust on the film appeared black. Size frequency distributions of particles larger than 100 $\mu$m were obtained in this way.

The additional analyses used in this paper included the following procedures:

- organic content of the suspended matter was estimated by ashing at 500°C for ~8 h, with a correction of 8% of the total inorganic material for water removed from clay minerals during heating (DANKERS & LAANE, 1983).
- dissolved and particulate sugars were determined after acid hydrolysis of the water and suspended matter sample on a Biotronik sugar analyser using routine analytical techniques. Hydrolysis conditions were 2 N HCl, 100°C, 3.5 h. Total sugars were calcu-



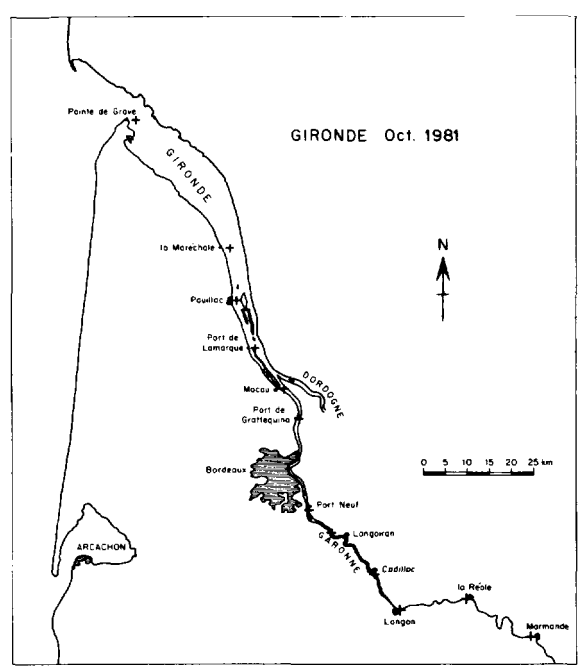




Fig. 2. Chlorinity (in ‰ $Cl^-$), suspended matter concentrations (in mg·$dm^{-3}$) and pipette/Coulter counter particle size in the Gironde in October 1981 at the sampling stations indicated on the map.

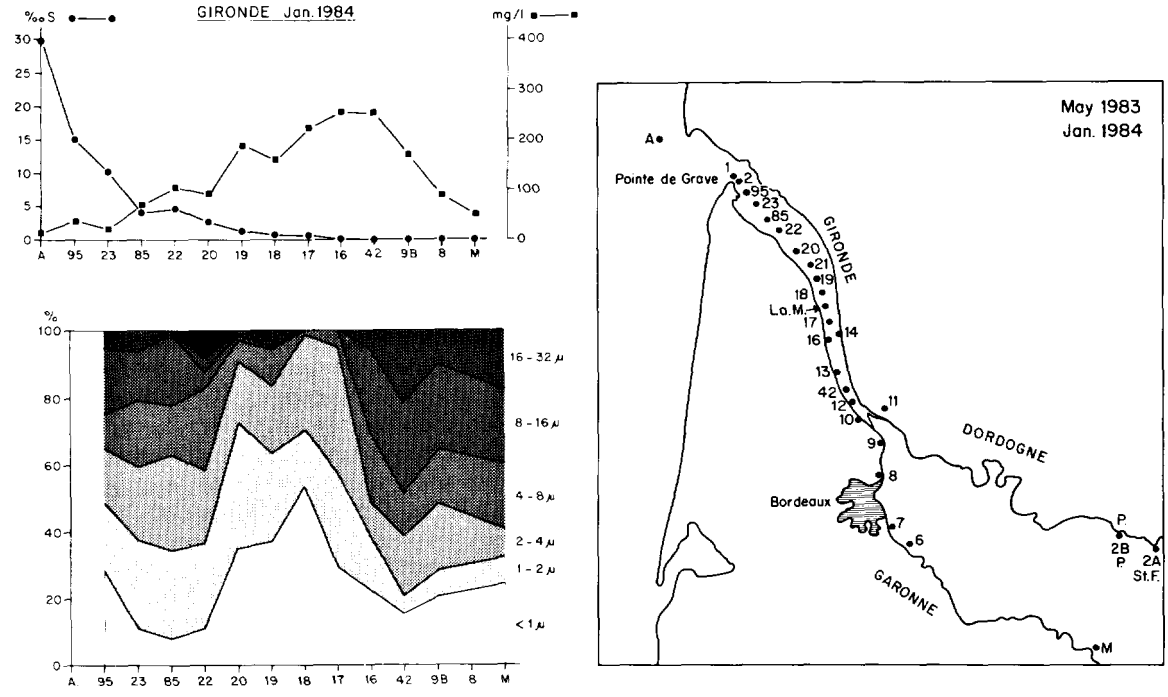



Fig. 3. Salinity, suspended matter concentrations (in mg·dm$^{-3}$) and pipette particle sizes in the Gironde in January 1984. The location of the sampling stations is indicated on the map.

lated as the sum of the individual monomers identified and quantified. Reproducibility of chromatographic analyses is better than 5%. The methods are described in detail in MICHAELIS & ITTEKKOT (1982).

- $\delta^{13}C$ of the organic fraction was determined mass spectrometrically after removal of carbonate by rinsing with dilute hydrochloric acid and combustion of the residue to $CO_2$. Values are given in ‰ relative to Vienna PDB, defined by NBS 19 carbonate = 1.95‰ *vs* VPDB (MOOK & TAN, 1990).
- chlorinity was determined by titration with silver nitrate in samples with an expected salinity of less than ~5. At higher salinity, total salinity was determined with a portable T/S meter or with a small Guildline CTD. The conversion of salinity into chlorinity or *vice versa* was done using Knudsen's Tables (US HYDR. OFFICE, 1959), which are based on the standard composition of seawater. An error is introduced below a salinity of ~5 because at low salinities the composition of the admixed river water influences the ratio between $Cl^-$ and the other ions. This effect was only taken into consideration in the Rhine river mouth.
- plankton samples were counted under an inverted microscope, directly on board or on land after storage with JKJ as preservative.
- ETS-activity was measured to get a relative measure for the respiration activity of living organisms in the suspended matter (VOSJAN, 1988). The ETS method is an activity measure with a saturation of the electron transport system with electrons; therefore it gives a potential or maximal respiration rate at incubation 500°C during ~8 h, with a correction of 8% of the total incubation temperature. In our case the incubation temperature was 20°C (VOSJAN & NIEUWLAND, 1987; VOSJAN *et al.*, 1990).
- current velocity and direction were measured (at station 83-120, 10.11.83) with a Toho-Dentan current meter.

## 3. RESULTS

### 3.1. RESULTS OF ADDITIONAL PARTICLE SIZE MEASUREMENTS (PIPETTE, COULTER COUNTER)

In addition to the particle-size distributions already published (EISMA *et al.*, 1982, 1983; EISMA, 1986), particle-size distributions for the Gironde in October 1981 and January 1984, the Ems estuary in November 1982, the Rhône mouth in September 1984 and the Scheldt estuary in December 1986 are given in Figs 2 to 6. Similar distributions were found in the Ems estuary in November 1983 and May 1984, and in the Rhône mouth in February 1985, but they do not give additional information and for reasons of space are not reproduced here. The entire series of measurements includes winter periods in the Ems, Rhine, Gironde, Rhône and Scheldt estuaries and spring-

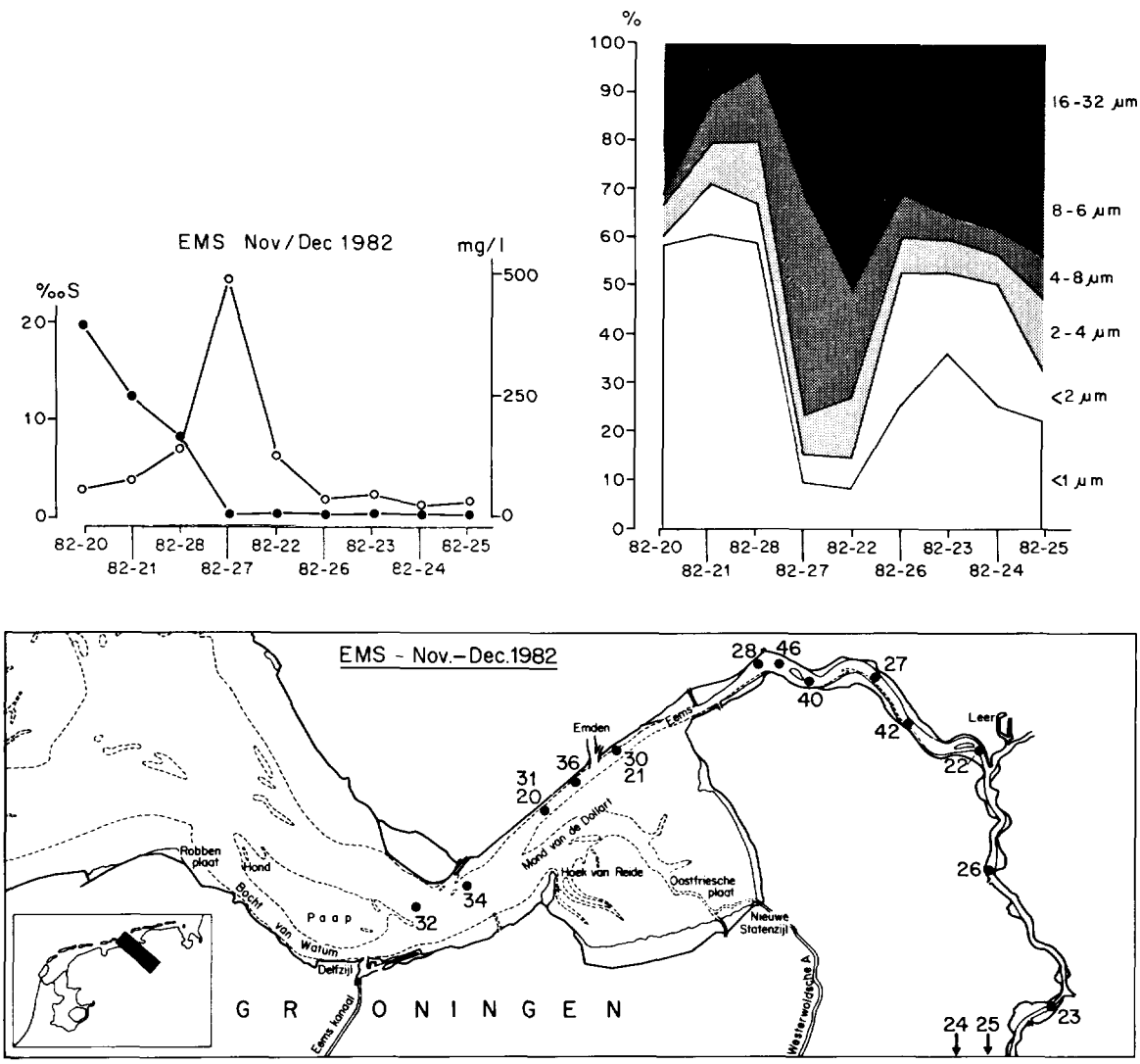



Fig. 4. Salinity, suspended matter concentrations (in mg·dm$^{-3}$) and pipette particle sizes in the Ems estuary in November-December 1982. The location of the sampling stations is indicated.

summer periods in the estuaries of the Ems, Gironde and Rhône. The distribution of salinity or chlorinity and the suspended matter concentration are also shown.

### 3.2. *IN SITU* PARTICLE SIZE (PLANKTON CAMERA)

In order to estimate to what extent particle size measured by pipette and Coulter counter is representative of the particle size *in situ* in the water (taking into account that particle break-up occurs during sampling and analysis), series of Benthos plankton camera photographs of suspended particles *in situ* were made in the Ems estuary in November 1982, in the Rhine mouth in January 1983 and in the Gironde in January 1984. The particle-size distributions determined from the photographs with the image analysis system described in EISMA *et al.* (1990) are given in Figs 7 to 9. In Fig. 10, the size distributions are reproduced in the same way as those obtained with pipette and Coulter counter, together with the distribution of salinity and total suspended matter concentration. Turbidity at very low salinity at one station in the Ems estuary (station 82-27: 0.3‰ $Cl^-$ or S=0.55) was too high (484 mg·dm$^{-3}$) to obtain photographs.

In the Ems estuary (Fig. 7), both the distributions obtained *in situ* and those obtained with pipette/Coulter counter showed an area with a change towards smaller particle size but were found at different places: in the pipette/Coulter counter data

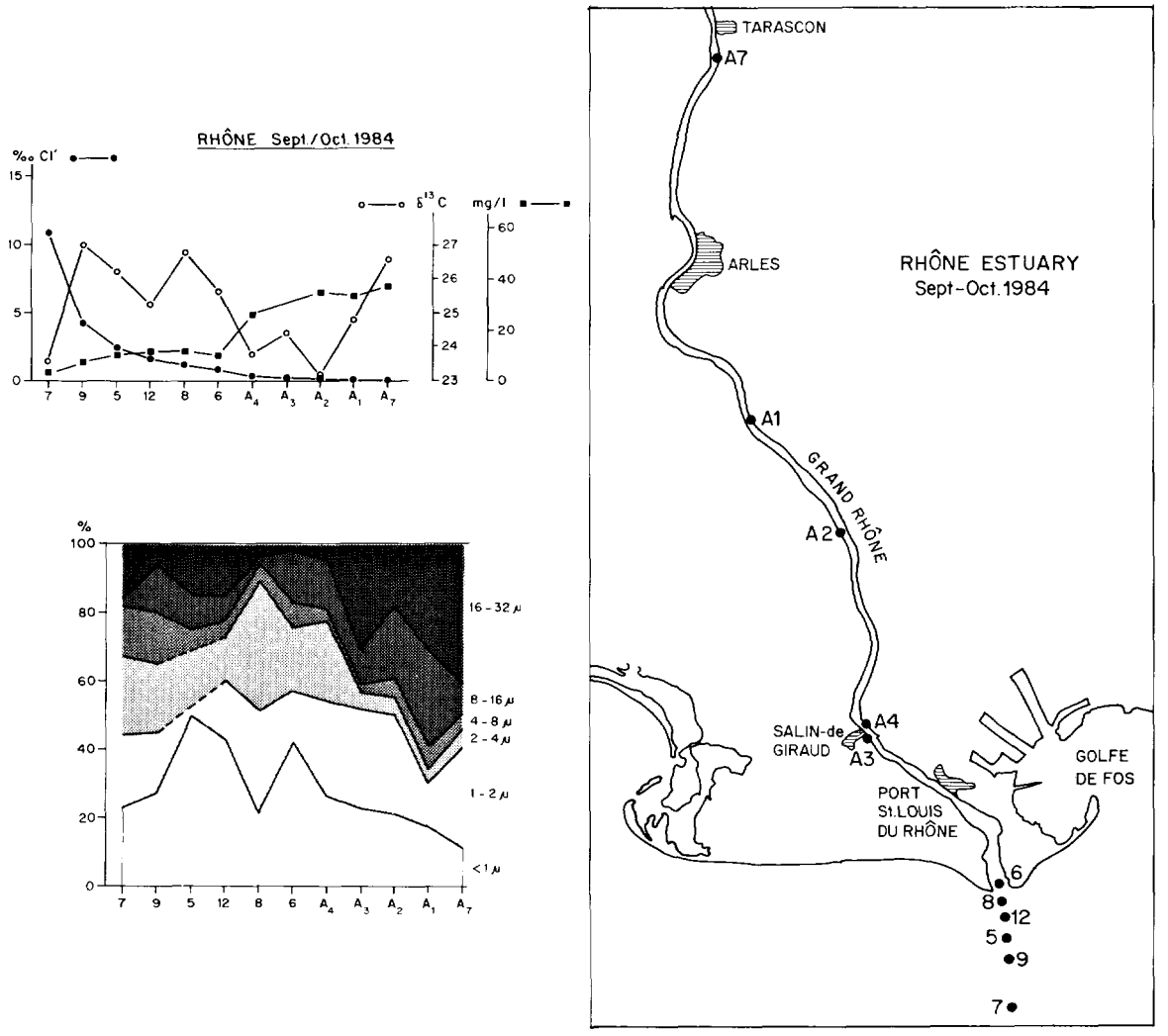



Fig. 5. Chlorinity (in ‰ $Cl^-$), suspended matter concentration (in $mg \cdot dm^{-3}$), $\delta^{13}C$ and pipette particle sizes in the Rhône river mouth in September-October 1984. The location of the samples is indicated on the map.

between stations 22 and 27 at salinities less than 1 and in the *in situ* distributions between stations 28 and 21 at salinities between 8 and 14. The *in situ* data for the Rhine mouth in January 1983 (for which no pipette/Coulter counter measurements are available) showed the reverse: an area with larger particle size at higher salinities (Fig. 8). The data for the Gironde (Fig. 9) again showed a zone of smaller particle size *in situ* at higher salinities (S-values between 4 and 10 at station 85-23), while in the pipette/Coulter counter data it occurred at lower salinities (S less than 1 to 3 between stations 17 and 20). This shows that there is no relation between the pipette/Coulter counter size distributions and the *in situ* plankton camera size distributions. It also confirms what had been found in earlier publications (EISMA *et al.*, 1983; EISMA, 1986): that flocs break up during sampling and size analysis, unless special methods are applied (diving, *in situ* measurements).

### 3.3. AUTOMATED-SCANNING-ELECTRON-MICROSCOPE ANALYSIS

Automated-scanning-electron-microscope analysis (EPXMA) of inorganic particulate material in suspension in the Ems estuary and in the Gironde had previously shown that the presence of a finer pipette/Coulter counter size at low salinities is not related to the source of the suspended matter (EISMA *et al.*, 1983, 1985). For the Rhône and the Scheldt, EPXMA was carried out in the same manner as for the Ems and Gironde (BERNARD *et al.*, 1986;

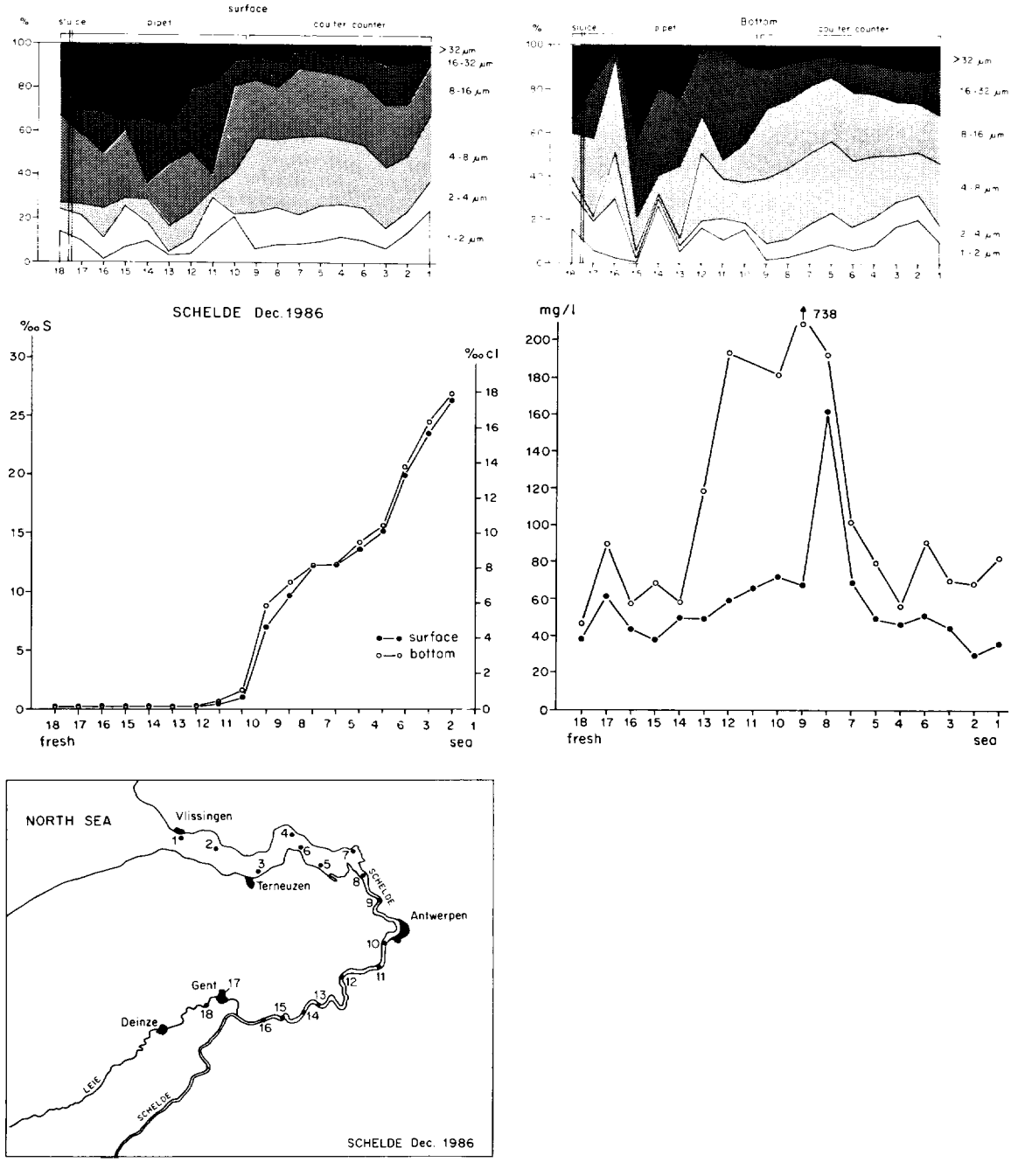



Fig. 6. Pipette and Coulter-counter particle sizes in the water of the Scheldt river and estuary in December 1986: -(top-left) surface water. -(top-right) bottom water. -(second row-left) Chlorinity (in ‰ $Cl^-$) in surface and bottom water in the Scheldt river and estuary in December 1986. -(second row-right) Suspended matter concentrations (in $mg \cdot dm^{-3}$) in the Scheldt river and estuary in December 1986. -(bottom) Sampling stations in the Scheldt river and estuary in December 1986. Station numbers indicated as on horizontal axis of the top figures.

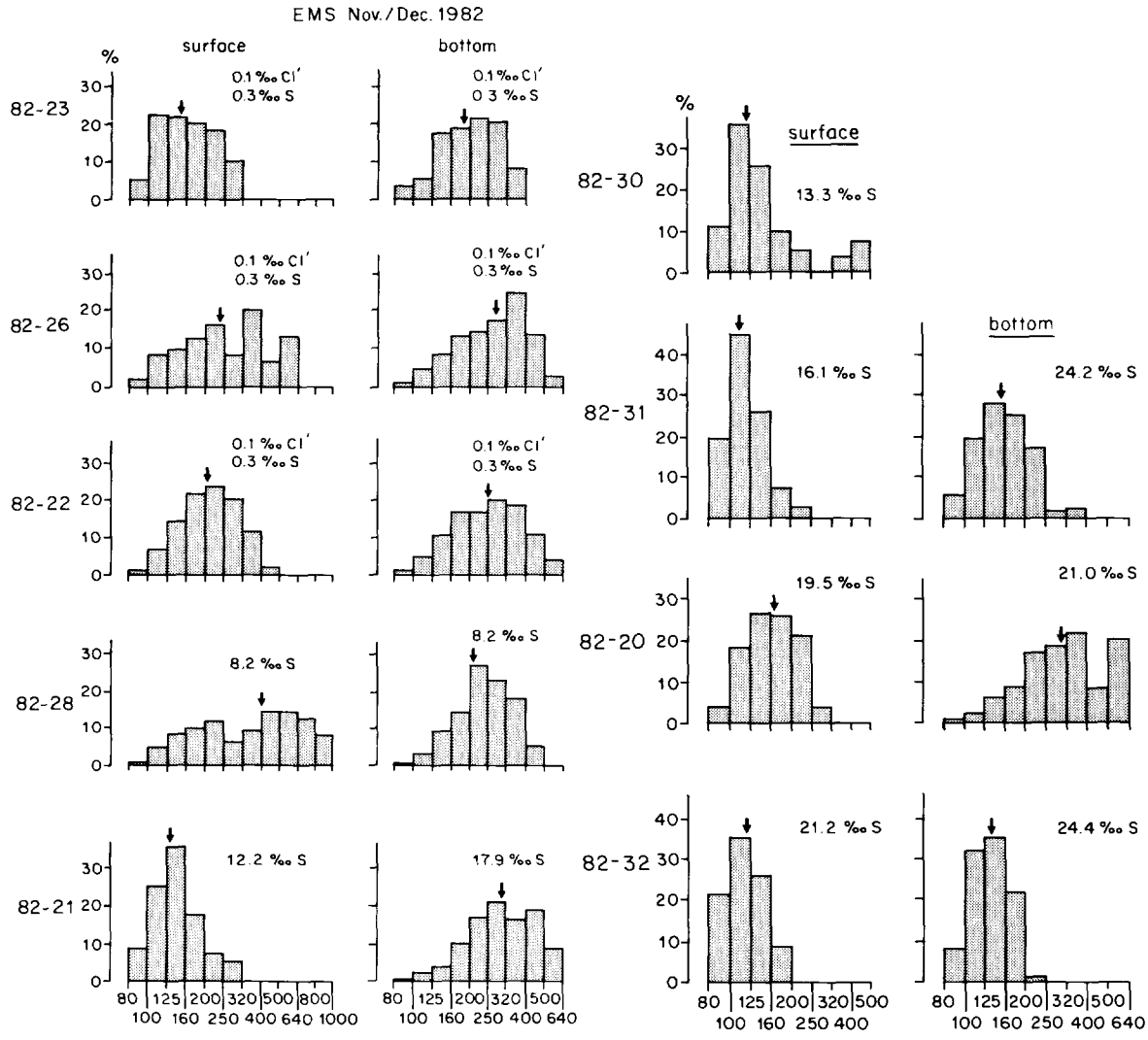



Fig. 7. *In situ* particle size distributions in the Ems estuary in November-December 1982. The location of the sampling stations is indicated in Fig. 4. The arrows indicate the median diameter.

BERNARD, 1989). The results for the Rhône are indicated in Fig. 11. The composition was variable from station A3 to station 7, but the only significant changes were the increase and decrease of the Ca-particles (presumably carbonate), suggesting an independent (biogenic) source of such particles in the river mouth. The composition at station A2 with a very high percentage of Ca-particles and correspondingly low percentages of Si-particles (group 9), Si+Al+K particles (group 5) and Ca+Si+Al particles (group 6) was exceptional. This probably points to a local sediment source. The shift to a finer particle size occurs at stations A2 to A4 (Fig. 5) but the deviating particle composition at station A2 alone is not sufficient to explain the finer pipette/Coulter counter particle size by an admixture of finer material from another source. In the Ems estuary, supply from the coastal sea dominates far into the freshwater section; in the Gironde, the suspended material comes from the Garonne river with a small admixture supplied by the Dordogne along the north side. On the basis of the $^{13}C/^{12}C$ ratio of the carbonate and organic fractions, SALOMONS (1975) and SALOMONS & MOOK (1981) have shown that in the Rhine mouth, material from the coastal sea and from the river are mixed along the estuary and that very little marine material reaches the saline-freshwater interface. In the Scheldt, there is a gradual mixing of river-supplied material and marine material, which already begins in the freshwater tidal area upstream of the fresh and saline water contact (BERNARD, 1989).

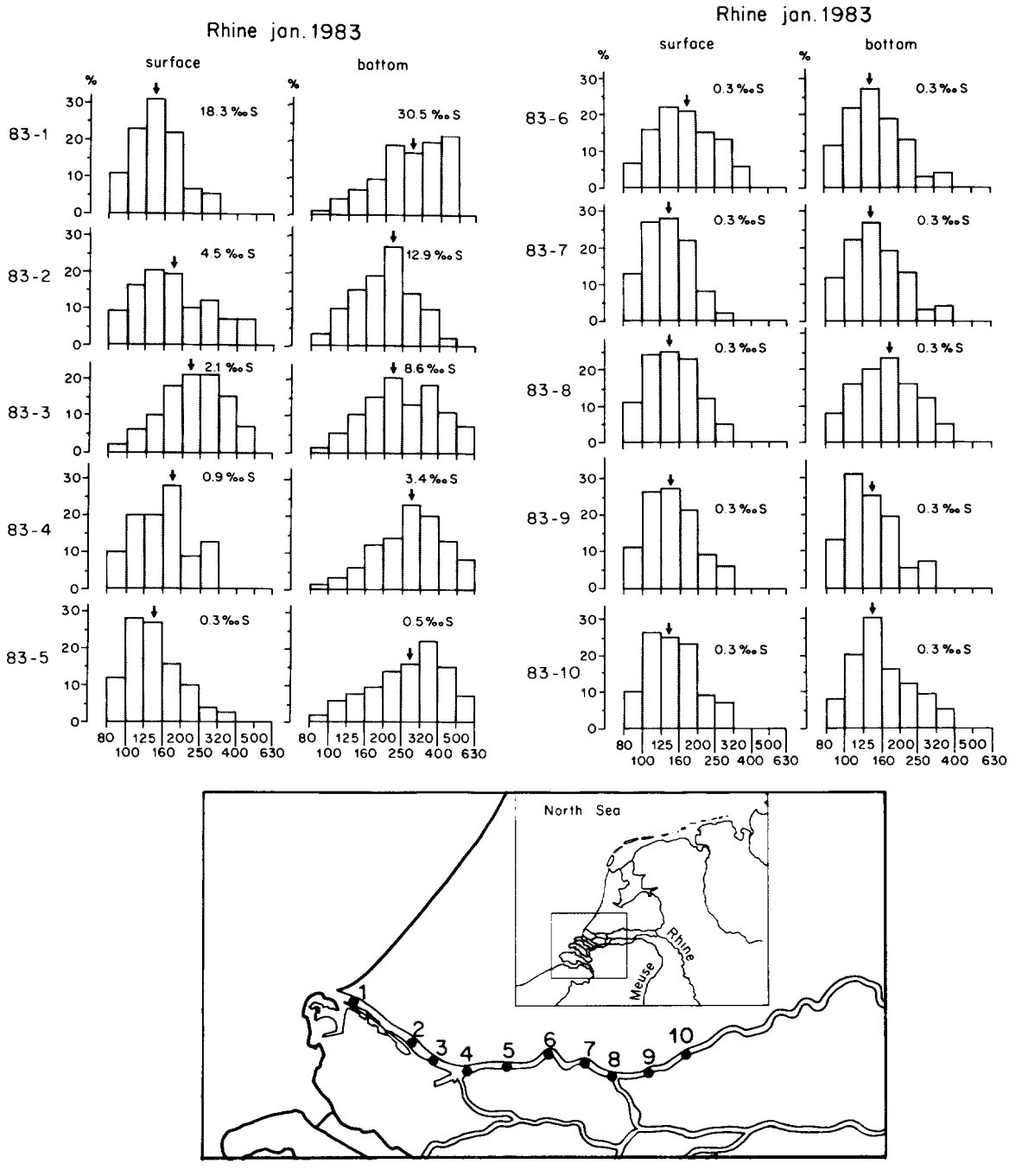



Fig. 8. *In situ* particle size distribution in the Rhine mouth in January 1983. The sampling locations are indicated on the map. The arrows indicate the median diameter.

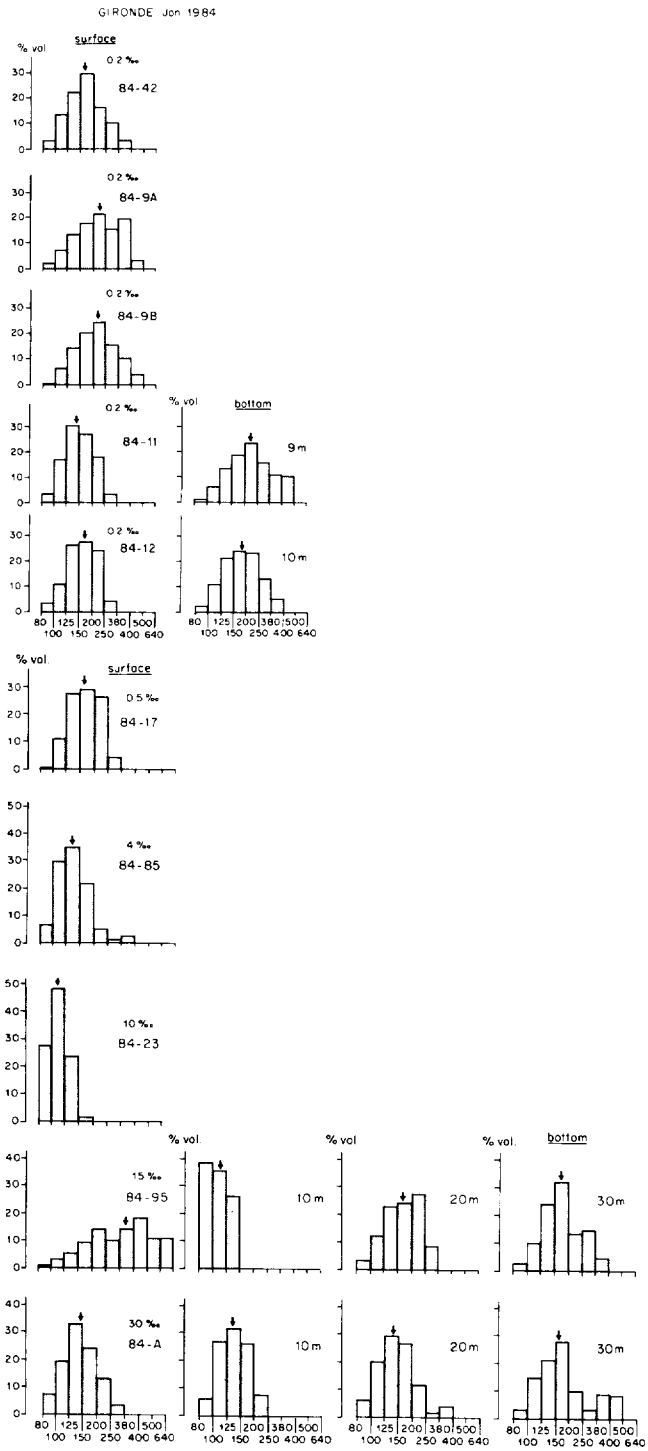



Fig. 9. *In situ* particle size distributions in the Gironde in January 1984. The sampling locations are indicated on the map of Fig. 3. The arrows indicate the median diameter.

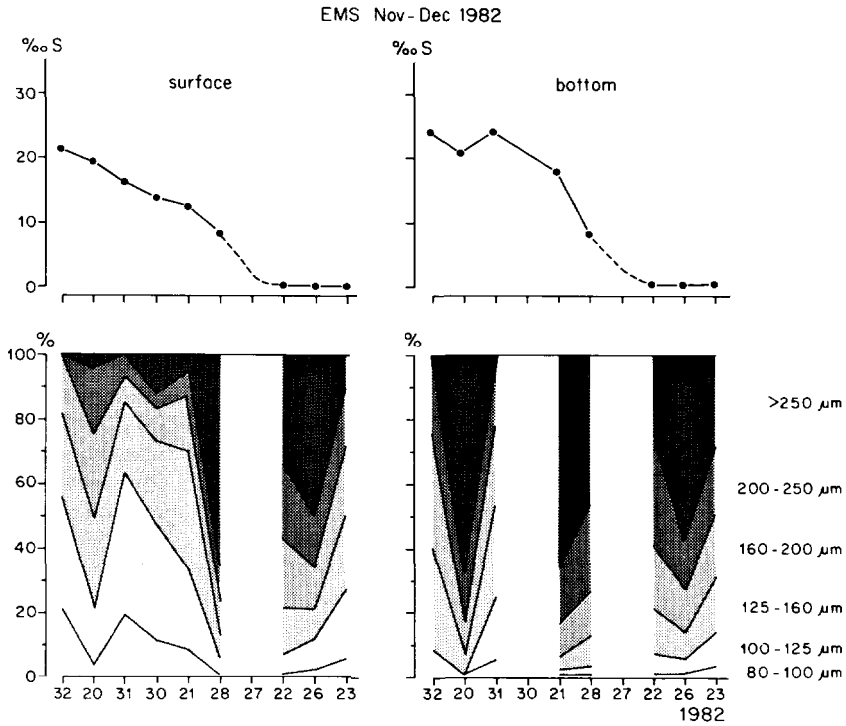



Fig. 10a. Salinity and *in situ* particle sizes in the Ems estuary in November-December 1982. The location of the sampling stations is indicated in Fig. 4.

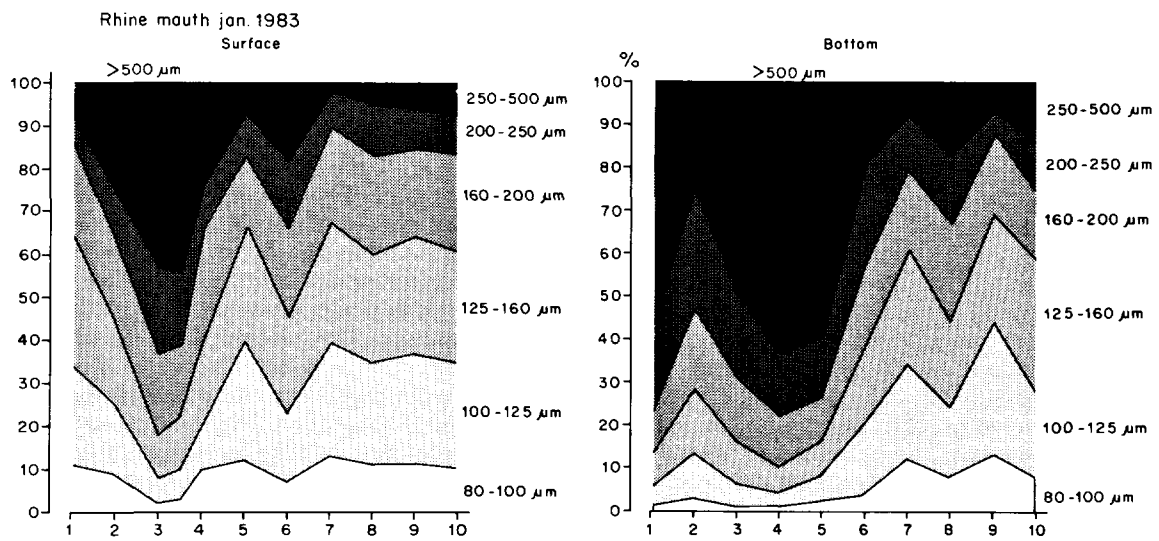



Fig. 10b. *In situ* particle sizes in the Rhine mouth in January 1983. The location of the sampling stations is indicated on the map of Fig. 8.

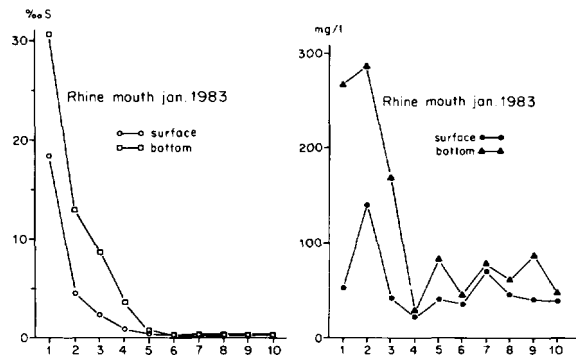



Fig. 10c. Salinity and suspended-matter concentrations in (mg·dm$^{-3}$) in the Rhine mouth in January 1983. The location of the sampling stations is indicated on the map of Fig. 8.

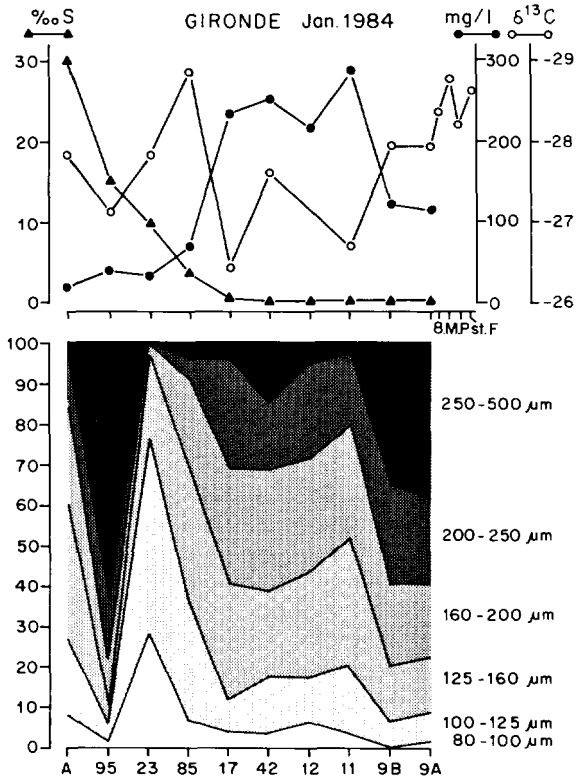



Fig. 10d. *In situ* particle size, salinity (in S units), concentration of suspended matter (in mg·dm$^{-3}$) and $\delta^{13}C$ in the Gironde in January 1984. The location of the sampling stations is indicated on the map of Fig. 3.

### 3.4. DISSOLVED AND PARTICULATE CARBOHYDRATES

Measurements of dissolved carbohydrates were made in the Ems and Rhine estuaries in January-February 1982 (EISMA *et al.*, 1982, 1983; EISMA,1986) and subsequently in the Ems estuary in November/December 1982, November 1983 and May 1984, in the Gironde in May 1983 and in the Rhône mouth in February 1985, while particulate carbohydrates were determined in the Ems estuary in November/December 1982 and in the Gironde in May 1983. The measurements were made along the axis from fresh to saline water of each estuary, and in the Ems estuary included two time-series at anchor stations during a full tide (about 3 hours). These data (Figs 11 to 16; one time-series at station 82-46 has already been published, EISMA *et al.*, 1983) show maximum as well as minimum concentrations of dissolved carbohydrates at low salinities, while the concentration of particulate carbohydrates is clearly related to the total concentration of particulate matter. When expressed as a percentage of the total suspended matter content (normally 1 to 2%), this percentage is higher in the fresh water than in the saline water. This was found both in the Ems estuary in November/December 1982 (Fig. 12) and in the Gironde in May 1983 (Fig. 15b), and is compatible with a release of carbohydrates at low salinities.

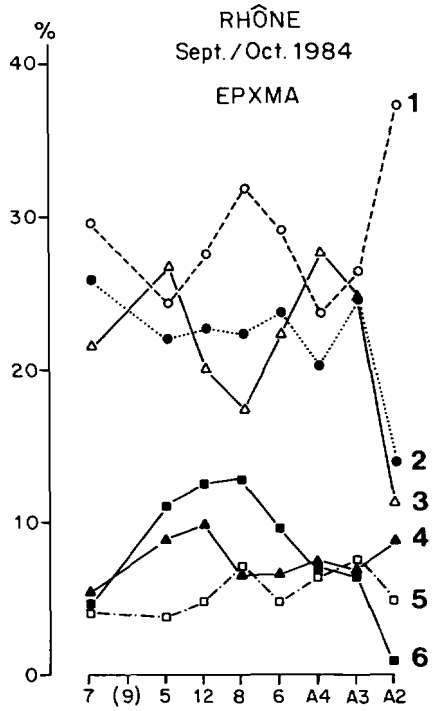



Fig. 11. Suspended particle composition determined with EPXMA analysis in the Rhône mouth at the sampling stations indicated on the map of Fig. 3. 1:96% Ca; 2:97% Si; 3:64% Si + 24% Al + 7% K; 4:45% Si + 26% Ca + 10% Al; 5:44% Si + 27% Fe + 21% Al + 2.5% Mg; 6:67% Ca + 23% Si + 5% Al.

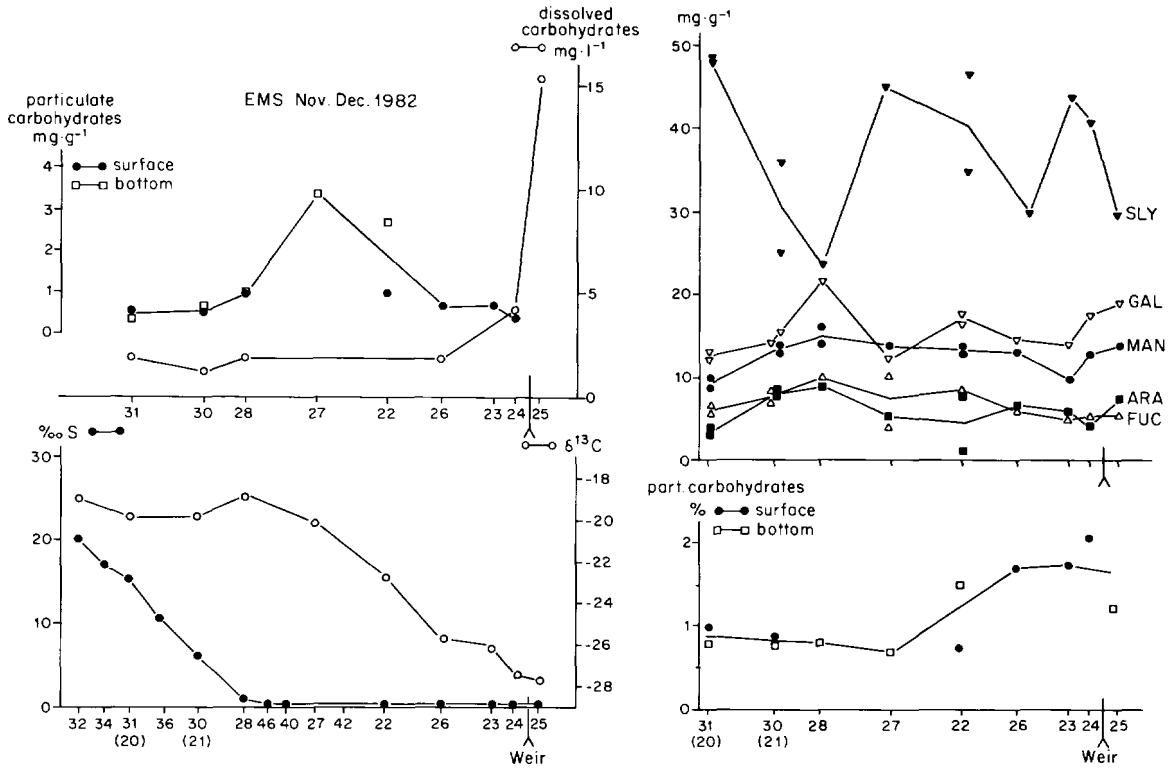



Fig. 12. Dissolved and particulate carbohydrates (in mg·dm$^{-3}$, resp. mg·g$^{-1}$, salinity, $\delta^{13}C$ and the percentage of particulate carbohydrates in the suspended matter in the Ems estuary in November-December 1982. The location of the sampling stations is indicated in Fig. 4.

### 3.5. DISTRIBUTION OF PLANKTON AND RESPIRATION ACTIVITY (ETS)

In the Ems estuary in January-February 1982, plankton numbers were highest in the river and the freshwater tidal area, and decreased towards the fresh and saline water interface. The lowest numbers were found in the brackish water (EISMA *et al.*, 1982, 1983; EISMA, 1986). In November 1983, the number of algal cells was higher and the difference between fresh and saline waters was much less marked (Fig. 17; Fig. 13a). In May 1984 the number of plankton cells was of the same order as in November 1983, but tended to increase towards the brackish water, while the number of freshwater species and *Cyclotella* sharply declined at the fresh and saline water contact, as can be expected (Fig. 18).

In the Gironde in January 1984, plankton counts were variable, with the lowest values in the river where S ~3, and the highest values also in fresh water where S ~10 (Fig. 3; Fig. 20). In the Rhône mouth in September-October 1984, the number of plankton cells was higher in the brackish water (Fig. 21). This was also found in February 1985 but the increase in the number of cells $<10$ $\mu$m began already in the fresh water (Fig. 16).

In these three estuaries, there was a general tendency for cell numbers to be greater in the brackish water, except during the winter in the Ems estuary when the higher numbers were found in the fresh water. The latter was also found for the ETS data in the Scheldt estuary in 1986 which were measured at the surface and the bottom (Fig. 6; Fig. 22). The activity decreased from the river to where S ~12; at higher salinities it remained about constant at very low values. In the fresh water, the ETS values were somewhat higher at the surface than at the bottom, whereas the reverse was found in the brackish water. No differences were found at salinities higher than ~12.

### 3.6. LOSS OF PARTICULATE ORGANIC MATTER

Loss of organic matter from the suspended particles at the transition from fresh to saline water was described for the Gironde in November 1980-September 1981 and in May 1983 (EISMA *et al.*, 1985; LAANE *et al.*, 1987). It was also found in the Gironde in October 1981 (Fig. 19) and in January 1984 (Fig. 20), but there was the added complication

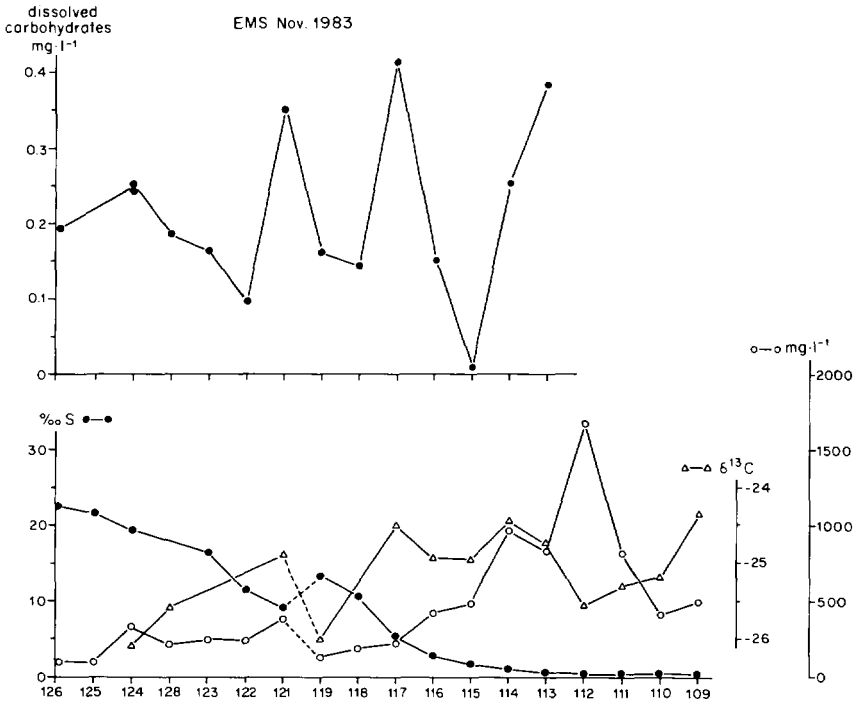



Fig. 13a. Dissolved carbohydrates (in mg·dm$^{-3}$), salinity, suspended matter concentration (in mg·dm$^{-3}$) and $\delta^{13}C$ in the Ems estuary in November 1983. The location of the sampling stations is indicated in Fig. 13c.

during the latter period that the organic matter content of the suspended matter was high again in the seaward part of the estuary. The plankton counts indicate that the loss is caused by the presence of plankton in large quantities which is not the case with the high organic matter contents in the freshwater part. A similar distribution of organic content was found in May 1984 in the Ems estuary (Fig. 18), but here plankton counts were high both in the freshwater part and in the seaward part of the estuary. In February 1982 in the Ems estuary and in December 1986 in the Scheldt estuary (Fig. 22b) there was a gradual decrease in organic matter content as the water became more saline, but in November 1983 in the Ems estuary there was no decrease at the transition from fresh to saline water. This was not found in the Rhine mouth in January 1982, while in the Rhône mouth in September 1984 and February 1985 the organic matter content increased together with the plankton counts (Fig. 21).

### 3.7. CHANGES IN ORGANIC MATTER COMPOSITION

Composition analysis of particulate organic matter in suspension in the Ems and Gironde estuaries indicated a change in the organic matter composition from fresh to saline waters (EISMA *et al.*, 1983, 1985). In both estuaries, land-derived compounds (lignin, phenoles, cellulose, xylose) were replaced by mainly aliphatic compounds of planktonic origin. The relative amounts of these components in the Ems estuary followed the mixing of material of marine and freshwater origin, while the compositional change in the Gironde occurred at the saline-freshwater interface. The $\delta^{13}C$ values for the organic matter closely followed the mixing of organic material from freshwater and marine origin. In the other series of measurements —in the Ems estuary and the Gironde during other periods as well as in the other estuaries studied here— the $\delta^{13}C$ also changed from more negative to less negative (generally from −30 to −28 in the fresh water to −24 to −18 in the saline water (MOOK & TAN, 1990; Figs 5, 11, 12, 13a, 14a, 15b, 17)), but no relation can be seen with the pipette/Coulter counter size distributions.

## 4. DISCUSSION

With one exception (Gironde, October 1981), all data show finer particle size at increased salinity compared to fresh water. This was also found by PIERCE & NICHOLS (1986) in the Rapahannock River estuary and by PULS & KUEHL (1986) in the Elbe river estuary. The data of KRANCK (1981) relating grain mode to

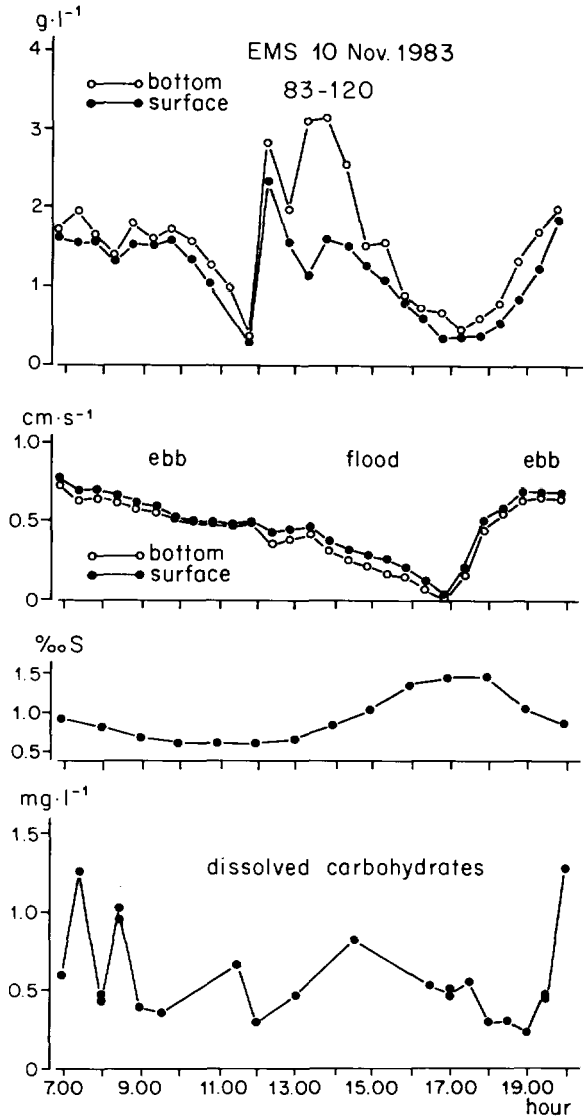



Fig. 13b. Suspended matter concentration (in g·dm$^{-3}$), current velocity (in cm·s$^{-1}$), salinity and dissolved carbohydrates (in mg·dm$^{-3}$) at stations 83-120 in the Ems estuary on 10 November 1983 during one tide (7.00-20.00 h). The station location is indicated in Fig. 13c.

natural (Coulter counter) floc mode indicate that in some Canadian estuaries Coulter-counter floc size at salinities above S=2 is generally smaller than at salinities below S=2. The reverse was observed in the Gironde in October 1981: the suspended material was finer in the river water and coarsened at the contact with more saline water. However, the turbidity maximum at that time was located further inland — approximately at stations 7 to 17— while in May 1983 and in January 1984 it was located downstream of Bordeaux (at stations 18 to 19 and 9 to 19, respectively; EISMA,1986 and Fig. 3). In October 1981 there was also large-scale resuspension of material from the bottom and along the shores of the river while the water level was rising. This was indicated by a high turbidity in the shallow parts and the presence of large clouds of resuspended material in the deeper areas. Resuspended bottom sediment can be finer grained because of consumption or degradation of organic matter present in the flocs whereby the floc structure is partly destroyed. It is therefore likely that at that time a more normal situation with a zone of relatively fine material at low salinities (which was found in May 1983 and January 1984) had been disturbed. The Gironde is exceptional because it receives water from two rivers, the Garonne and Dordogne. Mixing of saline water with water from the Garonne river mainly takes place along the south side of the Gironde, and from the Dordogne mainly along the north side. Both systems remain more or less separate to almost halfway up the estuary. The same range of finer grain size was present at low salinities along both the north and south sides. It is remarkable that a finer Coulter-counter size was also found at low salinities in the Rhine river estuary, since the Rhine already had a salinity of S ~0.5 due to the salt discharges of the mining industry. This suggests that the finer Coulter-counter size is not related to the absolute salinity values but to the increase in salinity.

The particle-size samples were usually collected only at 1 to 2 m below the surface. This was done to minimize the influence of exchange with bottom sediment, but had the drawback that a vertical gradient, if it existed, was not observed. Therefore, in the Scheldt estuary in December 1986, both surface and bottom waters were sampled and analysed. The Scheldt is a macrotidal estuary (tidal range 4 to 5 m) where the strong tidal currents tend to keep particles mixed over the vertical. The Scheldt data (Fig. 6) show no evidence of the particles in the bottom water having a different size: the distributions in the surface and bottom waters are very much alike, although in the bottom water somewhat more irregular which may be caused by some resuspension of bottom sediment. Fig. 6 shows that total suspended matter concentrations at stations 10 to 12 in the low-salinity region are about three times higher in the bottom water samples than in those of the surface water: a gradient in concentration is present without a gradient in pipette/Coulter counter size. The bottom water samples were collected at about 1 m above the bottom, which leaves the possibility of a size gradient being present very near to the bottom.

The shift towards a finer pipette/Coulter counter size in the Ems, Rhine, Scheldt estuaries and in the Gironde is independent of the origin of the suspended material as indicated by EPXMA analysis, but in

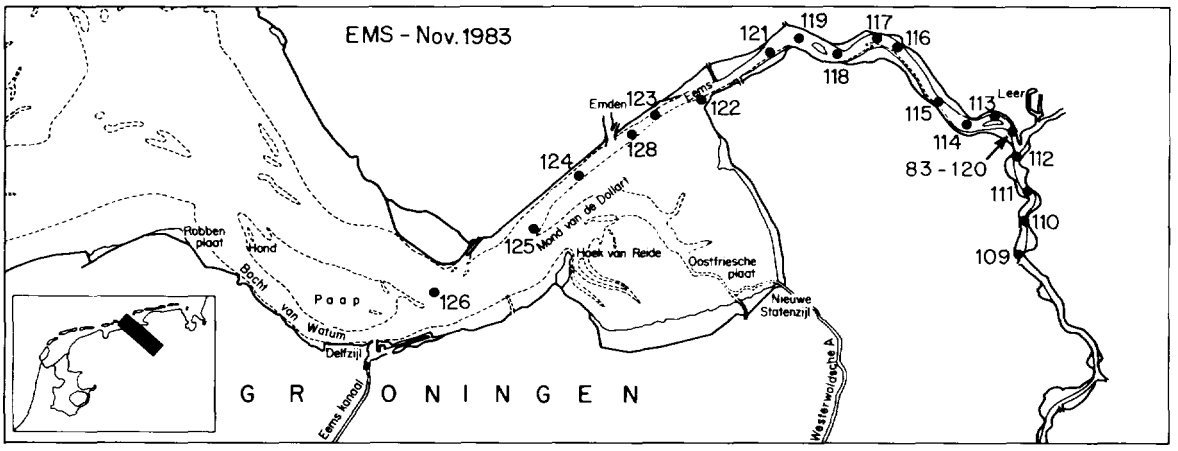



Fig. 13c. Sampling stations in the Ems estuary in November 1983.

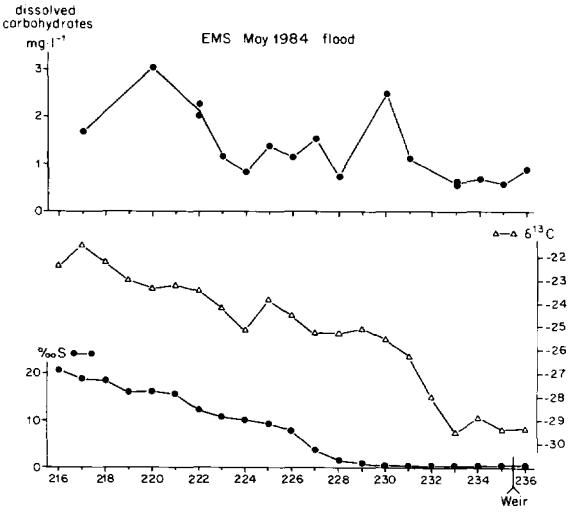
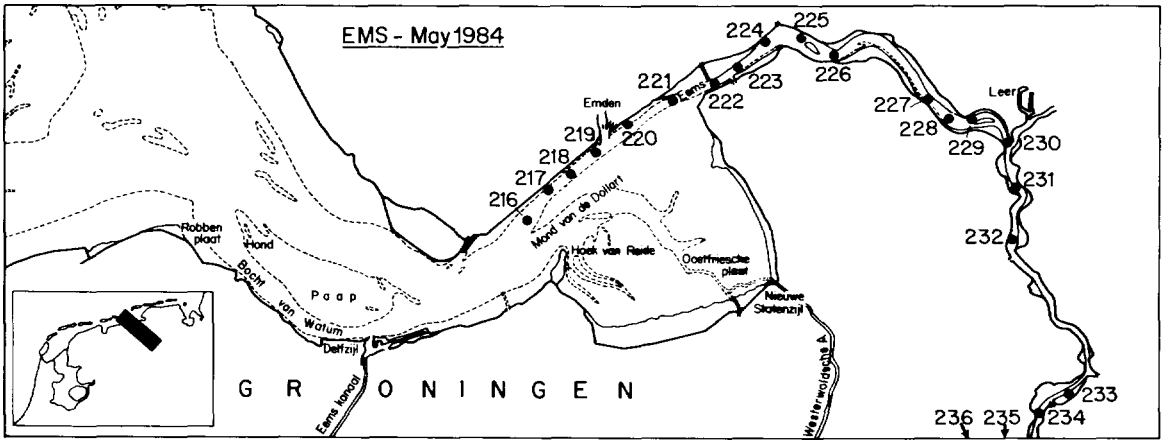


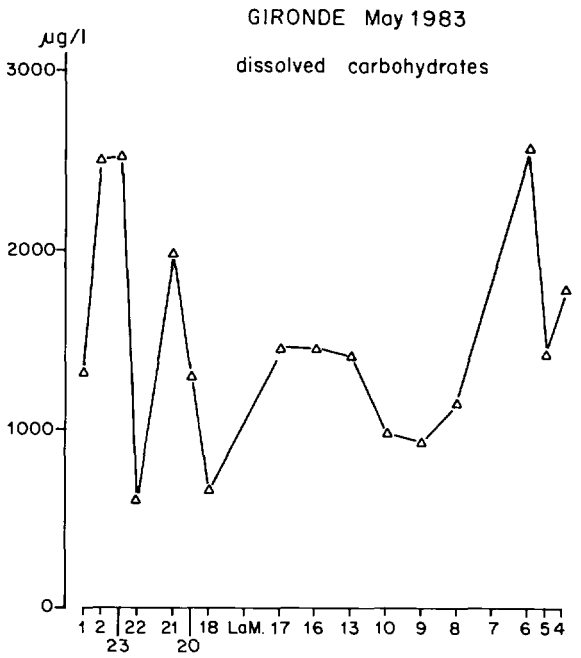

Fig. 14a. Dissolved carbohydrates (in $mg \cdot dm^{-3}$), salinity, and $\delta^{13}C$ in the Ems estuary during high tide in May 1984. The location of the sampling stations is indicated in Fig.14b.

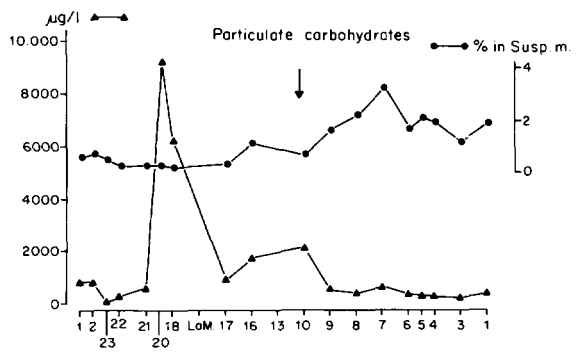
the Rhône river mouth this shift occurs at stations A2 to A4, where A2 has a different composition. As discussed above, the deviating particle composition at station A2 alone, but, is not considered to be sufficient to explain the change in pipette/Coulter counter size by an admixture of finer material from another suspended sediment source.

The presence of finer pipette/Coulter counter size distributions at low salinities, first found in the Ems and Rhine estuaries, was related to a maximum of dissolved carbohydrates which was found at the same localities and at the same time (January-February 1982 (EISMA *et al.*, 1982, 1983; EISMA, 1986)). It was assumed that these carbohydrates came from polysaccharides or long- chain organic compounds in the suspended material (such as humic and fulvic acids), and are mobilized as ion strength increases (Leenheer, pers. comm.). While the carbohydrates go into solution, the flocculated material becomes more fragile due to loss of 'glue' (EISMA *et al.*,

Fig. 14b. Sampling stations in the Ems estuary in May 1984.





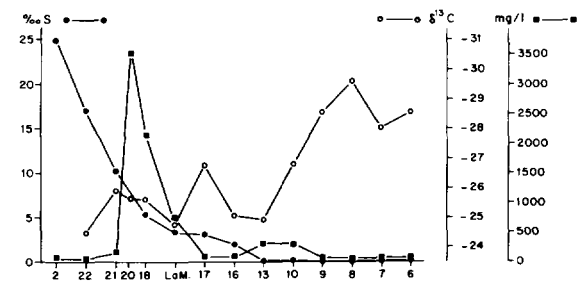
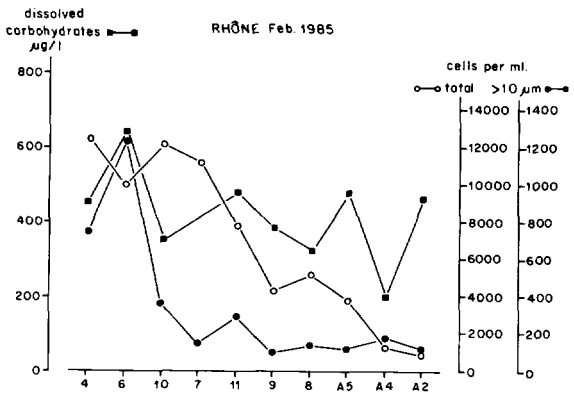
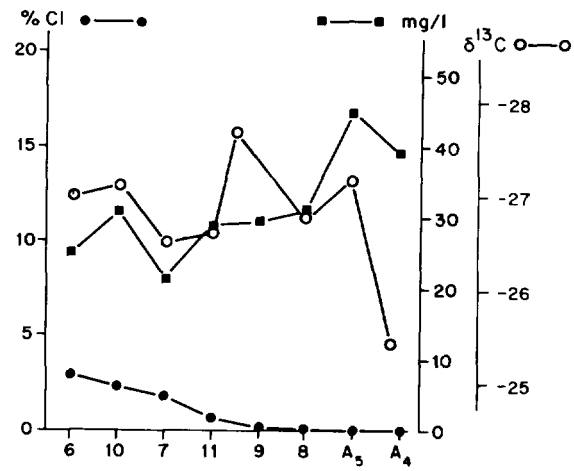




Fig. 15. (top) Dissolved carbohydrates in the Gironde in May 1983. (middle) Particulate carbohydrates (in $\mu gr \cdot dm^{-3}$) and the percentage of carbohydrates in the suspended matter in the Gironde in May 1983. (bottom) Salinity, suspended matter concentration (in $mg \cdot dm^{-3}$) and $\delta^{13}C$ in the Gironde in May 1983. The location of the sampling stations is indicated in Fig. 3.



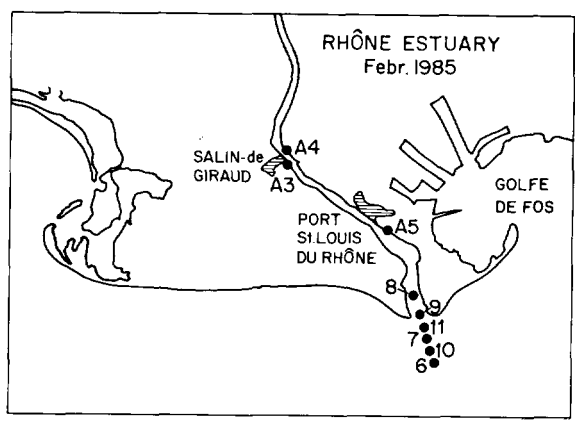




Fig. 16. -(top) Dissolved carbohydrates (in $\mu g \cdot dm^{-3}$), total number of algal cells and number of algal cells > 10 $\mu$m at the Rhône mouth in February 1985. -(middle) Chlorinity (in ‰ $Cl^-$), suspended matter concentration (in $mg \cdot dm^{-3}$) and $\delta^{13}C$ at the Rhône mouth in February 1985. - (bottom) Sampling stations at the Rhône mouth in February 1985.

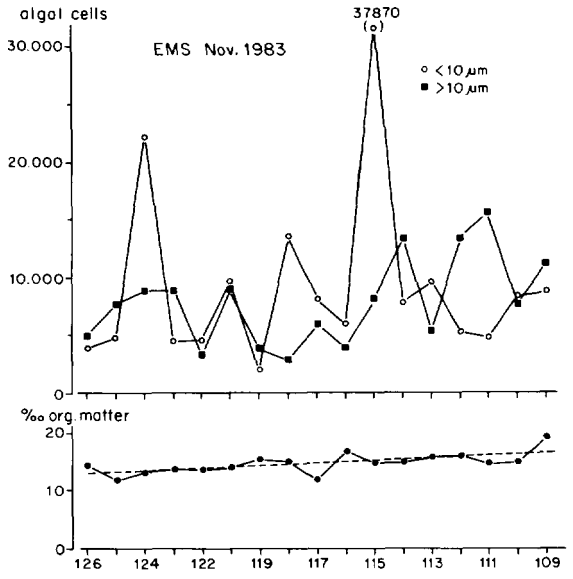



Fig. 17. Number of algal cells per $cm^3$ > 10 µm and < 10 µm, and proportion of organic matter in the suspended matter in the Ems estuary in November 1983. The location of the sampling stations is indicated in Fig. 13c.

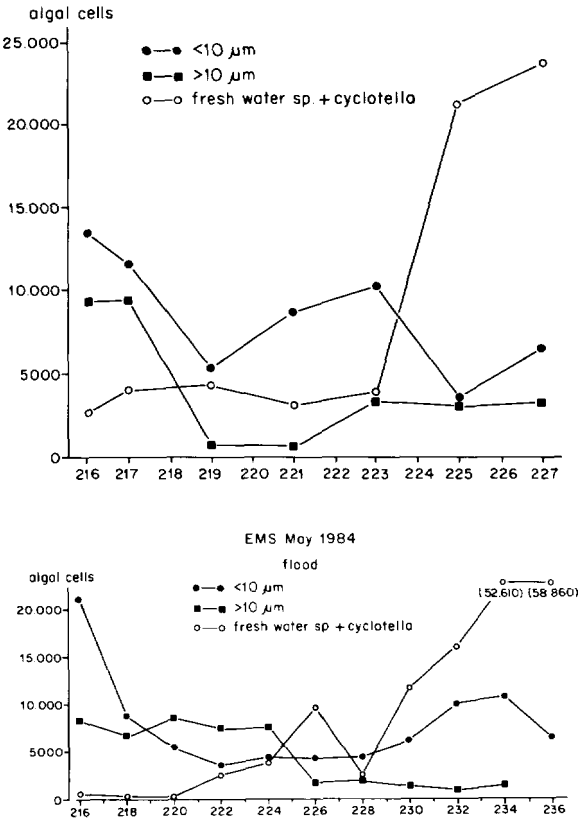



Fig. 18. Number of algal cells per $cm^3$ > 10 µm and < 10 µm, and number of freshwater algal cells + *Cyclotella* sp. per $cm^3$ in the Ems estuary during ebb tide (top) and flood (bottom) in May 1984. The location of the sampling is indicated in Fig. 14b.

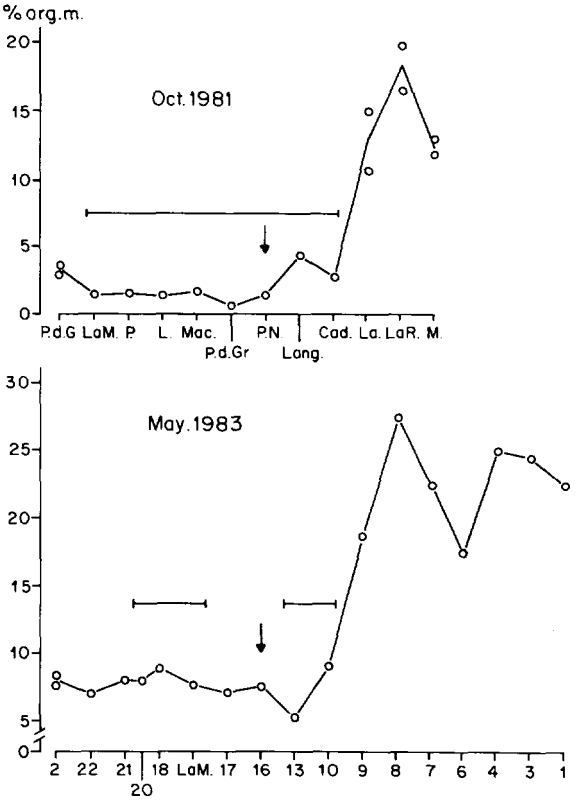



Fig. 19. Percentage of organic matter in the suspended matter in the Gironde in October 1981 and May 1983. The location of the sampling stations is indicated in Fig. 2 (October 1981) and Fig. 3 (May 1983). The horizontal bars and the arrows indicate the turbidity maximum and the saltwater contact, resp. (*cf.* Figs 2 and 15).

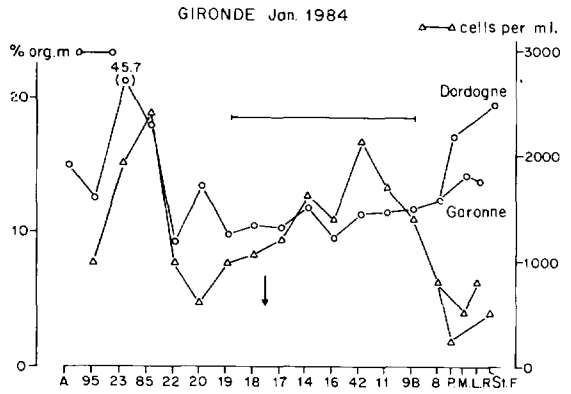



Fig. 20. Percentage of organic matter in the suspended matter and the number of algal cells per $cm^3$ in the Gironde in January 1984. The location of the sampling station is indicated in Fig. 3. The horizontal bar and the arrow indicate the turbidity maximum and the saltwater contact, resp. (*cf.* Fig. 3).

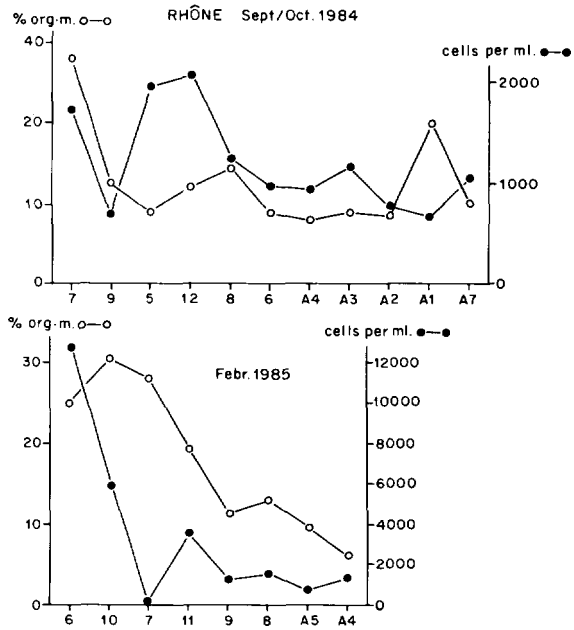



Fig. 21. Number of algal cells per $cm^3$ and the percentage of the organic matter in the suspended matter at the Rhône mouth in September-October 1984 and February 1985. The location of the sampling stations is indicated in Fig. 5 (September- October 1984) and Fig. 16 (February 1985).

1983). The dissolved carbohydrates may also come from resuspended bottom sediment, which would have a similar effect on the suspended matter Coulter-counter size distributions. Recent data from January 1988 for the Ems estuary (Spitzy, pers. comm.) confirm the presence of a dissolved carbohydrate maximum in the water at low salinity during the winter.

The fact that no maxima of dissolved carbohydrates were found in the Ems estuary in November/December 1982 and in the Gironde in May 1983, although the data on particulate carbohydrates indicated mobilization of carbohydrates at low salinity, can be related to biological activity and rapid uptake of dissolved carbohydrates, which in a northern estuary like that of the Ems will have a seasonal effect. In that estuary in February 1982, living plankton (algae) were mainly present in the fresh water (EISMA *et al.*, 1983). Their numbers had been reduced to almost zero where the dissolved carbohydrate maximum was present. ETS measurements, which give an indication of biological activity, decreased in a similar way to very low values in the saline part of the Scheldt estuary in December 1986 (Fig. 17). Plankton data for November 1983 and May 1984 in the Ems estuary (Figs 18 and 19), however, showed an abundance of plankton both in fresh and saline water, while data on ETS showed no clear relationship to salinity. In the Ems estuary in May 1984, there was a numerous plankton population in the fresh water in the innermost parts near the Weir at Herbrum during the flood, which extended seawards during ebb to almost the fresh-saline water contact. In the Rhône mouth (which has no tides), the increase of plankton growth was related to a decrease in turbidity in the river plume (Fig. 16), where the suspended matter settles to the bottom forming a nepheloid layer (ALOISI *et al.*, 1979).

It is therefore concluded that mobilization of carbohydrates from particulate matter normally takes place at the fresh-saline water contact, as is indicated by a maximum of dissolved carbohydrates at low salinities during the winter and by a decrease of the carbohydrates content of the suspended particulate matter during the rest of the year. Where biological activity is high (during spring/summer/autumn at higher latitudes and at lower latitudes also during the winter), the maximum of dissolved carbohydrates is not observed because the mobilized sugars are quickly reused. In addition, a maximum at low salinities when observed in winter is in the form of a sharp peak: there is no strong diffusion of dissolved carbohydrates, indicating their residence time in the water is short (in the order of a day or less), and even shorter when biological activity is greater.

A higher fragility of suspended flocs may also be related to a loss of organic matter, however, a decrease in total organic content was not regularly found at low salinities. It is clear that the primary production of organic particles can strongly influence the organic matter content of the suspended matter in such a way that any loss at the fresh-saline water contact by mineralization or consumption is (temporarily) obscured. It can also be obscured by an in-

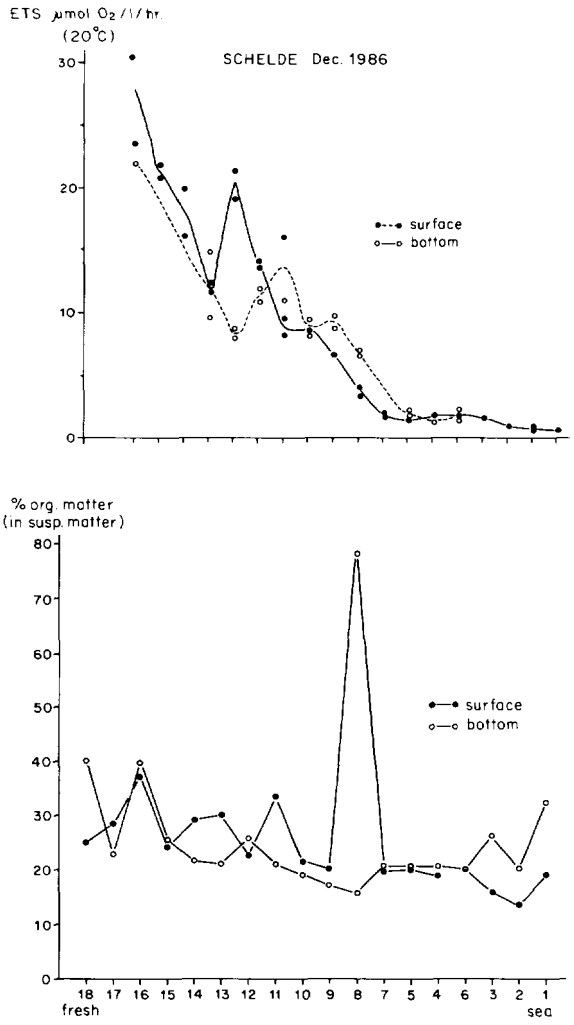



Fig. 22. (top) ETS (in $\mu$mol $O_2 \cdot dm^{-3} \cdot h^{-1}$; 20°C) in the Scheldt river and estuary in December 1986. (bottom) Percentage of organic matter in the suspended matter in the Scheldt river and estuary in December 1986. The location of the sampling stations is indicated in Fig. 6.

flux of particulate organic material from the sea, which is the case in the Ems and Scheldt estuaries, where the mixing of particles of marine and freshwater origin takes place in the freshwater part of the estuary and reaches far inland due to tidal mixing in combination with repeated deposition and resuspension. In fact, a marked zone with strongly decreasing organic matter contents of the suspended matter at low salinities could only be distinguished in the Gironde. Such a loss therefore cannot explain the higher fragility of the suspended particles at low salinities as is generally found in the estuaries studied. Since the organic matter composition shows no relationship to the pipette/Coulter counter size distributions, one can confirm the conclusion reached earlier (EISMA, 1986) that specific organic compounds (polysaccharides, humic and fulvic acids, and possibly others) are of importance for floc formation and their fragility, and not the bulk organic matter. Aging effects, resulting in stronger bonding and more resistant flocs, and little contact with the bottom sediment may explain the presence of less fragile flocs in the northern North Sea as compared to the coastal waters in the Southern Bight (EISMA & KALF, 1987). It is not likely, however, that aging has a large effect in estuaries where there is repeated exchange of suspended matter with the bottom sediment and residence times are relatively short.

No relation was found between the pipette/Coulter counter size distribution and the *in situ* Plankton camera size distributions: the first had a maximum size of about 125 $\mu$m while the Plankton camera size distributions reached almost 1000 $\mu$m. Recent data for the Scheldt estuary, obtained with another *in situ* camera system, giving size distributions upwards of 3 to 5 $\mu$m (EISMA *et al.*, 1990), showed that more than 80% of the particulate matter in suspension was present in the form of particles (flocs) larger than 100 $\mu$m. This indicates that during sampling and size analysis most of the suspended material is broken into fragments and single grains: the pipette and Coulter-counter size distributions are primarily an indication of the degree to which the suspended particles (flocs) are broken apart, *i.e.* of their firmness or fragility. HANNAH *et al.* (1967) used the Coulter counter as a measure of floc strength based on the shear that develops during stirring of the suspension and during the passage through the aperture.

The *in situ* size distributions appear unrelated to the fragility of the flocs as indicated by the pipette/Coulter counter data, and no relation can be seen with the mobilization of carbohydrates, the organic matter content of the suspended particles, or the composition of the organic matter in the particles. Nor does ionic strength (salinity) appear to influence floc size: this seemed so only in the Rhine mouth in January 1983 when the floc size became larger at the fresh-saline water contact. This can be explained by nearby dredging; it was not found in the Ems estuary in November 1982 nor in the Gironde in January 1984. Recent data for the Scheldt estuary (EISMA *et al.*, 1991) also show that ion strength is not a significant factor. Since all these factors are of no importance in determining *in situ* floc size, the question remains which factors are important: *in situ* flocs show variable size distributions and a variable maximum size (the minimum size was determined by the camera).

The only systematic study known to the authors on natural *in situ* floc distributions in an estuary is by

GIBBS *et al.* (1989). It is based on data obtained in the Gironde in May 1983 with a combination of *in situ* holography and a microscope technique to observe flocs after careful sampling. The measured particles ranged in size from less than 10 $\mu$m to a maximum of about 200 $\mu$m. This was much smaller than that obtained in the three estuaries studied with the Benthos plankton camera: here, maximum size in most samples was well above 300 $\mu$m and only in a few samples less than 200 $\mu$m. In addition the *in situ* maximum size of flocs in the Scheldt, measured with another camera system (EISMA *et al.*, 1990), was well above 300 $\mu$m. This makes it likely that in spite of careful sampling, some floc break-up occurred in the samples of GIBBS *et al.* (1989).

GIBBS *et al.* (1989) also observed very fine material in the fresh water in the Gironde which coarsened at S values between 0.1 and 5. As seen above, we did not find this in the Gironde in January 1984, in the Ems estuary in November 1982 nor in the Scheldt estuary in 1989, but only in the Rhine mouth in January 1983. Therefore, the general conclusion of GIBBS *et al.* (1989) that fine-grained particles discharged by the rivers coagulate upon encountering the low salinities in the upper estuary cannot be shared.

A full discussion of the factors that determine floc size distributions in estuaries, is given in part II of this paper (EISMA *et al.*, 1991).

## 5. CONCLUSIONS

Particle-size distributions of suspended matter observed in five northwest-European estuaries (Ems, Rhine, Scheldt, Gironde and Rhône) confirmed earlier observations that particle sizes, determined by pipette analysis and Coulter counter, become finer at the contact of fresh and saline water. This was found in the bottom water as well as at the surface. The only exception (the Gironde in October 1981) was probably caused by exceptional conditions during the sampling period with much resuspension of bottom sediment in the freshwater part of the tidal area.

Measurements of *in situ* particle size in three estuaries (Ems, Rhine, Gironde) indicated no relation between the *in situ* distributions and the distributions obtained with pipette or Coulter counter. The *in situ* maximum size was 600 to 800 $\mu$m, and the pipette-Coulter counter measurements were about 125 $\mu$m —the pipette/Coulter counter methods measured the size of floc fragments formed during sampling and analysis. Nevertheless, the results are not arbitrary and show definite trends that can be related to the behaviour of carbohydrates in the estuaries. In the winter, a peak in the concentration of dissolved carbohydrates was found at the same place; during the other seasons, only a decrease was observed in the carbohydrate content of the suspended matter. Changes in the total content of organic matter in the suspended matter and changes in the bulk composition of the particulate organic matter, as indicated by organic analysis or by the stable carbon isotope ratio, did not affect the pipette/Coulter counter size of the flocs. It is concluded that both pipette and Coulter-counter size distributions are an indication of the fragility (or firmness) of estuarine flocs.

The increased fragility of the flocs at low salinities does not influence the *in situ* size of the flocs. In addition, there is no consistent evidence that salt flocculation is an important factor in river mouths.

## 6. REFERENCES

ALOÏSI, J.-CL., CL. MILLOT, A. MONACO & H. PAUC, 1979. Dynamique des suspensions et mécanismes sédimentogénétiques sur le plateau continental du Golfe du Lion.—C.R. Acad. Sc. Paris **289:** 879-882.

BERNARD, P., 1989. Automated electron probe X-ray microanalysis combined with multivariate analysis for application in marine research. Thesis. University Antwerpen: 1-209.

BERNARD, P., R. VAN GRIEKEN & D. EISMA, 1986. Classification of estuarine particles using automated electron microprobe analysis and multivariate techniques.—Env. Sci. Techn. **20:** 467-473.

DANKERS, N. & R. LAANE, 1983. A comparison of wet oxidation and loss on ignition of organic material in suspended matter.—Sc. Techn. Letters **4:** 283-290.

EDGERTON, H., P. ORNTER & W. MCELROY, 1981. An *in-situ* plankton camera.—Oceans: 558-560

EISMA, D., 1986. Flocculation and de-flocculation of suspended matter in estuaries.—Neth. J. Sea Res. **20:** 183-199.

EISMA, D. & J. KALF, 1987. Distribution, organic content and particle size of suspended matter in the North Sea.—Neth. J. Sea Res. **21:** 265-285.

EISMA, D., J. KALF & M. VEENHUIS, 1980. The formation of small particles and aggregates in the Rhine estuary.—Neth. J. Sea Res. **14:** 172-191.

EISMA, D., G.C. CADÉE, R. LAANE & J. KALF, 1982. Preliminary results of Aurelia- and Navicula cruises in the Rhine and Ems estuaries, January-February, 1982.—Mitt. Geol. Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderb. **52:** 633-654.

EISMA, D., J. BOON, R. GROENEWEGEN, V. ITTEKKOT, J. KALF & W.G. MOOK, 1983. Observations on macro-aggregates, particle size and organic composition of suspended matter in the Ems estuary.—Mitt. Geol. Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderb. **55:** 295-314.

EISMA, D., P. BERNARD, J.J. BOON, R. VAN GRIEKEN, J. KALF & W.G. MOOK, 1985. Loss of particulate organic matter in estuaries as exemplified by the Ems and Gironde estuaries.—Mitt. Geol. Paläont. Int. Univ. Hamburg, SCOPE/UNEP Sonderb. **58:** 397-412.

EISMA, D., T. SCHUHMACHER, H. BOEKEL, J. VAN HEERWAARDEN, H. FRANKEN, M. LAAN, A. VAARS, F. EIJGENRAAM & J. KALF, 1990. A camera and image analysis system for *in-situ* observation of flocs in natural waters.—Neth. J. Sea Res. **27:** 43-56.

EISMA, D., P. BERNARD, G.C. CADÉE, V. ITTEKKOT, J. KALF, R. LAANE, J. M. MARTIN, W.G. MOOK, A. VAN PUT & T. SCHUMACHER, 1991. Suspended-matter particle size in some West-European estuaries; Part II: A review on floc formation and break-up.—Neth. J. Sea Res. **28:** 215-220.

GIBBS, R.J., D.M. TSUDY, L. KONWAR & J.M. MARTIN, 1989. Coagulation and transport of sediments in the Gironde Estuary.—Sedimentology **36:** 987-999.

HANNAH, S.A., J.M. COHEN & G.G. ROBECK, 1967. Measurement of floc strength by particle counting.—J. AWWA July 1967: 843-858.

KRANCK, K., 1981. Particulate matter grain-size characteristics and flocculation in a partially mixed estuary.—Sedimentology **28:** 107-114.

LAANE, R.W.P.M., H. ETCHEBER & J.C. RELAXANS, 1987. Particulate organic matter in estuaries and its ecological implication for macrobenthos.—Mitt. Geol. Paläont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderb. **64:** 71-91.

MICHAELIS, W. & V. ITTEKKOT, 1982. Biogeochemistry of world rivers: field and analytical techniques. In:E.T. DEGENS. Transport of carbon and minerals in major world rivers.—Mitt. Geol. Paläontol. Inst. Univ. Hamburg, SCOPE/UNEP Sonderbd. **52:** 69-90.

MOOK, W.G. & F.C. TAN, 1991. Stable carbon isotopes in rivers and estuaries. In: E.T. DEGENS, S. KEMPE & J.E. RICHEY. Biogeochemistry of major world rivers. John Wiley, New York.—SCOPE **24:** : 247-266.

PIERCE, J.W. & M.M. NICHOLS, 1986. Change of particle composition from fluvial into an estuarine environment: Rapahannock River, Virginia.—J. Coastal Res. **2:** 419-425.

PULS, W. & H. KUEHL, 1986. Field measurements of the settling velocities of estuarine flocs.—Proc. Third Int. Symp. River Sed. Univ. Mississippi, March 31-April 4: 525-536.

SALOMONS, W., 1975. Chemical and isotopic composition of carbonates in recent sediments and soils from Western Europe.—J. Sed. Petrol. **45:** 440-449.

SALOMONS, W. & W.G. MOOK, 1981. Field observations of the carbon isotopic composition of particulate organic carbon in the southern North Sea and the adjacent estuaries.—Mar. Geol. **41:** M11-M20.

U.S. HYDROGRAPHIC OFFICE, 1959. Instruction Manual for Oceanographic observations.—H.O. Publ. No. 607: 1-210.

VOSJAN, J.H., 1988. The ATP and ETS method in the study of surface layers and deep-sea basins of East Indonesian waters.—Arch. Hydrobiol. Beih. Ergebn. Limnol. **31:** 221-228.

VOSJAN, J.H. & G. NIEUWLAND, 1987. Microbial biomass and respiratory activity in the surface waters of the East Banda Sea and North West Arafura Sea (Indonesia) at the time of the South East Monsoon.—Limnol. Oceanogr. **32:** 767-775.

VOSJAN, J.H., S.B. TIJSSEN, G. NIEUWLAND & F.J. WETSTEIJN, 1990. Oxygen regime, respiratory activity and biomass of microorganisms, and the carbon budget in the Fladen Ground area (northern North Sea) during spring.—Neth. J. Sea Res. **25:** 89-99.

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