Chapitre III

Sedimentological investigation

by

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Introduction

In this chapter are presented five reports which represent part of the sedimentological investigations conducted during 1972.

A first report by F. Gullentops comments the bottom-topography of the Southern Bight and stresses the necessity to dispose of an accurate bathymetric map. A brief review is given of the geological history of the Southern Bight.

A second report by F. Gullentops describes a Flowsheet for the analysis of recent sediments as it has been developed for this project and is being used for the analysis of some 2000 bottom samples.

A third report by M. Moens discusses the actual knowledge on sedimentation and erosion velocities of mud in the marine environment. This status questions can already be used as a first approximation in the mathematical model and prepared for eventual experimentation.

A fourth report by M. Moens discusses the results of sediment suspension analysis obtained during the campaign 1972. Even though not all stations were sampled as planned some interesting conclusions are proposed.

A fifth report by A. Bastin gives the results of a preliminary investigation on the sorption capacity characteristics of muds compared in fresh- and saltwater environment and determined with radio-isotopes.

A.- SOUTHERN NORTH SEA BOTTOM RELIEF

In a multidisciplinar research of the dynamics of a sea a good knowledge of the sea-bottom relief is an essential prerequisite. Depth influences hydrodynamical, sedimentological and biological phenomena. And so do of course changes in depth and the rates of these changes which determine in fact bottom relief.

As a basis for some disciplines a static image of this relief, a bathymetric map, may suffice. The bottom relief, however, has much more to tell. It is in itself a dynamic equilibrium between a long geological past and the actual forces operating now in the sea. A complete understanding of the bottom topography supposes a full knowledge of both. This stage has not yet been attained but it may be usefull to give a short account of the most salient facts and hypotheses on the most recent geological history and explanation of the bottom topography.

For the bathymetry we will use, with courtesy of the *Royal Dutch*, a map compilated by Houbolt on the basis of British Admirality charts.

The geological past which interests us here starts with the breakthrough of the Straits of Dover. Hypothetically this is put in the penultimate glaciation (- 150.000 years) because at least at that moment a good mechanism for the breakthrough occurred. It is indeed proven that during this coldest glaciation British and Scandinavian ice-masses joined in the North Sea West European rivers and ice meltwaters were blocked in their northern outflow. A large lake must have formed in the southern North Sea, the rising water of which found an outflow on a low point situated on the actual Straits of Dover. The huge overflow created an incision which drained the ice dammed lake.

During the last interglacial the sea level rose a few meters higher than now and the straits were enlarged by tidal currents and wave action, but were still narrower than now.

During the last glacial period the southern North Sea dried up again due to the lowered sea level (- 100 m). An important river formed by Thames, Rhine and Meuse together with the meltwaters of the Humber ice lobe eroded the still existing deepwater Channel. It may be that it was joined for some

time by the overflow waters of a new ice-dammed lake to the north but this is not proven yet.

Important quantities of sand were deposited on the old sea bottom. A huge alluvial fan of the Rhine is still discernible in the general bathimetry.

The very rapid ending of the last glaciation caused a rapid rise of sea level and a renewed transgression of the sea through the straits. During the Boreal period (8000 BP) the Southern Bight depended only from the Channel and extreme tidal currents must have run through the straits.

A new configuration appeared when the sea level rose above the Humber, Texel and Dogger bank heights to reach during the Atlantic Period (6000 BP) the highest sea level establishing approximately our actual coasts and current systems.

During the last 2000 years the sea breached repeatedly the coastal barriers and only then was formed the Scheldt estuary. The erosion of the tidal currents swept out to the sea new masses of sands which built up the outward Delta.

In the sea the tidal currents rearranged in streamline patterns the huge quantities of sand brought in during the glacial period. All of them however are not necessary in equilibrium with the actual dynamics. Some certainly are fossil as the Brown Bank Boreal beach barrier. Others may still reflect slightly different current systems of Atlantic times. But the majority without doubt is in equilibrium with actual current patterns. If directions are quite clear from the trend of the banks, the sense of movement is in most cases subject to discussion. Real displacement of the banks with cartographic methods is only seldom established due to the low accuracy of old bathymetric charts. The movement of the Falls to the south and especially Sandettie to the north seems certain. This is a very important system as it has built up through the deep water Channel and forms a major danger for the North Sea navigation. If well understood this system might also form a clue for the Southern Bight tidal current system.

The Knolls of East Anglia and the Flemish Banks have in common their linked pattern in which Van Veen recognized flood and ebb currents. Although these displace important quantities of sand, the migration is in a closed system, with flood and ebb currents nearly equal.

More seaward the Well Banks and the Hinder Banks are more rectili-
near and admittedly progressive in direction of a stronger flood current.

The Zealand Banks are enigmatic and might be relicts of an older
Atlantic system or even due to erosion as Houbolt suggests.

By this very short account to this large working group we intended
only to show that a better understanding of the sea-bottom morphology
will also contribute to the solution of the general problem of the mathe-
matical model.

B.- A FLOWSHEET FOR ANALYSIS ON RECENT DETRITAL SEDIMENTS

As a contribution to the Belgian effort of the study and control of pollution the government subsidies two important research programmes that aim to establish a mathematical model of the sea, applied to the Southern Bight of the North Sea and a mathematical model of a river, applied to the Samber, major tributary of the Meuse.

In these programmes has also been incorporated the study of the sediments. The reason is double. First the sediments in suspension may be considered as polluants. Very often their quantity, in rivers, estuaries and coastal waters, has been greatly increased by human interference due to domestic and industrial waste waters, and by accelerated soil erosion. They can reach concentration levels so as to influence considerably the water turbidity, and lower the transparency to a point of intervening and even prohibiting the development of organisms. By sedimentation these suspensions form clayey sediments and can cover previously sandy bottoms with mud, intervening once more in the development of the benthos.

Secondly the sediments in suspension are constituted for a large part of argilaceous and organic matter. Due to their physico-chemical characteristics of free valences and large specific surfaces, these substances are capable of adsorbing cations, among which also noxious heavy metals as Cu, Zn , Pb .

By sedimentation of the suspension-material these cations are extracted from the sea and sedimentation can be regarded as a natural purification of the sea. However, the organic substances can be decomposed bacteriologically on the sea bottom and the noxious cations may be put in solution again. Or the mud may be eaten by lithofagic benthos that absorb and concentrate the noxious elements and introduce them in the biological cycle and the food chain.

It is quite clear that a pollution research programme has to incorporate the study of the sediments, their characteristics, and dynamics. And that this study will concentrate essentially on the muddy sediments and to a lesser degree on the coarser sediments, the sands, transported along the bottom.

In both programmes we have been charged with the study of certain sedimentologic parameters. A flowsheet of analysis has been established and a method of valorisation of the analysis devised. Although no new analytical techniques were used we think it worthwhile to publish our way of working.

Indeed in the next two years some two thousand samples will be analyzed in this way and quite a lot of information will be gained on the southern North Sea. Other workers in neighbouring countries however are confronted with the same problems and the huge effort produced will be more usefull if the analysis and the extracted parameters were comparable.

In establishing an analysis flowsheet we are confronted with three premisses.

1. The exposed aim of the research.

2. The great quantity of samples which need simple, rapid and sophisticated analysis techniques giving the maximum of information.

3. The fact that the disponible samples will be of several types :

a) Samples of water ranging from 10 to 25 ℓ , taken regularly at certain points and depths of the North Sea and the Samber. The quantity of material in suspension varies largely but can be as low as 1 mg/ℓ and be insufficient for complete analysis. Only certain parameters will be defined.

b) Samples of suspension material obtained by continuous centrifugation of thousands of liters water on board of the vessel. These can be used for complete analysis.

c) Bottom samples taken by very different devices and yielding again enough material for the whole analysis.

1.- The analysis

The flowsheet (fig. 1) gives the succession of operations listed by numbers and of quantities listed by letters :

$$A \quad : \text{sample as it arrives in the laboratory,}$$
$$A_w : \text{watersample,}$$
$$A_c : \text{centrifugation sample,}$$
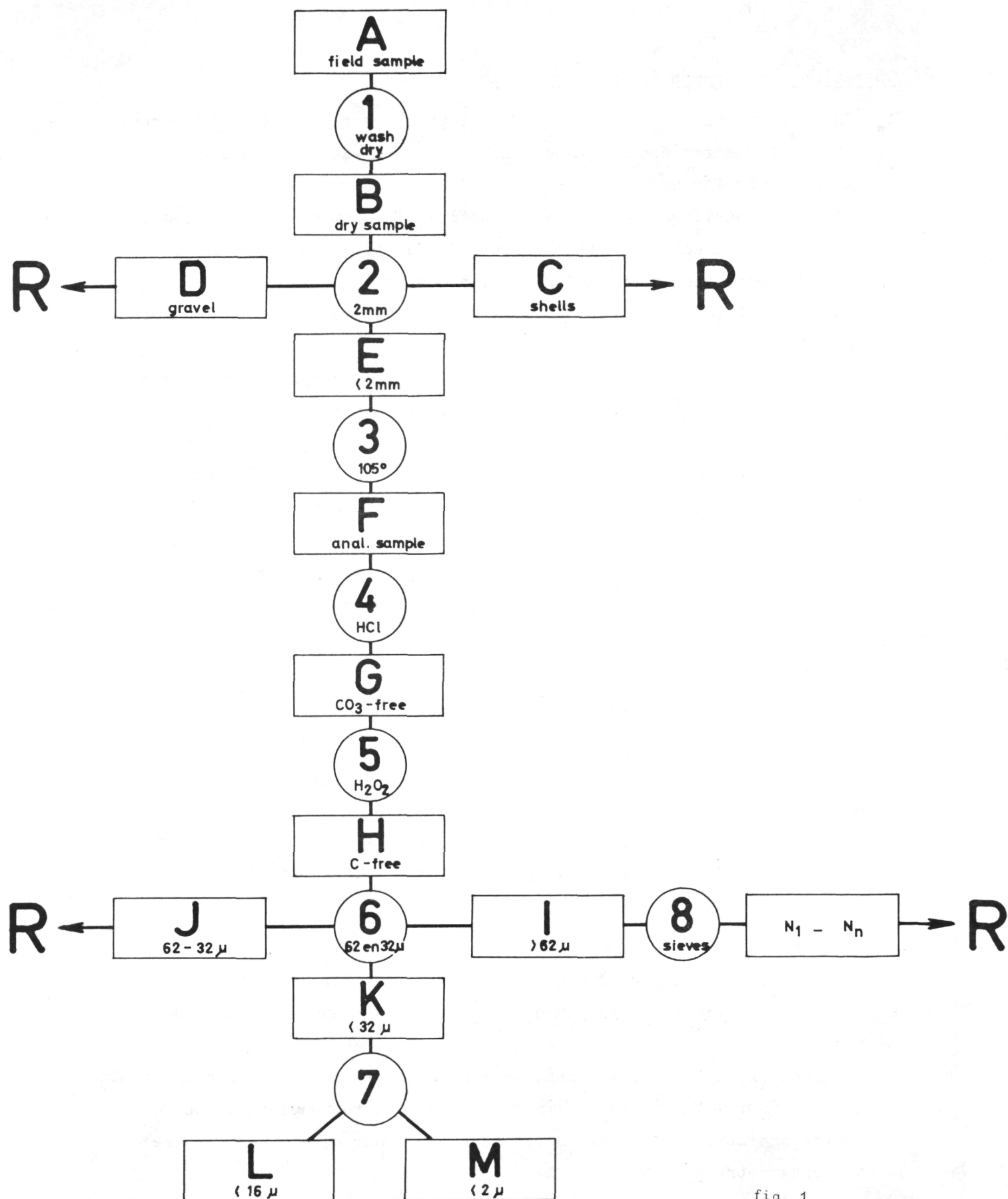$$A_b : \text{bottomsample.}$$

fig. 1.

Operation 1 — Preparation of the sample

1_w The watersample is filtered on filter paper by the method of inverted
bottles. The residue is washed with distilled water and transferred
to a beaker for drying.

1_c Off the centrifugation sample a quantity of about 10 mg , or less,
is taken, washed with distilled water on a filter paper so as to eli-
minate sea-salts and transferred to a beaker for drying.
The rest of the sample is dried at room temperature and stocked for
eventual other analysis.

1_b Muddy bottomsamples are treated as 1_c . If the sample however con-
tains shells or pebbles their percentage is estimated. The variability
of sampling makes that exact percentages are not significant. A rela-
tive accuracy of 25 % should be aimed at which is largely sufficient
for characterizing the shelly or gravely bottom nature.
Sandy bottomsamples containing only small amounts of mud are comple-
tely washed with tap water on filter paper so as to eliminate sea salts
and dried at room temperature, yielding the *clean sample B* .

Operation 2

This total sample B may contain shells and shell fragments and
pebbles. These are then sieved off by hand on a 2 mm sieve and by rough
weighing the *quantity of shells C* and the *quantity of pebbles D* ob-
tained. Both are stocked for eventual further study.

From *fraction E* , *finer than 2 mm* , a representative sample is
taken, between 10 and 20 mg , by splitting and transferred to a beaker.

Operation 3

We have now obtained representative aliquots for analysis. This
sample is now dried at $105°$ in a drying oven in a numbered glass beaker
of known weight.

After extensive experiments, we choose to dry at $105°$ because :
1) an equilibrium weight is obtained which can be reproduced in the fol-
lowing operations. This is important because our determinations are
all gravimetric;

2) the drying is achieved much more rapidly than at 60° ;

3) a more stable state is obtained less liable to weight change during cooling and weighing of the samples.

After drying the beaker is weighed again yielding the analysis *quantity F* . With normal samples we aim at a weighing accuracy of 0.01 mg , which certified the 0.1 % ; the very small water-suspension samples are weighed to 0.1 mg , certifying at least the 1 % .

Operation 4

The sample, if calcareous, is now first decalcified. The reasons for this operation step are :

1) if small shell fragments are present, as is very usual in sandy marine sediments, their platy character gives them a diameter much greater than the hydraulical equivalent sand grains. The granulometrical characterization of the sand is thus better without shell fragments, if analysis is made by sieving;

2) the following digestion of organic material by H_2O_2 is better on a carbonate free sample, also as to exclude the formation of Ca-oxalate which would precipitate;

3) to allow later an easier peptisation of the clay fraction;

4) finally, to determine the carbonate content.

Decalcification is achieved by cold 1 N HCl , filling up until the reaction is finished. The attack should be as short as possible so as to minimize the solution of other minerals especially iron compounds.

After completion of carbonate reaction the sample is filtered and washed with distilled water until the pH of the filtrate approaches neutral.

By filtering in a hard filter paper, type Whatman 41 , no colloïds are lost, the eventually present clay fraction being flocculated and the residue can easily be washed back in the glass beaker.

Experiments of burning the washed filter paper showed that no appreciable clay matter was withhelt in the filterpores.

The residue is again dried at 105° and weighed giving *carbonate free sample G* . The difference F - G is a good approximation of the

$CaCO_3$-content , taking into account that other minerals present may also have gone into solution to a much lesser degree.

Operation 5

The organic content is generally important in muddy sediments and ranges from fresh organic matter to all degrees of decay and decomposition. It has to be eliminated so as to enable peptisation and in a way as to give some quantitative information on the amount present.

Digestion by H_2O_2 has the advantage of giving the total loss of organic matter. Other methods give the amount of organic compound but not the amount of organic matter due to the various stages of decay. Furthermore digestion by H_2O_2 can be achieved in a flowline of analysis.

We use a fixed quantity of 100 cc 15 % H_2O_2 , which is allowed to react without heating. If necessary, a second aliquot of reagent is used. After completion of combustion the beakers are evaporated in the oven to 105° and weighed.

Evaporating the technical H_2O_2 , that we use, leaves a small but variable residue of stabilizing salts. Each bulk delivery is controlled so as to correct the dried sample weight, yielding finally the *carbon free sample H* .

It should be emphasized that previous decalcification is necessary, otherwise Ca-oxalate may be formed and precipitated.

Taking all these precautions the determined weight loss G - H can be considered a good approximation of organic matter content.

Operation 6

The next step is wet sieving of the sediment residue. Its aim is to separate the sandfraction from the silt and clay fractions which will require separate techniques for further analysis. At the same time this first separation produces important informations.

Instead of using only the normal 62 µ sieve we use also the 32 µ sieve. This makes sedimentation techniques more easier but also gives immediate information on the presence of a silt fraction in the suspension material. If clayey the sample is extensively prepared so as to achieve optimal disaggregation and peptisation.

Because the sample has gone through three cycles of drying at 105°
the first step is a prolonged (several days) soaking with a small amount
of distilled water. If tenacious some H_2O_2 is added and the sample
boiled using the very active mechanical action of O_2-bubbles forming.
100 cc of distilled water are added with 20 cc of peptisation solution
(Na-carbonate + oxalate) and boiling continued on a sandbath. The samples
are finally shaken on a shaking table.

The sample is then washed on to the 62 μ sieve of a Rhewum vibra-
tion siever. Maximum 800 cc of distilled water are flushed through the
sieves, while working, and the passing suspension water collected. The
residues on the two sieves are washed in beakers evaporated at 105° and
weighed giving the quantities I , *sand coarser than* 62 μ , and J ,
coarse silt *between* 62 *and* 32 μ .

At the same time the fraction K , smaller than 32 μ is obtained
as K = H - I - J .

The fraction J is stocked for eventual further study, the fraction
I being used for operation 9, dry sieving.

Operation 7

The aim of the next step is to gain further information on the grain-
size of the fraction smaller than 32 μ . Because the sedimentation methods
are excessively time consuming the work is reduced in two ways :
1) No analysis is made if the fraction K amounts to less than 5 % ;
2) on a routine basis only two cuts are made at 16 μ and at 2 μ .

The suspension water having passed the 32 μ sieve has been supple-
mentary peptised by the vibration of the siever. It is finally treated
with an ultrasonic shaker or a laboratory mixer. The suspension is then
brought to 1 ℓ , poured in a sedimentation column and by a substraction
method 50 cc of suspension finer than 16 μ and finer than 2 μ sub-
stracted, dried to 105° and weighed. After correcting for the amount of
peptising chemicals and transforming to quantities per liter we obtain the
weight fraction L , *smaller than* 16 μ *and* M , *smaller than* 2 μ .

It results that the fraction   32-16 μ = K - L ,

16- 2 μ = L - M ,

< 2 μ = M .

Operation 8

Fraction I is now used to characterize further the grain-size
distribution of the sands by dry sieving. Generally we use quarter-ϕ
sieves, but to reduce the work in this scheme we confined the analysis
to half-ϕ sieves, yielding the weight fractions M_0 to M_n. After
transforming them to weight percentages of the sand fraction they will
be used to identify the type of distribution curve on probability paper.

In a first stage only two parameters will be extracted from it,
a measure of central tendency and a measure of sorting.

The separate fractions are stocked for later mineralogical and
morphometrical investigations.

2.- The parameters

From the analytical quantities, which have been obtained previously,
a number of sedimentological parameters can be calculated. These parameters
will be used for defining the sedimentological characteristics, for stu-
dying the distribution in space of these characteristics and for corre-
lation with chemical and biological properties as defined by other groups
in the same projects.

2.1.- Direct parameters

1) Shell percentage Sh

Either directly estimated in muddy sediments or calculated as

$$Sh = \frac{C \times 100}{B} .$$

2) Pebble percentage Pb

Either directly estimated or calculated as

$$Pb = \frac{D \times 100}{B} .$$

3) Calcium carbonate content Ca

Defined on the fraction smaller than 2 mm

$$Ca = \frac{F-G \times 100}{F} .$$

4) Organic matter content Or

Equally defined on the fraction smaller than 2 mm

$$Or = \frac{G-H \times 100}{F} .$$

5) Sandfraction Zd

Defined on the fraction smaller than 2 mm and free of carbonates and of organic matter, instead of on the total sediment. This parameter becomes a more significant, detrital variable by eliminating the influence of variable organic matter and carbonate content

$$Zd = \frac{I \times 100}{H} .$$

6) Suspension fraction Ps

In the neighbourhood of 62 µ is generally situated a break in the grainsize distribution due to the difference in saltation and suspension transports. In Western Europe, this is reinforced by the presence of an important siltfraction derived from fossil eolian loess.

$$Ps = \frac{H-I \times 100}{H} .$$

Ps is evidently complementary to the sand fraction.

7) Coarse silt fraction Sc

The fraction between 62 µ and 32 µ

$$Sc = \frac{J \times 100}{H} .$$

8) Medium silt fraction Sm

The fraction between 32 µ and 16 µ

$$Sm = \frac{(H-I-J-L) \times 100}{H} .$$

9) Fine silt fraction Sf

The fraction between 16 µ and 2 µ

$$Sf = \frac{(L-M) \times 100}{H} .$$

10) The clay fraction Cl

The fraction smaller than 2 µ

$$Cl = \frac{M \times 100}{H} .$$

It is evident that

$$Zd + Sc + Sm + Sf + Cl = 100 \ .$$

From this arrises that all eventual analytical errors are combined in
the fraction Sm which is not measured directly but is only known by
calculation. Grainsize curves giving an abnormal situation in this
fraction are probably evidence for analytical errors, mostly due to
loss of material during one of the operations or a faulty weighing.
These samples should be rerun.

2.2.- Derived parameters

As derived parameters we consider those which are obtained by
calculation from the previous ones and can be used to characterize more
sensitively certain sedimentological properties. A great number of them
can be defined from the available analytical data and direct parameters.
We give only a choice here.

11) The sand median Mez

A measure of central tendency of the sand fraction must be known
as a parameter proportional to the transport capacity of bottom currents,
so proportional to their velocity. The mode Moz characterizes best the
top of a frequency curve and is defined following the graphical method
of Gry, where the derivative becomes zero.

On a routine basis however we use the sand median Mez defined
as the 50-percentile on the cumulative curve of the sand-fraction
alone. In this way Mez approaches Moz as the influence of the bimodal
suspension population is excluded.

In the presence of bimodal sand populations it is certain that Mez
remains a crude estimate of central tendency.

12) Sandsorting Soz

The sandsorting gives in first approximation a valuable idea on the
variability of bottom currents and is worthwhile to note. We must certainly
remember that mixing of different layers during sampling extends this va-
riability in time. We prefer the simple notation

$$Soz = \frac{\phi_{84} - \phi_{16}}{2}$$

which justly does not take into account the tails of the distribution in which mixing becomes still more important. Even so it should be remembered that bimodal sand populations, as so often occur for instance in tidal currents, will show a sorting much worse than that of the two separate populations.

This sorting coefficient is easily determined on the cumulative curves of the sand fraction and has the advantage to be usable as σ in statistical calculations.

13) The coarse silt ratio Ser

This ratio compares the fractions of the suspension devided by the 32 μ limit

$$Ser = \frac{Sc}{Ps} .$$

It is not a very sensitive measure because the loess-silts have a mode close to 32 μ and small changes in this silt material have a big influence on the Ser .

We use it however because on watersuspension samples the 32 μ limit is the finest division.

14) The coarse and medium silt ratio Scmr compares the fractions of the suspension material divided by the 16 μ limit

$$Scmr = \frac{Sc + Sm}{Ps} .$$

More sensitive because most of the detrital siltfraction is above 16 μ in the loess.

15) The clay ratio Cr

Let us compare the clay fraction, finer than 2 μ , to the total suspension material

$$Cr = \frac{Cl}{Ps} .$$

It seems quite superfluous to analyze the suspension fraction in so different ways. Our aim however is to discover differences in the mud composition which might reflect slight differences in provenance of the suspension material and to analyze the influence of flocculation on the grainsize distribution.

16) <u>Clay organic ratio Ocr</u>

Let us compare the content of organic matter to the clay content

$$Ocr = \frac{Or}{Cl} \ .$$

Assuming the decayed organic matter is mostly present in the finest fraction it is interesting to establish a comparison between the two.

In fact the total organic matter, being without doubt interesting for general classification, for biological use, for correlation with chemical analysis, is too much influenced by other variables as sand and silt content. For distinguishing real qualitative differences between muds these variables have to be excluded, which is tried with this ratio.

Acknowledgments

C.- *LITERATURE REVIEW ON SEDIMENTATION AND EROSION OF MUD*

1.- Sedimentation

1.1.- Flocculation

Suspended matter in the sea is not dispersed into its elementary particles, but aggregated into units, called floccules. Several mechanisms cause this aggregation of the particles [E. Verger (1968)] :

- flocculation by the high electrolyte content of the sea; mainly due to Ca^{++} and Mg^{++} ions;
- biological causes :
  - mussels, oisters, etc. agglomerate suspended particles by their mucus,
  - many mollusk species leave faecal pellets; mud globules aggregated in their alimentary canal,
  - diatoms can gather mud around their frustules by excreted mucus;
- particulate organic matter can act as a mean of aggregation with inorganic particles.

Flocculation by electrolytes is the most important mechanism, biological factors may be acting in definite areas, such as tidal flats, estuaries, etc. Flocculation by electrolytes in physico-chemically controlled by the following factors, and becomes more important as [Migniot (1968)] :

- concentration of the flocculating electrolyte increases,
- valency of present ions is higher,
- hydrated ions are smaller,
- temperature rises,
- dielectric constant decreases,
- pH decreases,
- adsorption capacity of present anions decreases.

1.2.- Influence of the elementary particles on flocculation

The size of floccules is usually given as an *equivalent diameter*. This means that they are considered to have the same settling velocity as quartz spheres of this diameter. The real diameter of these complexes however
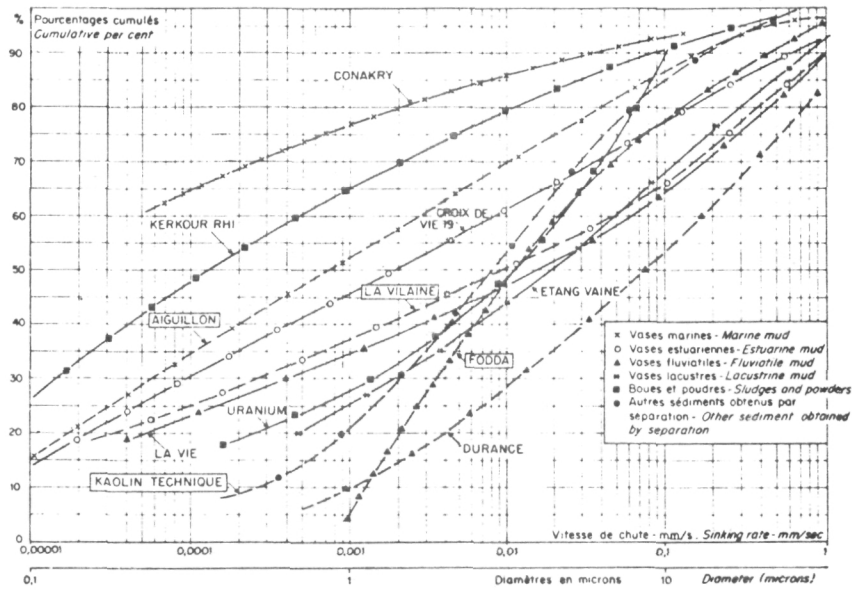
fig. 1.- Examples of sinking rate curves for deflocculant media. From Migniot (1968).
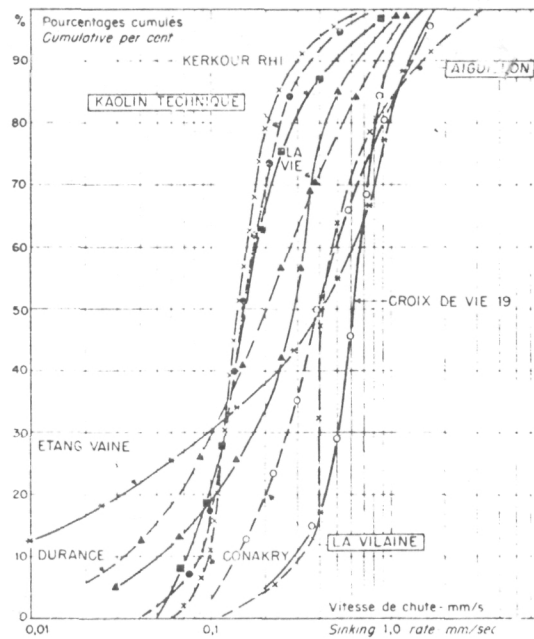

fig. 2.- Examples of sinking rate curves for flocculant media. From Migniot (1968).

is much greater, as specific weight of some components is lower than that of quartz (*e.g.* organic matter) and water content may be up to 95 % [Postma (1967)].

Migniot (1968) found by flume experiments on different pelitic sediments that flocculation reduces grain-size variation (fig. 1 and 2). The *factor of flocculation* is defined by Migniot as :

$$F = W_{f\ 50\%} : W_{d\ 50\%}$$

with $W_{f\ 50\%}$: mean settling velocity of floccules in a flocculating environment and $W_{d\ 50\%}$: mean settling velocity of individual particles in a peptizing environment.

At 20 °C and a concentration of 10 g/ℓ sediment, salinity 30 % : $F \simeq 250\ d^{-1.8}$ (fig. 3) with d : equivalent diameter in μ . Thus F increases as d decreases.
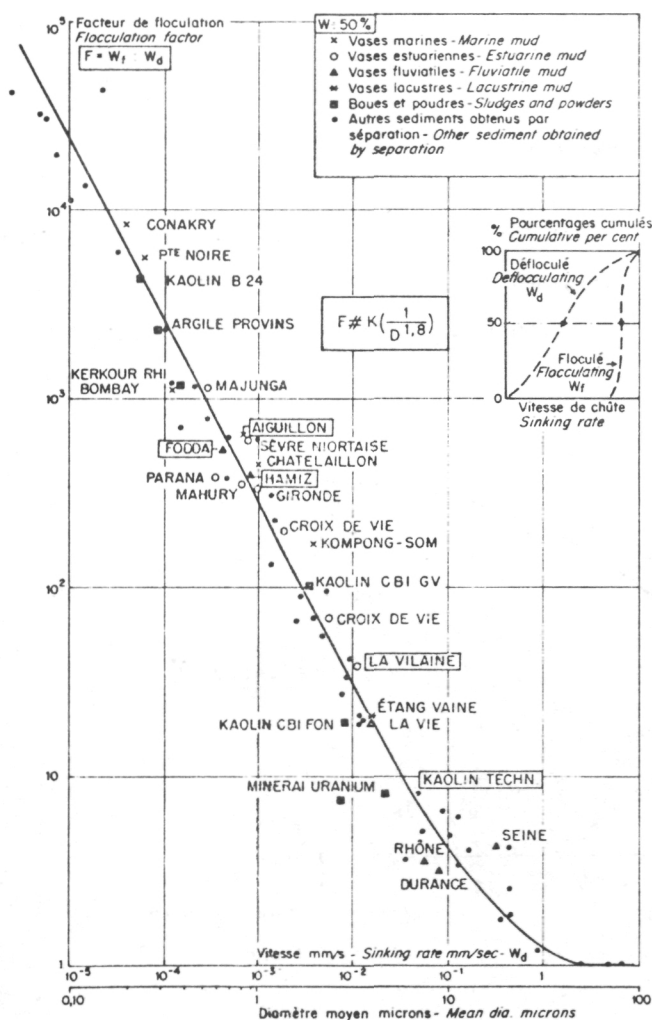

fig. 3.- Effect of particle size on flocculation. From Migniot (1968).

As to Migniot, mineral matter brought into a flocculating environment would have a mean settling velocity between 15×10^{-3} to 60×10^{-3} cm/s . This corresponds to a mean grain size of 13 to 26 μ , concentration being 10 g/ℓ .

Flocculation would not act upon particles greater than ± 30 μ and would also be influenced by the concentration of the suspension. F increases with increasing concentration until 15 g/ℓ and decreases at higher concentrations (fig. 4).
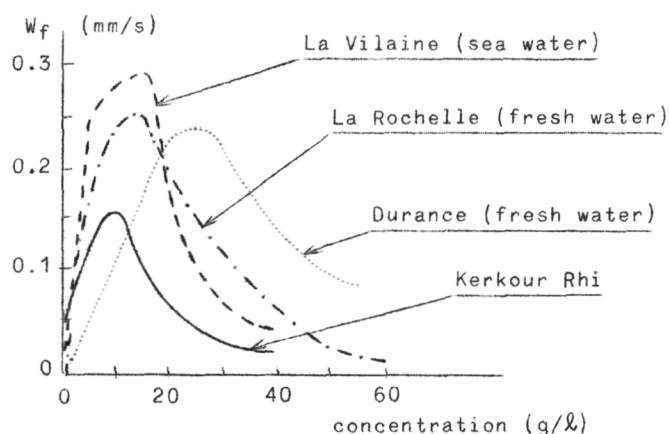

fig. 4.- Effect of solid particle concentration on floc sinking rate. From Migniot (1968)

Small concentrations of flocculating matter suffice to flocculate a suspension; *e.g.* 10 ‰ salinity makes 0.5 g/ℓ sediment reach its maximum settling velocity (fig. 5 and 6). Provided a high salinity of
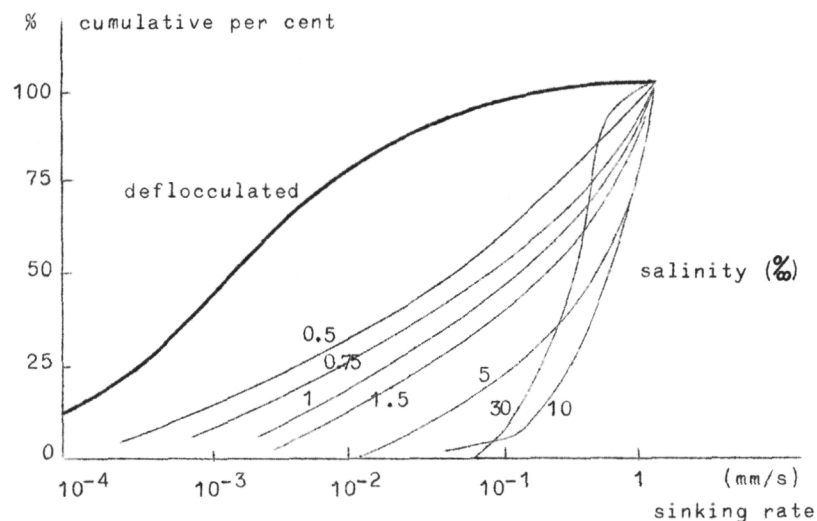

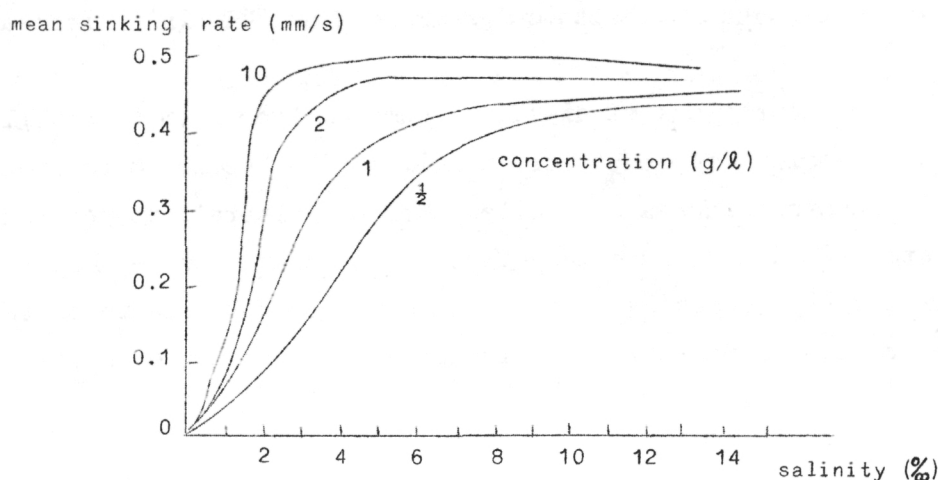fig. 5.- Effect of salinity on sinking rate. From Migniot (1968).

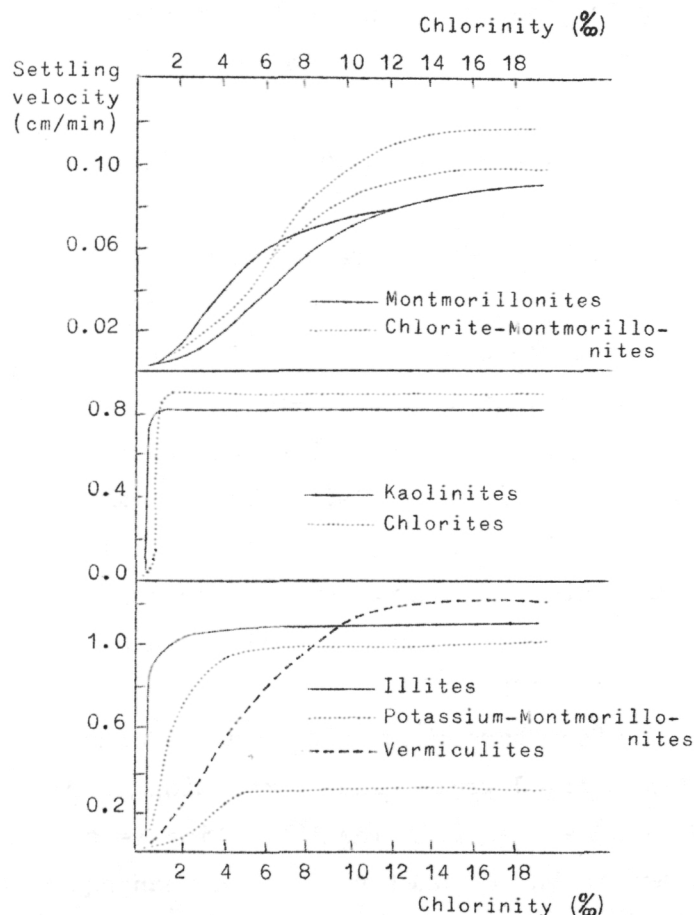fig. 6.- Effect of salinity on sinking rate. From Migniot (1968).

fig. 7.- Settling velocities of clay minerals
in sea water at different chlorinities
(26 °C, pH = 7.2-8.8, 2 g clay/liter).
From Postma (1967).

a very concentrated suspension, macro-flocculation may occur causing the decrease of the sinking rate.

The influence of mineralogy of the particles on their flocculation was studied by Whitehouse *et al* (1960) [see Postma (1967)]. They found suspensions of 2 g clay minerals per liter of sea water at 26 °C reaching different maximum representative settling velocities depending upon salinity and mineralogy. For illite, a velocity of 1.85 cm/s was reached at 4 ‰ chlorinity (eq. diam. ≈ 13 μ), whereas kaolinite reached 1.35×10^{-4} cm/s (eq. diam. ≈ 11 μ) at 2 ‰ chlorinity.

Montmorillonite did not reach such constant maximum

settling velocity, but flocculation progressed as chlorinity increased
(fig. 7).

Small concentrations of dissolved humic matter seem to stabilize
kaolinite suspensions in sea water. Stabilization becomes more prominent
as kaolinite content increases, while other clayminerals suspensions
would be stabilized to a much lesser degree [Rivière and Vernhet (1951)].
Furthermore, Berthois and Pacheco (1968) suppose that organic matter with
a high $\frac{C}{N}$ ratio suppresses the influence of temperature on settling rate.

1.3.- Literature data

Gripenberg (1934) attributed an equivalent diameter of 5 to 15 µ
to flocculated matter in the sea [see Svendrup *et al* (1942)].

Svendrup, Johnson and Fleming (1942) considered that elementary
particles with equivalent diameter greater than 15 µ do not share in
flocculation and consequently sink at their own rate.

At the Gulf of Paria mean median floccule size is estimated at
15 µ eq. diam. by Van Andel and Postma (1954).

Through grain size analyses of Dutch tidal march deposits, Van
Straaten (1954) inferred that the mud was deposited as floccules with
an equivalent diameter between some and 40 µ .

Microscope counts made in not specified coastal areas by Jerlov
(1955) resulted in a mean geometric diameter of 16 µ [see Jerlov (1963)].

By the same procedure, Prickard and Giovando (1960) obtained mean
diameters of 7 to 17 µ [see Jerlov (1963)].

Several authors found constant ratios existing between the sub-
fractions of the fraction lesser than 25 µ in recent marine mud depo-
sits along the Dutch coast [see Favejee (1960)].

One explanation could be that after throughout mixing and floccu-
lation in the sea, the mud obtained a fixed grain size composition. Par-
ticles greater than 25 µ would thus have an individual settling velocity.

Investigations about the Demerara Bar Channel revealed a mean equi-
valent diameter approximately equal to 8 µ for flocculated matter
(chlorinity 10 to 20 ‰) and 1 to 1.5 µ for the same but unfloccu-
lated material (chlorinity 0.2 to 0.5 ‰) [see Postma (1967)]
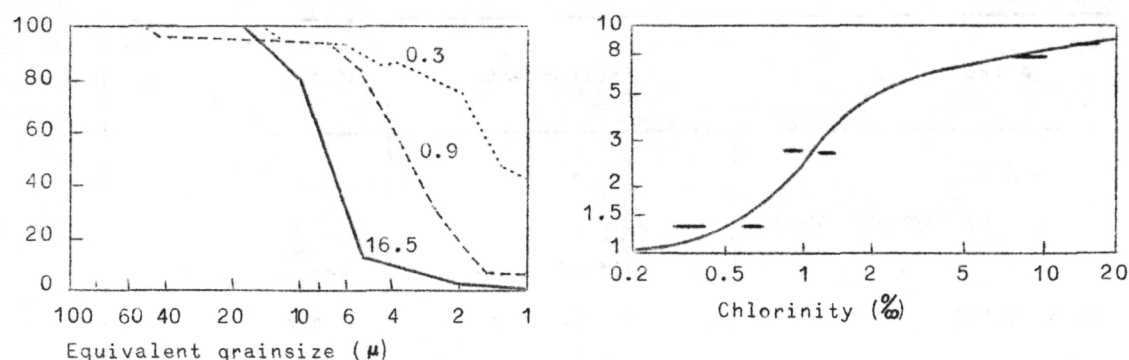(fig. 8).

fig. 8.- Left : equivalent particle-size distributions measured at different chlorinities
by the pipette method; scale at left indicates the weight percents of silt, finer
than indicated size. Right : relation between median equivalent particle size and
chlorinity; scale at left indicates median equivalent particle size μ ; silt con-
centrations : 1 mg/ℓ (Demerara Coastal Investigation, 1962). From Postma (1967).

Berthois and Pacheco (1968) found median equivalent diameters of
approximately 11 , 22 and 33 μ at temperatures of respectively 5 ,
20 and 25 °C for sediments of the Loire Estuary. For mud of a Green-
land Fjord a median equivalent diameter of 4 μ was found. These labo-
ratory experiments were executed in distilled water, sediment concen-
trations were not communicated.

A concrete estimation about the settling velocity of flocculated
matter in the southern North Sea was made by McCave (1970). Based on the
results of Postma's experiments (1961) in the Borndiep and Marsdiep and
on those of Sheldon (1968) in the Crouch Estuary he computed a settling
velocity of 1.8×10^{-3} to 6.4×10^{-3} cm/s (equivalent diameters 5
to 10 μ). His estimation of a representative mean settling rate was
4×10^{-3} cm/s with an upper limit to the mean of 1×10^{-2} cm/s . This
corresponds to an equivalent diameter of 7 to 8 μ and 12 μ respec-
tively at 10 °C mean temperature of North Sea water.

Terwindt and Breusers (1972) on the other hand report a mean fall
velocity of mud in Dutch tidal waters of 1.5 m/h or 4.2×10^{-2} cm/s
which corresponds to an equivalent diameter of about 20 μ.

Author	Environment	Equivalent diameter of the floccules (μ)	Flocculated fraction (μ)
Gripenberg (1934)	labo	5-15	
Svendrup, Johnson, Fleming (1942)			< 15
Van Andel, Postma (1954)	Golf of Paria	mean diam. 15	
Van Straaten (1954)	Dutch wadden	some to 40	
Jerlov (1955)	coastal waters (?)	geom. mean 16	
Prickard, Giovando (1960)	coastal waters (?)	geom. mean 7-17	
? (1960)	Demerara Bar Channel	± 8	
Favejee (1960)	Dutch coast		< 25
Postma (1961)	Dutch waddensea	6-12	
Berthois, Pacheco (1968)	Loire-estuary	11-33 (median)	
Berthois, Pacheco (1968)	Fjord, Greenland (labo)	4 (median)	
Sheldon (1968)	Crouch-estuary	mean diam. 5-10	
Migniot (1968)	labo	13-26	< 30
McCave (1970)	Southern North Sea	mean diam. 7-12	
Terwindt, Breusers (1972)	Dutch tidal waters	mean diam. 20	

2.- Erosion

2.1.- Mud properties in relation to its erodability

Migniot (1968) who investigated the erosion of different muds
(table 1) by water movement, found that for older deposits in streaming
water :

$$U_{*c} \simeq KT_s^2$$

where U_{*c} is the critical shear velocity in cm/s ; K the factor depen-
ding on the nature of mud-water complexes, ranging in proportion from 1
to 10 ; T_s the mud concentration in g/ℓ .
For recent unconsolidated deposits :

$$U_{*c} \simeq KT_s .$$

Table 1

From Migniot (1968)

Origine	Pourcentages		Médiane μ (Pélite)	Analyses chimiques			Minéraux des argiles
	Sable (%)	Pélite (%)		$CaCO_3$ (%)	Mat. organ. (%)	Fe (%)	
Vase marine de L'Aiguillon	0	100	0,85	30	2	1,5	kaolinite : 35 % illite : 65 %
Vase "La Rochelle"	2	98	0,45	25	4	1,6	illite, kaolinite
Vase Conakry (Guinée)	0	100	0,15	20	1	6,0	kaolinite
Vase estuarienne de La Vilaine	8	92	1,6	15	1,5	1,3	illite : 50 % kaolinite : 50 % traces de chlorite
Vase estuarienne du Mahury (Guyane)	2	98	0,9	4	2,5	-	kaolinite : 60 % illite : 40 %
Vase fluviale de l'oued Fodda (Alg.)	0	100	0,65	21	4,7		kaolinite : 29 % illite : 26 % montmorillonite : 21 % chlorite : 24 %
Vase de retenue de barrage du Hamiz (Algérie)	1	99	0,60	20	0,2	-	illite, kaolinite, chlorite, interstratifié; montmorillonite, illite
Limon Durance (après tamisage)	-	100	11,00	20			poudre détritique, quartz, etc.
Argile de Provins (brute)	0	100	0,70	0	-	-	kaolinite
Argile de Provins (séchée et broyée)	0	100	0,30	-	-	-	kaolinite
Boue de Kerkour-Rhi (Inde)	2	90	0,35	60	-	traces	montmorillonite : 70 % illite : 30 % présence de phosphates

If initial rigidity is greater than 20 dyn/cm^2

$$U_{*c} \simeq 0.5 \, T_y^{\frac{1}{2}} \qquad (C\,G\,S \text{ units}).$$

For values of $T_y \simeq 10 \text{ dyn/cm}^2$

$$U_{*c} = T_y^{1/4} \, .$$

Furthermore he found that differences in mineralogy and grain size composition between the muds must be responsible for notable differences in their erodability.

Mud deposited in sea water needed a 1.7 times higher velocity to be eroded than this same : mud laid down in fresh water. Experiments with mixtures of sand and mud showed that only the water content of the mud was of great importance. More than 30 % of sand caused the decrease of U_{*c} (table 2).

Table 2

From Migniot (1968)

Concentration de vase T_s (g/ℓ)	Pourcentage de sable (%)	Concentration globale vase + sable	Vitesse de reprise	
			$\bar{U}$ (cm/s)	U_* (cm/s)
465	13,6	525	55	2,3
475	22,5	582	60	2,5
470	39,5	697	57	2,4
471	52,5	830	49	2,05
470	66	1000	45	1,0
sable pur	100	2000	32	1,35

Terwindt and Breusers (1972) who carried out comparable experiments came to almost identical conclusions :
- thicker mud layers have smaller initial consolidation rates and lower values of U_{*c} (table 3);

Table 3

From Terwindt and Breusers (1972)

Percentage sand in mud	Thickness mud layer (cm)	Consolidation time (h)	U_{*c} (m/s)
37	2	2	0.019
37	2	2 ½	0.021
7	20	2 ½	0.008
2	2	2	0.009-0.014

- increasing sand content of the mud gives a more rapid initial conso-
  lidation and higher values of U_{*c} . A U_{*c} maximum is reached at a
  sand content of 40 % and higher contents lead to decreasing values
  of U_{*c} ;
- for one particular mud sample, U_{*c} increases linearly with mud con-
  centration of the bed material.

These experiments were carried out with 3 muds (table 3, first
three lines) gathered in the estuary and harbours of the southwest part
of the Netherlands.

Clay mineralogic composition was about 70 % illite, ≃ 15 %
montmorillonite and 15 % kaolinite.

2.2.- Wave activity and current velocity as controlling factors of mud erosion

Based on observed wave oscillograms, Draper (1966) computed peak
particle speeds at the southern North Sea bottom (due to wave action)
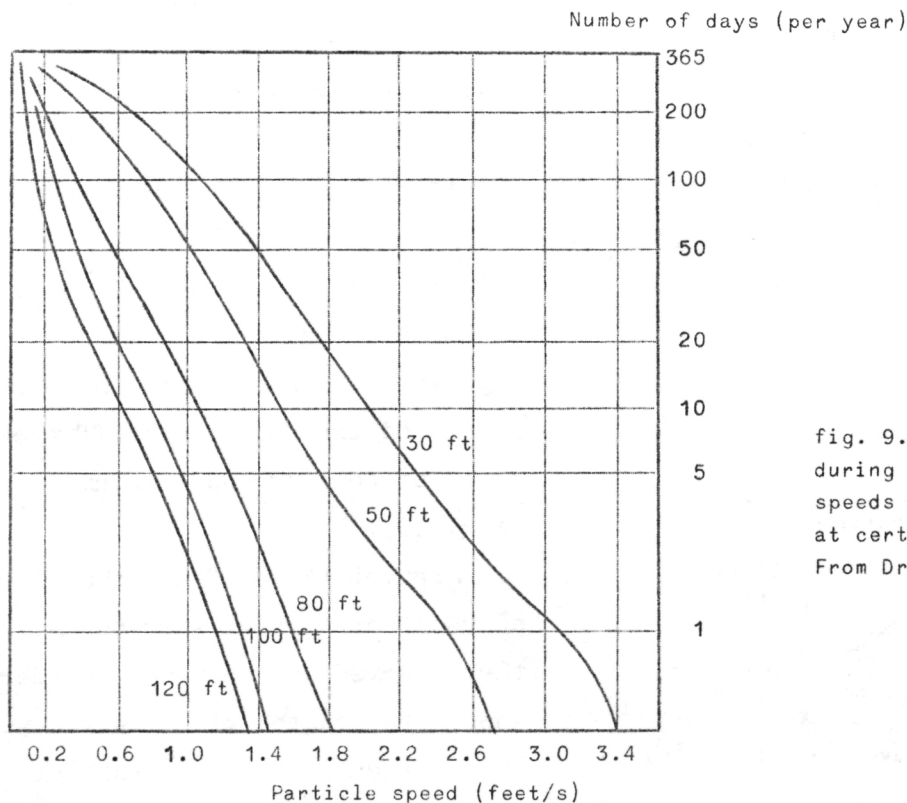which can be reached once in any time interval (fig. 9 et 10). Thus at

fig. 9.- Percentage of the time during which water particle speeds exceed any given value at certain depths. From Draper (1966).
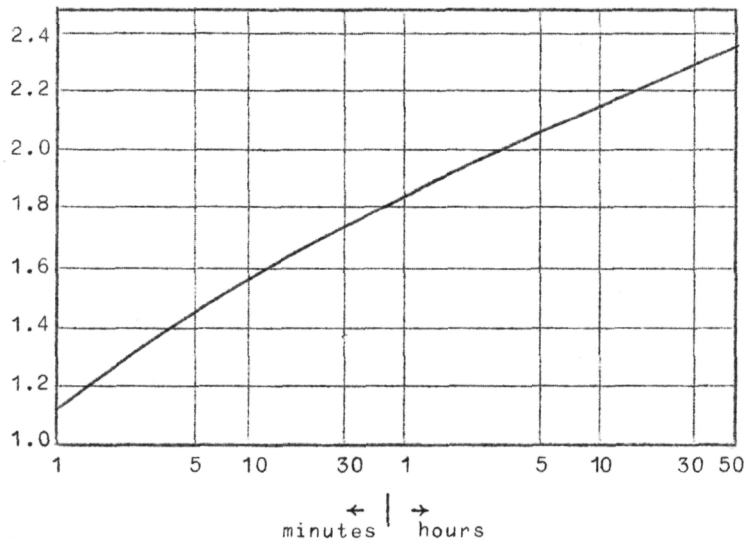
Particle speed factor

fig. 10.- The particle speed factor is the ratio of the most probable value of maximum particle speed to the significant peak particle speed, as a function of the length of time. To obtain the probable maximum value of particle speed in any particular situation, the value of significant peak speed obtained from fig. 9 must be multiplied by the relevant particle speed factor.
From Draper (1966).

a depth of $\simeq$ 10 m , a speed of 54 cm/s is exceeded during 20 days each year. Once in every hour of this period, a speed of 100 cm/s can be reached.

McCave (1971) stated that for waves, the maximum geomorphic-sedimentologic work will be done when the product of mass rate of sediment movement and frequency of occurrence gives a maximum. Based on Draper's results he computed that the most effective waves for the southern North Sea are those which occur between 10 and 20 % of the time, giving peak particle speeds of 30 to 40 cm/s . The maximum values of the effectiveness plot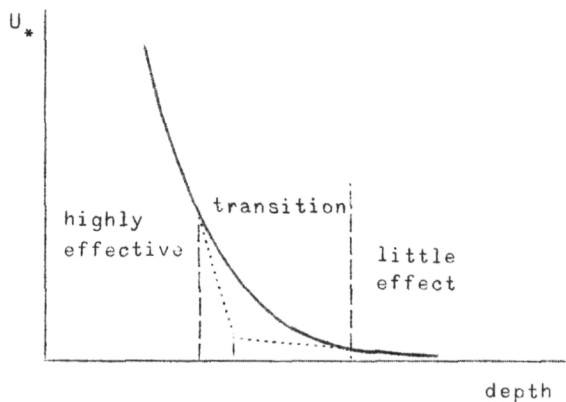ted as a function of depth (fig. 11) show that the area above $\simeq$ 15 m is in the highly effective zone, *e.g.* the nearshare strip and the crests of the sand banks off the south of Holland and Belgium (fig. 12).

Migniot (1968) found that for a muddy bottom a greater depth than the observed one must be considered when wave lengths with a given period are calculated. An initial
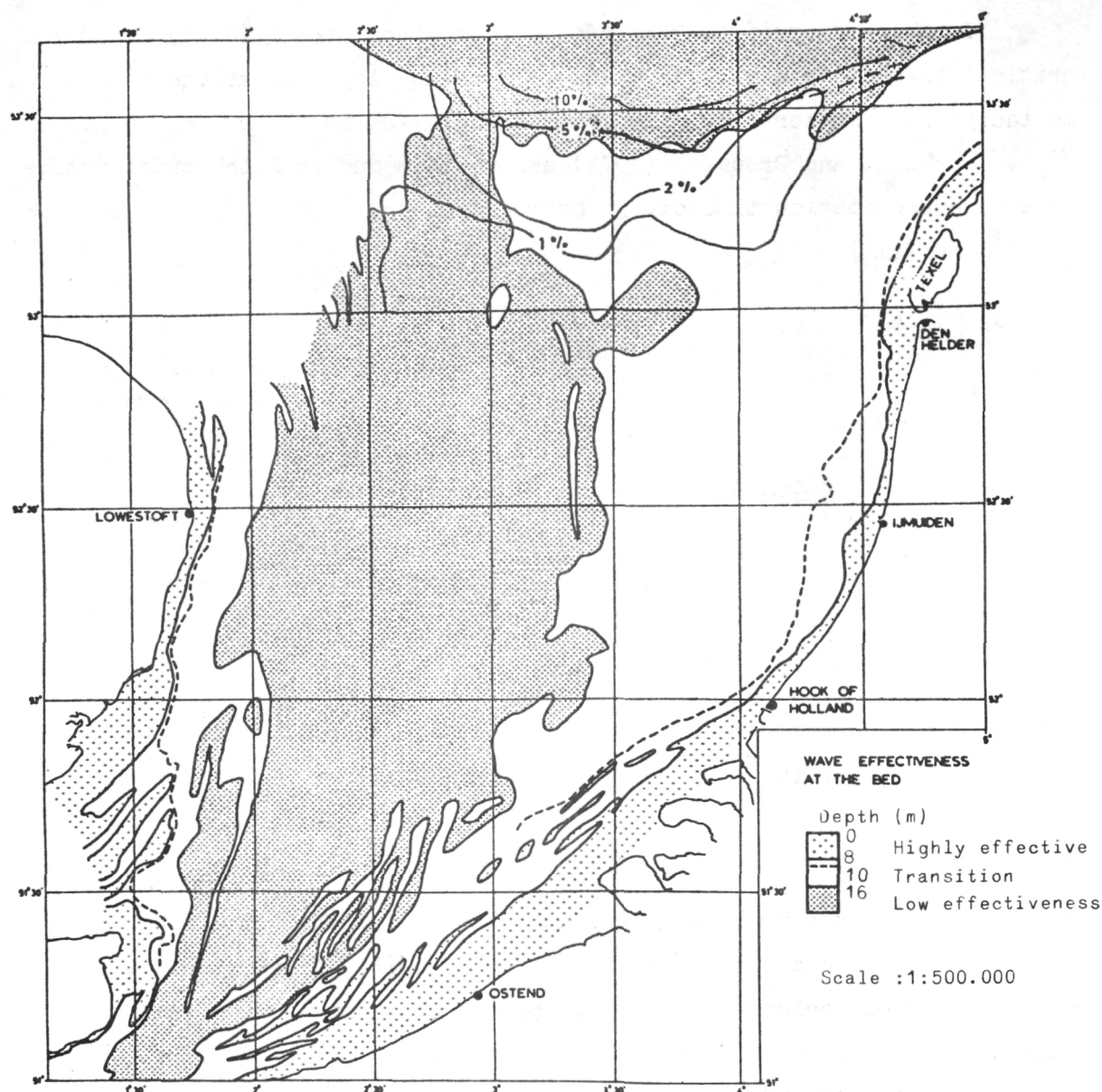

fig. 11.- From McCave (1971).

fig. 12.- Regions of high, transitional and low wave effectiveness at the bed
(Southern Bight of the North Sea). Between 53°N and 53°40'N contours
of percent mud (% < 50 μ) in the bottom sediments are shown. There is
a fairly rapid increase in mud percent in the region of low wave ef-
fectiveness. From McCave (1971).

rigidity of 20 N/m^2 is needed for the mud to act as a rigid bottom.
Orbital movements of the waves can develop into an unconsolidated mud
and prevent consolidation. Owing to their thixotropic properties, older
deposits can thus be fluified. For instance, Migniot (1968) found that
water content of muds decreased with increasing depth in the sea.

In the *Haringvliet*, Terwindt, Breusers and Svasek (1968) found a critical shear stress of 11 dyn/cm^2 for sand-clay laminations with a median grain diameter (for mixed samples) of 20 to 60 μ (U_{*c} = 3.3 cm/s).

Terwindt and Breusers (1972) assume that mud in Dutch tidal waters, after a consolidation time of 3 hours (fig. 13) have a U_{*c} of 2 cm/s ($\tau_c \simeq 4$ dyn/cm^2).
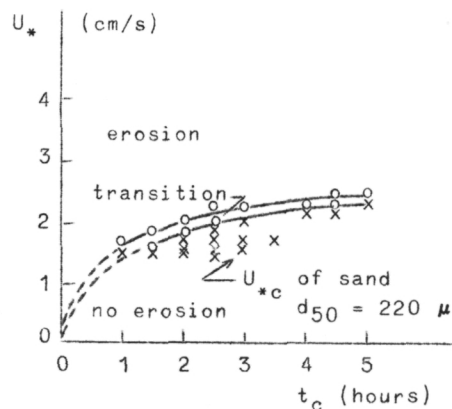
fig. 13.- Critical shear velocity U_{*c} in relation to consolidation time t_c.
ρ_w = 1010 kg/m^3
c_0 = 16.5 g/ℓ
Waterdepth = 25 cm
Thickness of mudlayer = 2 cm
o Strong erosion of mudlayer
x No or slight erosion of mudlayer
From Terwindt and Breusers (1972).

By means of the formula

$$\frac{U_y}{U_*} = 5.75 \log \frac{y U_*}{0.108 \nu}$$

where U_y is the current velocity at a height y above the bed, U_* the shear velocity and ν the kinematic viscosity of the water, the critical current velocity $U_{50,c}$ at 50 cm above the bottom can be calculated and is about 60 cm/s . Where this current strength is exceeded, no preservation of mud layers can occur.

In an offshore tidal channel in the *Haringvliet*, lenticular and sand-clay lamination only occur at water depths greater than 5 m below. Terwindt *et al* (1972) thought that wave action prevented permanent deposition of mud layers at lesser depths.

3.- Sedimentation and erosion mechanisms in the North Sea

3.1.- The German Bight

For this area, McCave (1970) calculated that the usually accepted mechanism of deposition during slack tide only could not account for a

rate of deposition of 15 cm per 100 years , encountered in that area.

Assuming a suspended sediment concentration of 2 mg/ℓ , a mean settling velocity of 4×10^{-3} to 1×10^{-2} cm/s and a near surface density for the mud of 1.5 g/cm^3 , the rate of deposition is 1.34 to 5.36 cm per 100 years if every slack tide has a still water period of 30 min .

The continuous model, however, based on Einstein's hypothesis (1967, 1968) [see McCave (1970)] of a plane existing near and parallel to the bed below which particles must settle, gives a rate of deposition of 16.8 cm per 100 years . Median diameters in the area are generally less than 40 μ and the average maximum shear velocity is 1.05 cm/s in the absence of waves. At this value, silt and fine sand cannot be moved.

This model however should only be valid at $U_* < 1.2$ cm/s and continuous deposition should temporarily be interrupted by storm and wave activity.

3.2.- Dutch tidal waters

Terwindt and Breusers (1972) stated that sedimentation of mud from suspension starts in a considerable degree if current velocity drops below 20 cm/s . In the area under consideration this should be the case during 2 hours on the average. With a fall velocity of 1.5 m/h , mud present over 3 m above the bed might reach the bottom. The maximum measured mud content near the bottom during slack water was 1 cm^3/ℓ . A layer of 0.3 cm of unconsolidated mud may thus be formed during one slack water period. As mud layers of 1.0 to 2.5 cm (original thickness 2 to 5 cm), carrying sharply bounded sand layers occur in the area, mud deposits must be preserved and formed over several tidal cycles. It was found that mud can carry a sharply defined sand layer after 3 hours of consolidation and this time is sufficient to make the mud resist to current strengths of 60 cm/s at 50 cm above the bottom. Not withstanding the fact that this value is normally exceeded in Dutch tidal water, mud deposits may be preserved in some circumstances :
- the troughs of sand ripples (flaser bedding) may protect them for erosion,
- admixture of sand may accelerate compaction and increase resistance to erosion,

- $U_{50,max} > U_{50,c}$ may only occur :
    - at spring tides,
    - at high river discharges into an estuary,
    - when storms cause a piling up of water near the coast,
    - at higher wave activities.

4.- Conclusions

It seems to us that :

- suspended matter concentrations and full velocity values accepted by Terwindt *et al* are too high in comparison with other data. For instance, in the area of the mathematical model we never observed concentrations higher than 150 mg/ℓ ;

- U_{*c} values may possibly be applied to muddy deposits off the Belgian coast. Nevertheless, the influence of waves must be taken into account as an important factor of mud erosion in coastal areas;

- prevailing conditions at muddy near coastal areas off the Belgian coast are quite different from those found in the German Bight : current strengths are stronger, the area is less deep and suspended matter concentrations are quite higher. Therefore, Terwindt and Breusers' model is more likely to hold here, namely current and wave action controlled deposition and erosion.

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D.- *RESULTS OF THE ANALYSIS OF SEDIMENT SUSPENSIONS OF THE CAMPAIGN* 1972

1.- Lateral distribution

Since the beginning of the investigation, some three hundred 25 ℓ-samples of sea water have been taken. Computed means for every station are shown on fig. 1. High concentrations of suspended matter were found in front of the Western Scheldt and the Belgian coast, this extension was not encountered.

In the open sea, concentrations are nearly negligible. The distribution of measured maximum and minimum concentrations (fig. 2 and 3) shows that the southern part of the area is a very dynamic one compared to the northern part.

Furthermore, the highest suspended matter content has been found during winter (table 1).

Table 1

Suspended matter content

(mg/ℓ)

	01	02	03	04	05	06	07	08	09
Winter	70,7	12,2	11,1	4,3	13,1	16,8	31,0	13,3	1,4
Summer	20,6 45,8 6,3	3,8	4,6 2,1	3,4 1,2	11,2 2,4	21,5 1,5	12,6 1,3	2,1	2,6 2,4

	16	17	18	19	20	21	22	23	24	25
Winter	0,6	0,6	4,6	0,9	0,8	0,2	0,8	1,9	2,5	1,8
Summer	2,5 1,6	1,6 1,4	2,4 0,4	0,5 0,5	0,3 0,9	1,2	1,3	2,4	0,6	1,0

The highly variable suspended matter content in the southern part can only be due to hydrodynamical conditions, among which wave effectiveness at the bottom is very important.

Terwindt (1967) also supposes that the high mud content of the water in winter can possibly be explained by the frequent eroding storms.
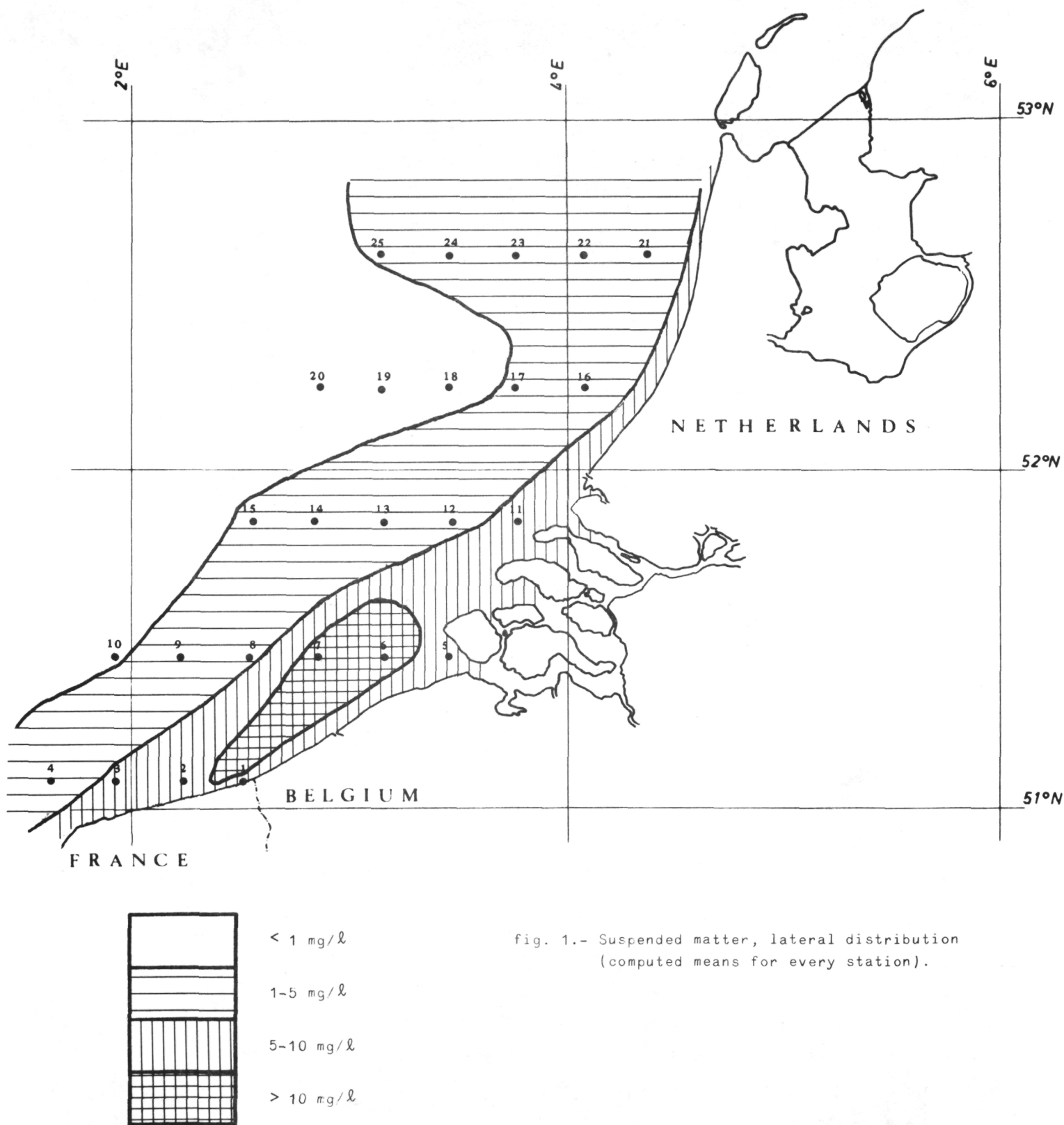
fig. 1.- Suspended matter, lateral distribution (computed means for every station).
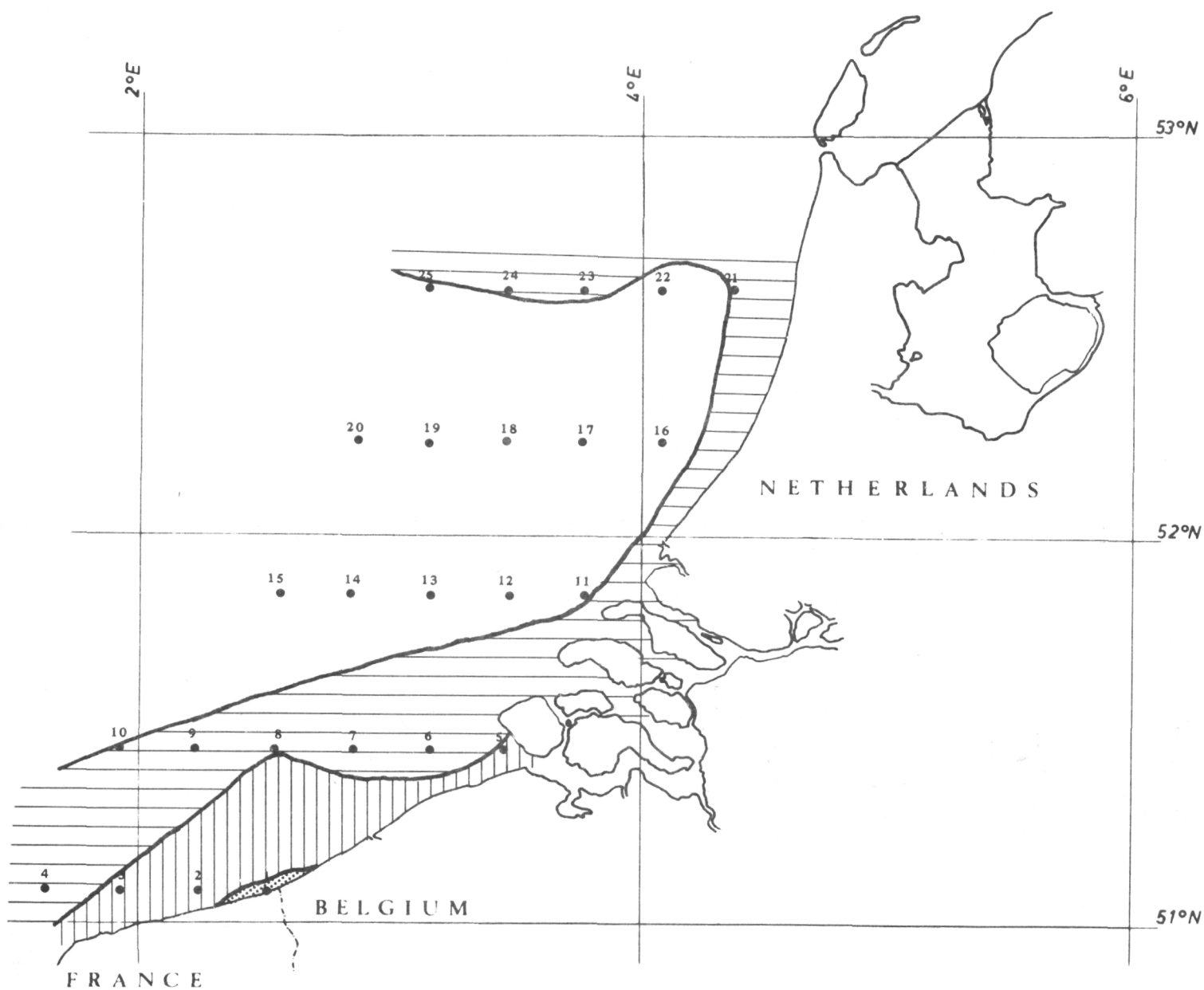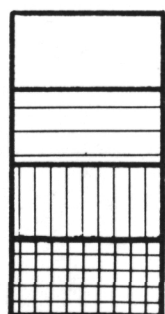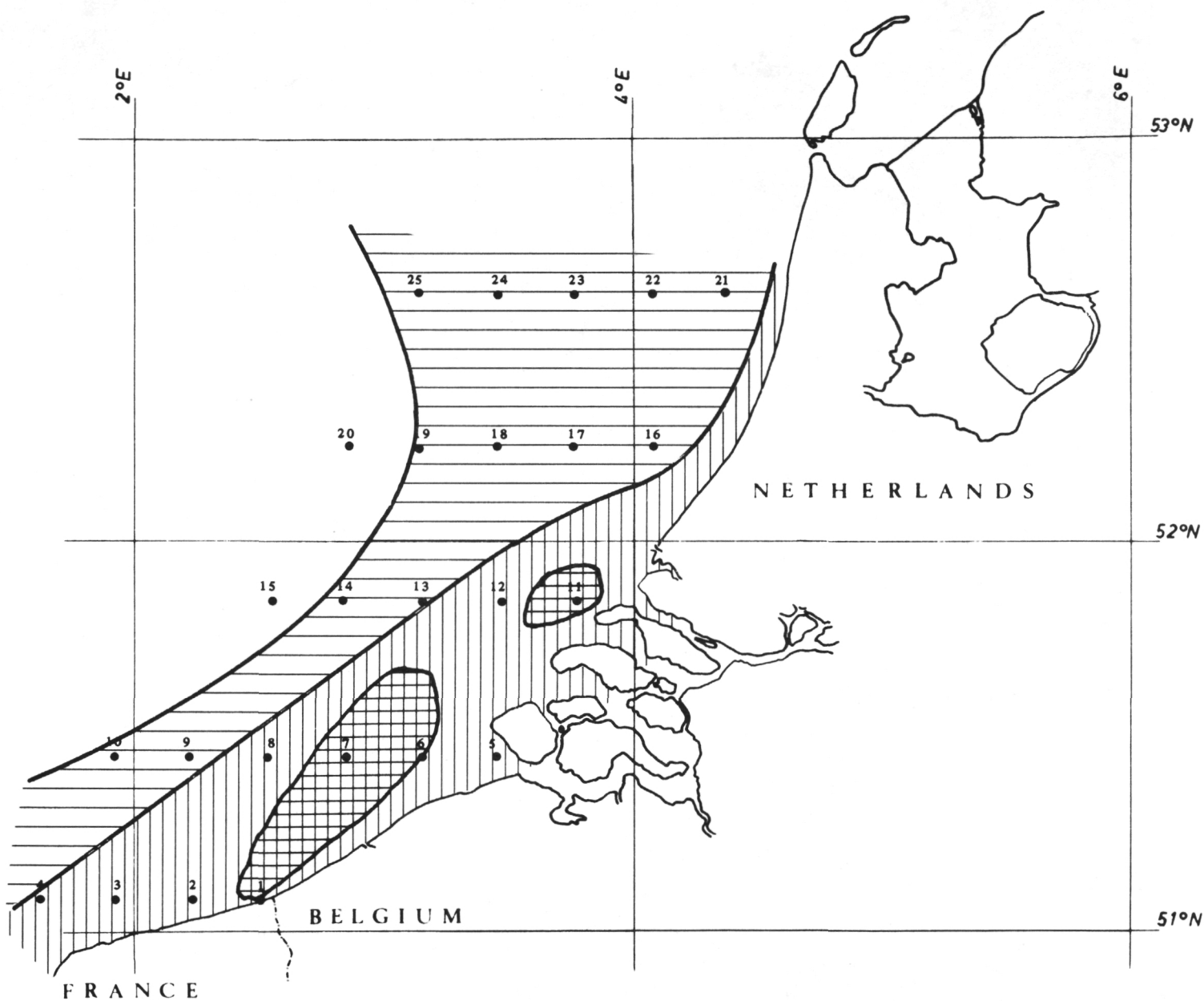
< 1 mg/ℓ

1-5 mg/ℓ

5-10 mg/ℓ

> 10 mg/ℓ

fig. 2.- Suspended matter, minimum concentrations.

< 1 mg/ℓ

1-2 mg/ℓ

2-5 mg/ℓ

> 5 mg/ℓ

fig. 3.- Suspended matter, maximum concentrations.

< 1 mg/ℓ

1-5 mg/ℓ

5-10 mg/ℓ

> 10 mg/ℓ

2.- Vertical distribution

A gradual increase of suspended matter content with depth, together with a tidal periodicity was found by Joseph (1955) [see D.J. Stanley (1969)] (fig. 4).
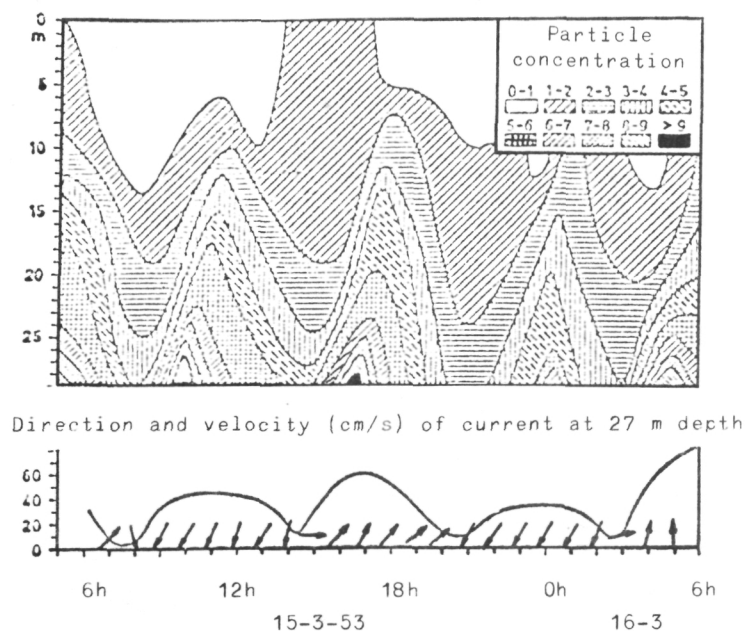

fig. 4.- Tidal periodicity in North Sea suspended sediment con-
centration. From Joseph (1955); cf. Stanley (1969).

As we sampled simultaneous over the encountered depth in every station by means of 5 samples, no such periodicity was found. One campaign around the Westhinder light vessel with an optical concentration measuring instrument and sampling at different depths in function of time did not reveal this periodicity either.

Gradual increase with depth was frequently but not always encountered at almost every station. This increase can be overshadowed *e.g.* by biological activity, wave action, turbulence and fresh water outflow at river mouths (Scheldt).

It is obvious from the foregoing that efforts to study sediment dynamics should be concentrated on the turbid near coastal area, especially were muddy bottom sediments are encountered.

In the open Southern Bight, sedimentation of mud must be of no importance as this zone is known as exclusively sandy [Stride (1963) and Houbolt (1968)].

3.- Grain size

The real grain size of flocculated material in the sea has already been the subject of one of our reports (*Techn. Rep. 1972, sed. 01*). An equivalent diameter of $\simeq 7\,\mu$ corresponding to a settling velocity of 4×10^{-3} cm/s was proposed. Conventional grain size analysis, applied on suspended sediments gathered by a centrifuge of course cannot give this real grain size distribution. Disintegration of the mass to its original components, floccules, is impossible. Moreover, the complex of clay- and silt-grade inorganic particles and organic matter is destroyed by this kind of analysis.

Because of the tight concentration of this complex, it was extremely difficult to peptize the material to its elementary particles. This is the reason why the results of these first analyses should be handled with utmost care, and no definite conclusions should be drawn from these figures.

Eighteen samples, taken during the first cruise of January 1972 were analyzed. Put into a sand-silt-clay diagram (fig. 5), they can be characterized as silty clays and clayey silts with a minor admixture of sand.

The distribution of the clay-fraction is shown in fig. 6. As these stations were sampled over a period of almost 3 weeks, the arising picture is not an instantaneous one.

The lowest clay content will probably be found in the coastal area. Reworking of silty bottom material can be responsible for this. The highest clay contents were found in a zone off the south of Holland, possibly because of absence of reworking.

Of course, more analysis are needed to draw definite conclusions.

In view of the high suspended matter content of the coastal zone, it is, in absolute figures, the richest in clay.

Dutch authors [*cf*. Favejee (1960)] found constant ratio's in North Sea suspended matter, between the subfractions less than $25\,\mu$. This is most probably due to throughout mixing before flocculation of the fraction less than $25\,\mu$. We think that only material derived from the same source can reveal constant ratio's.
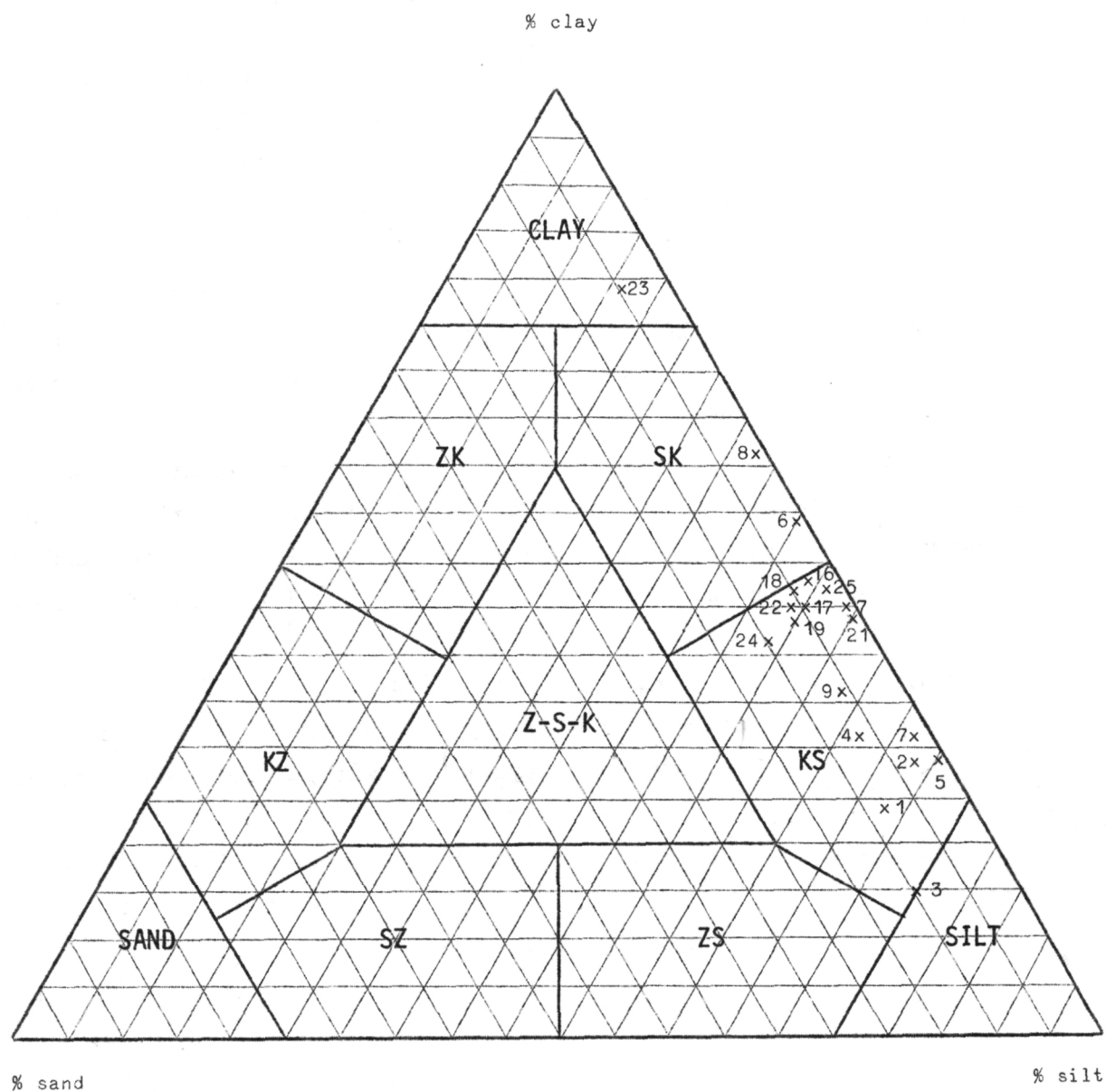
fig. 5.- Sand-Silt-Clay content of suspended matter.
          (Cruise 01/1972).
          K = Clay, Z = Sand, S = Silt.

fig. 6.- Clay content, cruise 01-72.
● Not sampled station.

10-20 %

20-30 %

30 %

fig. 7.- Organic C content, cruise 01-72.
● Not sampled station.

< 2 %

2-3 %

3-4 %

> 4 %
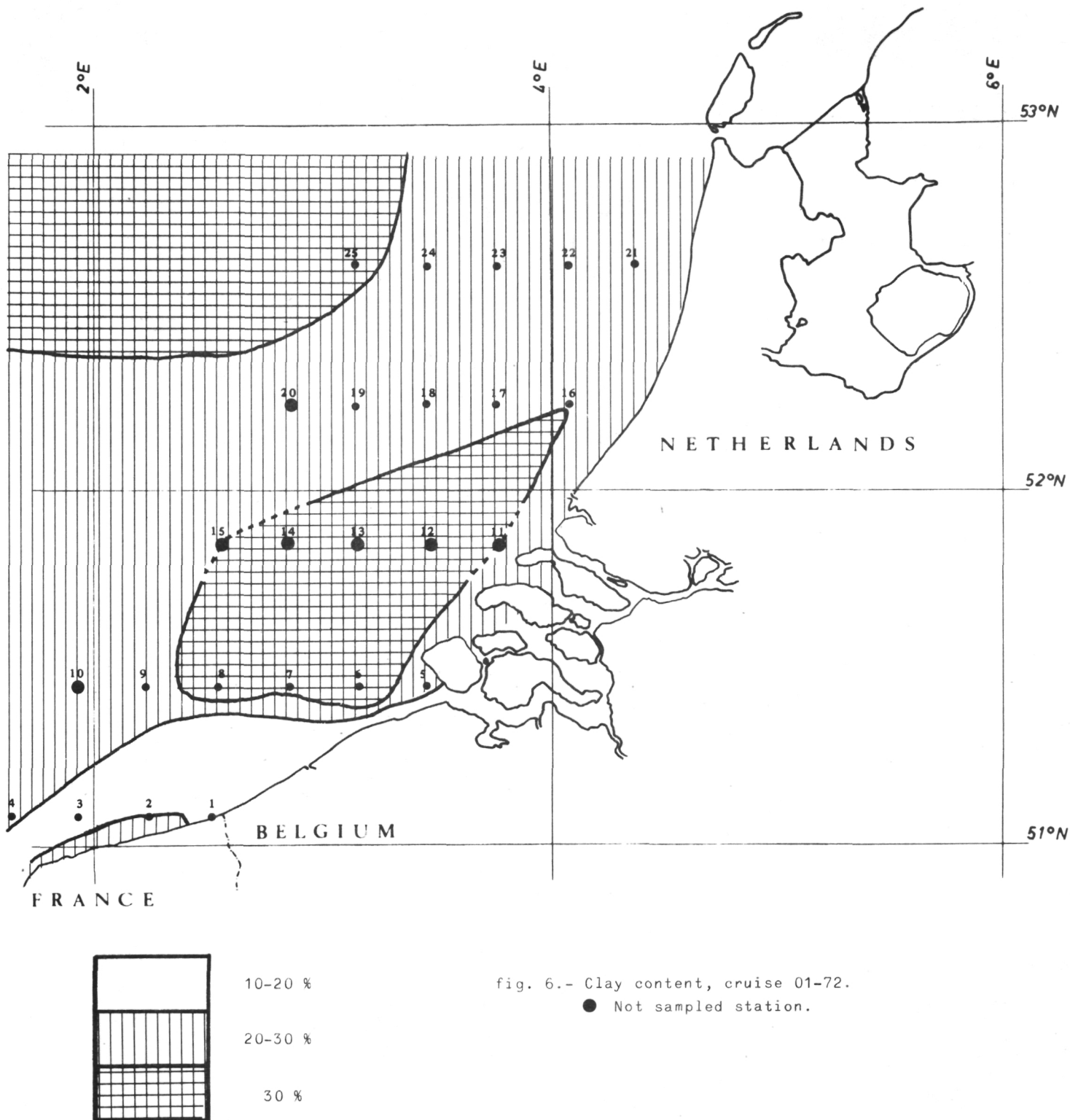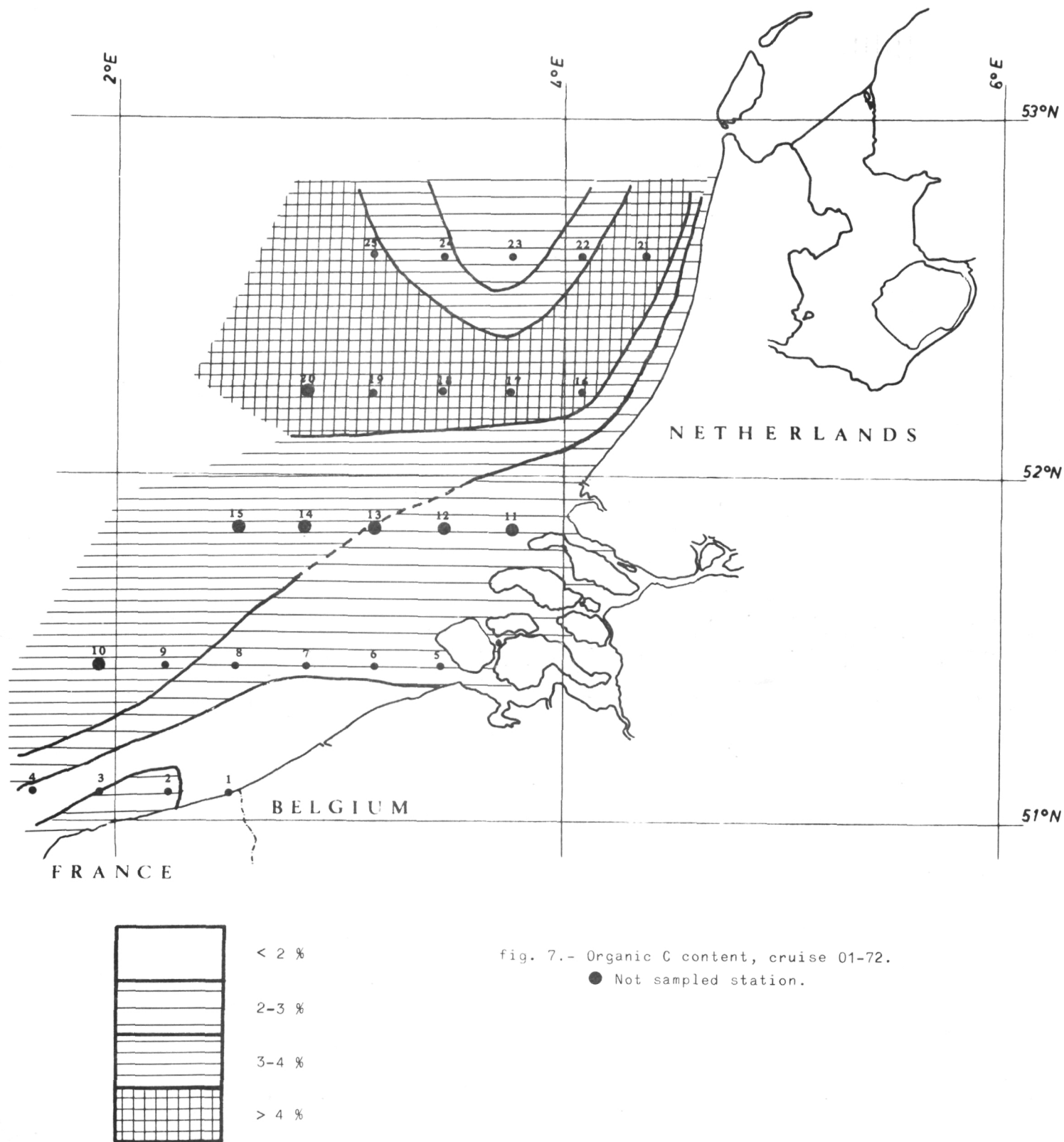
Most probably in consequence of insufficient peptization no such constancy was found by us.

4.- Organic content

The same samples were treated with the Walkeley and Black method in order to determine the organic C content. Results are presented in fig. 7.

Organic C from living organisms undoubtedly interferes with dead organic C in those figures, to what extend however is unknown to us.

The S.E. near coastal part shows a low organic C content, an increase is noted towards the N.W. open sea.

To the open sea, an increase in suspended matter content at the surface is coupled to a decrease in organic C content. On the contrary, this increase when appearing in the near coastal zone rich in suspended matter, brings along an increase in organic C content (fig. 8).

When in the open sea, suspended matter concentration increases, this will usually be due to an increase in the introduction of inorganic material. Nearer to the coast however, such an increase is also due to higher planctonic standing crop and higher productivity, together with dead organisms remaining in or returning to suspension, as to benthonic organisms that are constantly being stirred up [see reports IV of G. Houvenaghel, D. Steyaert and Ch. Van Beveren (1971)].

5.- Carbonate content

Loss of weight was measured after treatment of the samples with 1 N HCl . This loss is mainly due to destruction of carbonates. Calculated percentages of total sample weight are shown in fig. 9.

The highest contents were found in a tongue-like zone extending from north to south, subparallel to the coast.

Up to now we cannot explain this pattern. We only found a loose correlation between carbonate content and clay content and between carbonate content and organic C content.
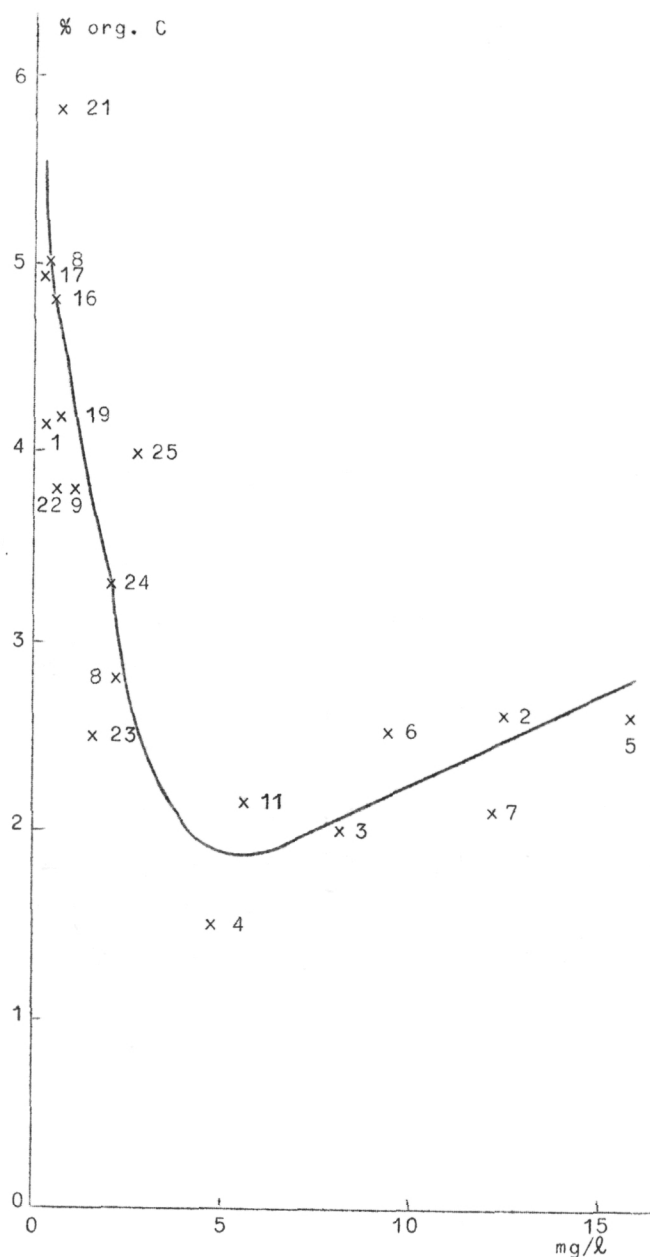
fig. 8.- Organic C as a function of suspended matter content.

Of course, more samples and better analysis of clay-content will be necessary.

In undecalcified suspended matter samples, we found small carbonate rhombohedrons, possibly due to chemical precipitation.

6.- Provenance

Information about the provenance of suspended matter can be gathered through different complementary investigations, e.g.

- mineralogical analysis,
- grain size analysis and calculation of ratios,
- chemical analysis of both the organic and inorganic fractions.

The optical analysis of the light minerals of the fraction less than 32 μ has just started. Calculation of ratios as stated above gave no results up to now.

A number of samples, taken in the Belgian near coastal zone and sent to us by Mr. J. Goovaere from the *Laboratorium voor Morfologie en Systematiek* of Prof. De Coninck at Ghent were analyzed. The ratio : percentage of clay in the fraction less than 62 μ was calculated and interpreted by Prof. F. Gullentops. Significant higher clay contents were found in an area, shown on fig. 10, pointing to a different provenance for this mud, possibly the Straights of Dover.

fig. 9.- Carbonate content, cruise 01-72.
● Not sampled station.

< 25 %

25-30 %
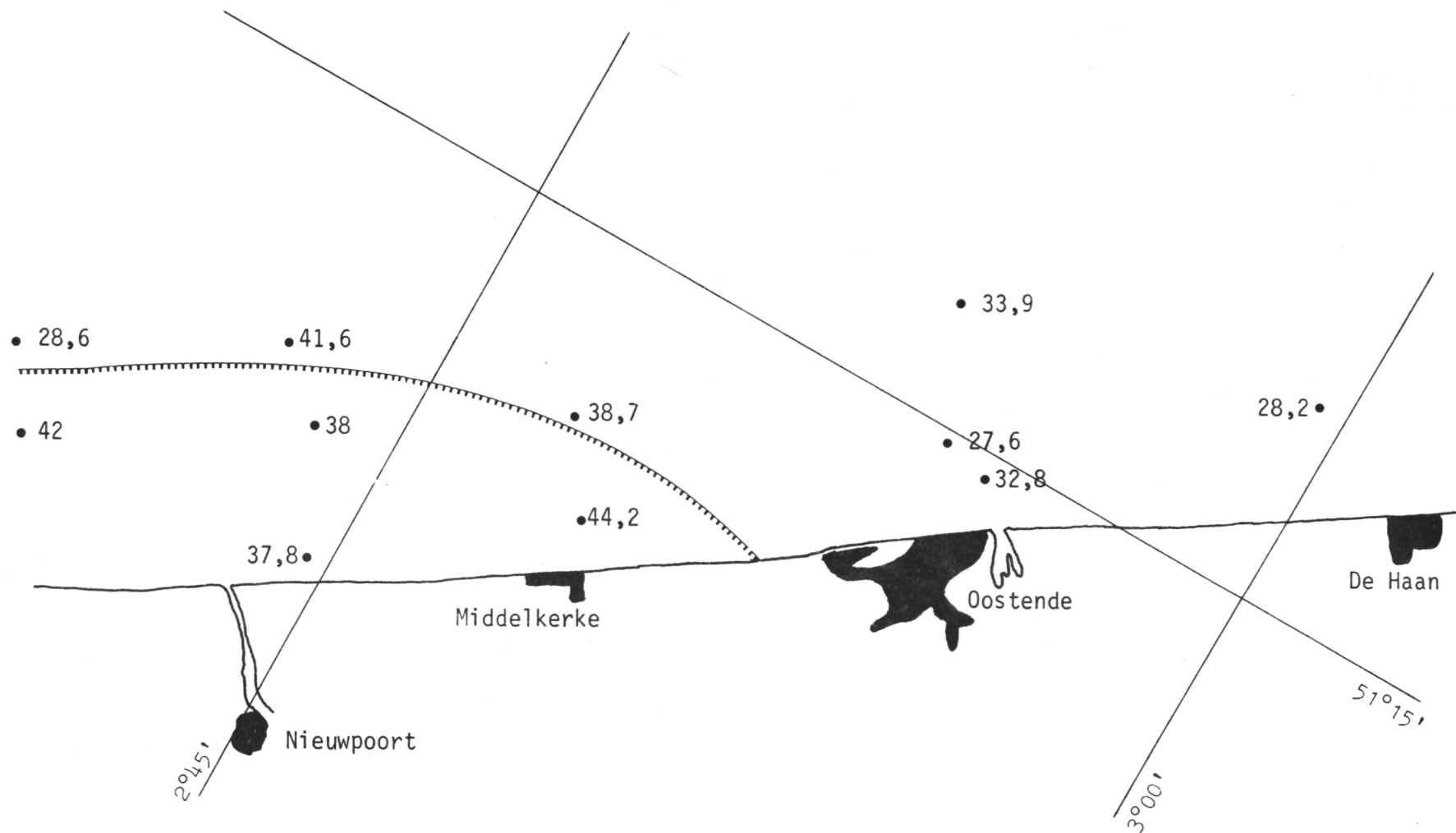
> 30 %

fig. 10.- Clay content of the fraction < 62 μ .

Chemical analyses have not been made yet.

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E.- SORPTION BY SOME NORTH SEA SEDIMENTS

1.- Introduction

The purpose of this job consists in gathering data on the sorption
of specific radioisotopes on natural bed sediments of the Scheldt and the
North Sea. For this will be used, especially the sediments' capacity and
the distribution coefficients of specific ions. The expression of sorption
will be understood here as any reaction between the sediment and the radio-
active solution, which will consequently cover both absorption and adsorp-
tion reactions.

The quantity of a specific radioactive substance that can be accepted
by suspended particles or by sediments does not depend exclusively on the
physical and chemical properties of the ion and of the sediment, but also
on a number of environmental factors. For radionuclides in cation shape,
which occurs most often, the sorption by sediments and the exchange ba-
lances between sediment and water are of great importance.

2.- Processing of sediments

The samples will be dried, for minimum one week, at a maximum tem-
perature of 50 °C . Then they will be finely ground in a mortar. For
part of the sample will be achieved a fractionation of less than 150 μ
by means of dry sifting, and a fractionation of less than 53 μ for
another part. Both fractions will be examined when determining capacity
and distribution coefficients. The sea water will be filtered immediately
upon arrival and again just before used for the tests.

3.- Sediments capacity determinations

The capacity will indicate the sediments potential sorption pro-
perties. Concentrations of 1-0.05 N will be used for capacity determi-
nations, depending on the method applied.

Process method
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Approximately 0.2 g of sediment will be weighed in a test tube. Excess ions present will be eliminated by rinsing with demineralized water. For this purpose will be added approximately 5 mℓ of water, the test tube will be thoroughly shaken during approximately ten minutes and then centrifuged. Pour off the clear supernatant liquid. This will be repeated until the rinsing water is free of chloride. Now will be added the CsCl solution (5 mℓ 1 N) previously marked with Cs^{137}. After thorough mixing, the test tube will be shaken during minimum four hours. Then centrifuge and pour off the supernatant liquid. This will be repeated another two times. Take care that minimum twenty times the capacity of the sample will be present in the solution.

Excess CsCl in the sample will be rinsed off with 10 mℓ shares of 95 % ethanol. Shake and centrifuge until the discarded ethanol is free of chloride.

Wash outer edge of the test tube with dilute HCl and rinse in demineralized water.

After drying, the test tube will be analyzed in NaI scintillation counter with well crystal. The initial solution too will be measured in the same crystal and with the same metering arrangement.

Capacity will be expressed in milliequivalents per gram :

$$Q = \frac{\text{sample : counts per minute and per gram}}{\text{solution : counts per minute and per meq.}}$$

Capacities will be determined with regard to CsCl 1 N and $Co(NO_3)_2$ 0.05 N . Use fractionation less than 150 µ of the sample for one, and fractionation less than 53 µ for the other operation.

4.- Cation exchange capacity

4.1.- In 0.05 N Co + Co^{60}
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Fraction < 150 μ

Sample	Capacity meq/g
5	0.21
1007	0.28
1021	0.031
1034	0.14
1035	0.024
1050	0.32
1065	0.22
1096	0.18

Fraction < 53 μ

Sample	Capacity meq/g
1034	0.25
1007	0.32
1065	0.26
1215	0.25

4.2.- In 1 N Cs + Cs^{137}

Fraction < 150 μ

Sample	Capacity meq/g
1097	0.32
1098	0.30
1100	0.085
1113	0.24
1114	0.22
1131	0.24

5.- Determination of distribution coefficient K_d

The distribution coefficient shows the ratio at equilibrium of the concentration in the solid phase and that in the fluid phase :

$$K_d = \frac{\text{Conc. in sediment}}{\text{Conc. in solution}} = \frac{C_o - C_e}{C_e}$$

where C_e is the equilibrium concentration in solution and C_o the concentration at the beginning in the solution. For the exchange of monovalent cations we may write :

$$M\text{-sediment} + Cs^+ \rightleftharpoons M^+ + Cs\text{-sediment}$$
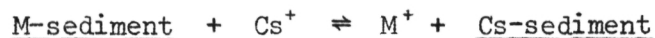
The equilibrium constant will then be :

$$K_M^{Cs} = \frac{[M^+] [Cs - sed]}{[M - sed] [Cs^+]} = \frac{K_d - Cs}{K_d - M} \ .$$

In sea water and river water, various other types of ions will be present in excess and their concentrations at the sediments exchange locations are generally unknown. For radionuclides in tracer quantities, however, the fraction of exchangeable locations they occupy will be extremely small. Consequently, we may consider, in the comparison here-above, $[M^+]$ and $[M - sed]$ as constants and we may write :

$$K_M'^{Cs} = \frac{[Cs - sed]}{[Cs^+]} = K_d - Cs$$

and this only if cesium is present in tracer quantities. In this case, the distribution coefficient will describe the equilibrium. This, however, will apply only for this specific sediment in water with this specific composition.

Process method

- Dependence of K_d on the sediment concentration. An increasing quantity of sediment will be shaken in sea water marked with Cs^{137}. For this we use small containers of 25 ml with 20 ml of sea water. After a certain time of shaking, the solution will be centrifuged or left to settle for an entire night. Part of the supernatant liquid (1-5 ml) will be pipetted off and measured. After the measuring, it will be poured back into the original solution and the shaking will be re-peated. This will be repeated until the value of K_d remains constant; it may be generally expected to occur after about seven days.

$$K_d = (\frac{\text{initial activity in the solution}}{\text{final activity in the solution}} - I) \times \frac{V}{g}$$

$$K_d \times C_e = Q .$$

- Dependence of K_d of the sediment concentration for solutions in demineralized water. Same process method as here-above but now not in sea water.

- Determination of K_d values in sea water for sediments. A fixed quantity (0.1 g) will be shaken with 20 ml of sea water with added tracer. Same process method as for determinations here-above.

- Influence of foreign ions on K_d values in demineralized water. High salt concentrations in sea water will reduce the K_d values

obtained to a large extent. Which ions will compete most strongly with cesium ? This will be investigated by similar tests with demineralized water and changing concentrations of Na , K and Ca .

Cs^{137} sorption at various sediment concentrations in distilled water
S D I   20/03/72   18 h 30 - 19 h 30

Sediment 0.1 mg	% Activity sorbed	K_d 10^3
122	93.5	23.4
240	96.6	23.5
314	96.9	19.8
393	97.4	18.9
594	97.9	15.6
622	98.0	15.3
853	98.1	12.2
1165	98.2	9.36
1550	98.4	7.55
2008	98.3	4.97
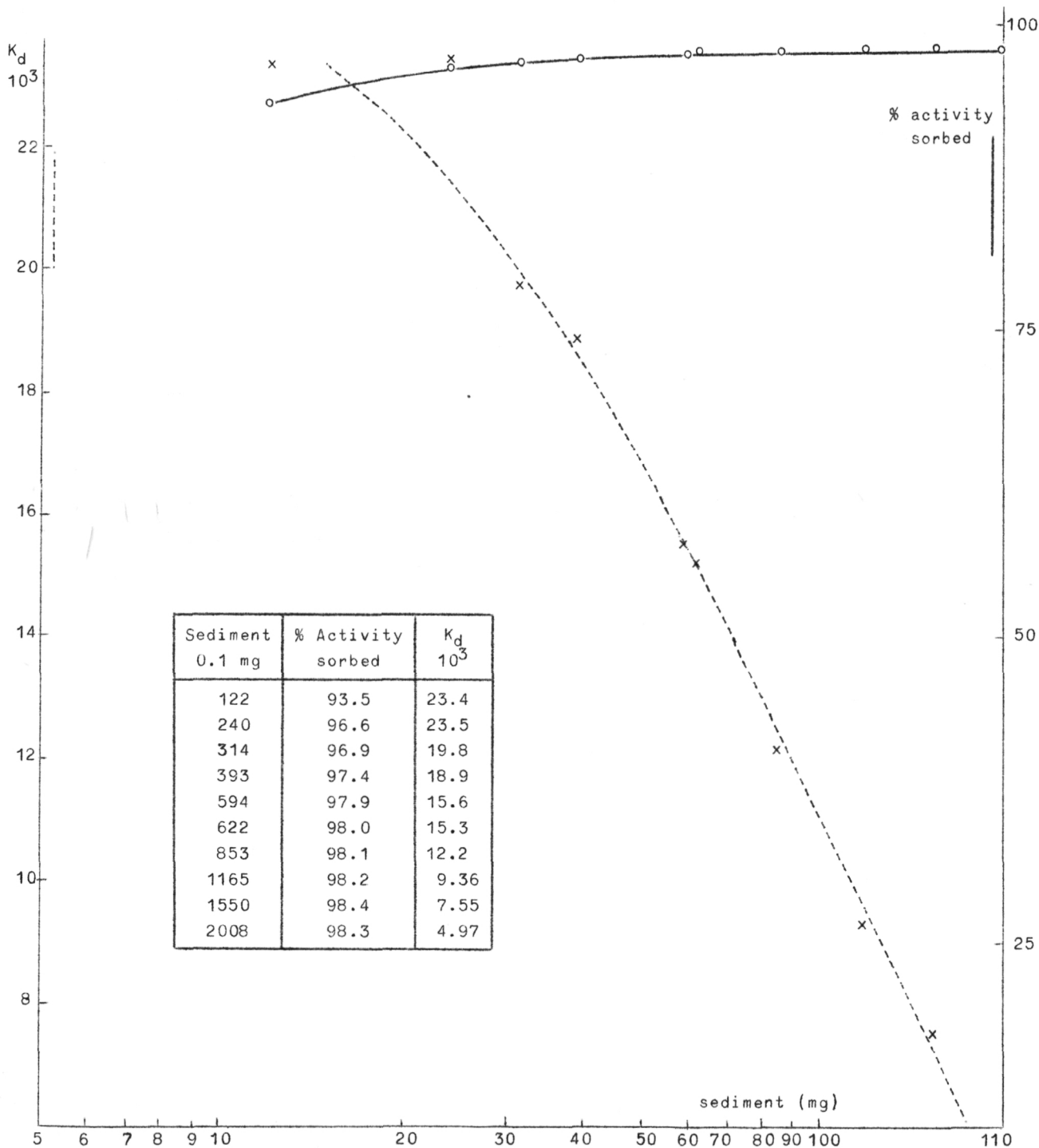
Cs^{137} sorption at various sediment concentrations in sea water
M 1097   < 53 μ

Sediment 0.1 mg	% Activity sorbed	K_d
24	15.3	819
36	15.0	524
114	28.5	512
249	43.9	503
734	68.3	498
980	74.3	504
1250	78.8	513
2013	87.1	517
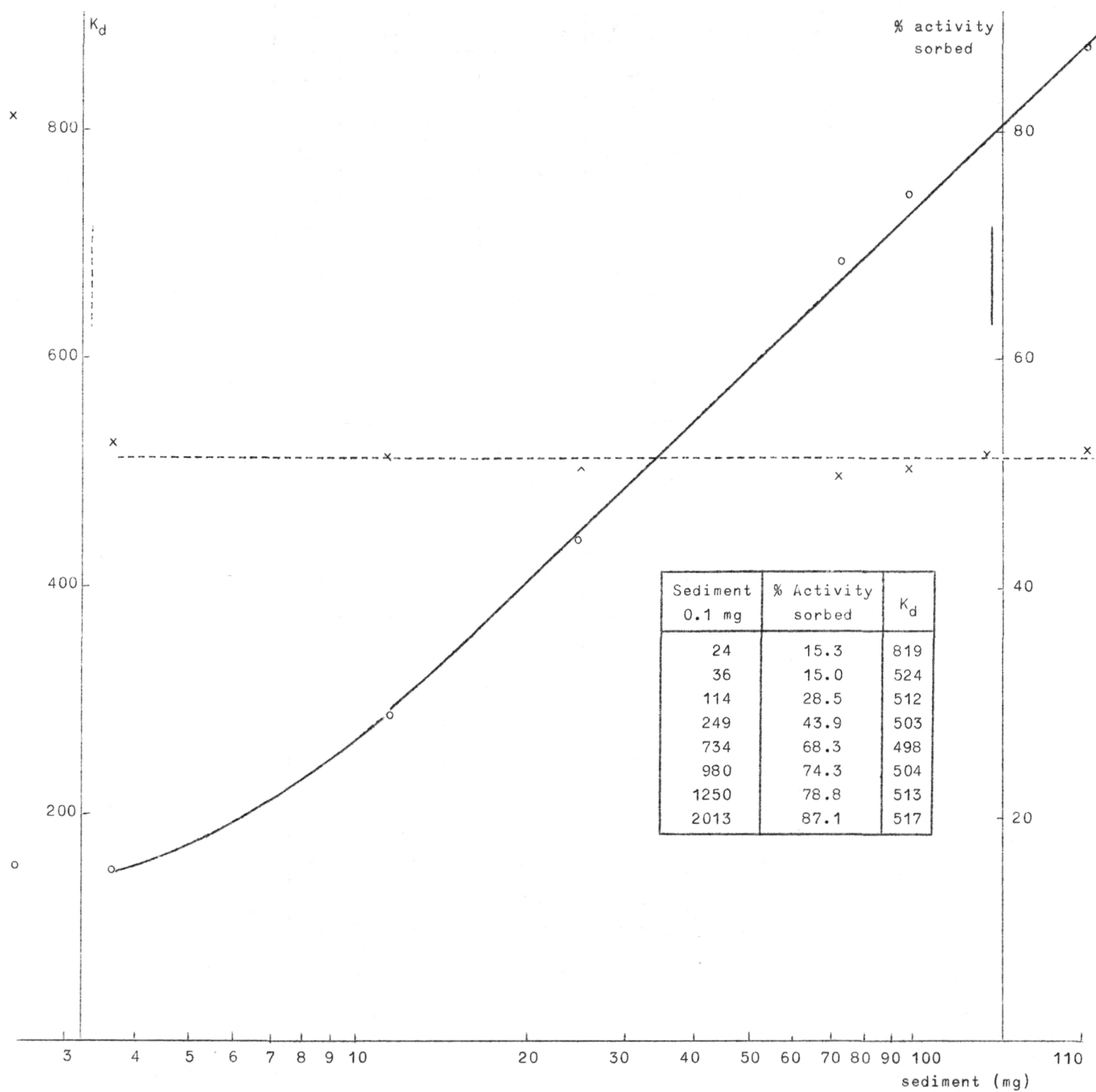
Per cent cesium sorption and associate K_d values

Sample < 150 μ	% Activity sorbed	K_d	Sample < 150 μ	% Activity sorbed	K_d
5	60.3	300	1133	41.5	140
1007	67.3	400	1149	77.7	690
1021	13.7	30	1151	75.0	580
1034	41.9	140	1153	69.0	430
1035	15.6	36	1172	46.6	180
1050	71.9	500	1194	53.2	220
1065	72.4	510	1196	67.5	400
1096	62.3	320	1211	62.6	330
1097	69.4	450	1215	77.4	690
1098	71.4	490	1251	40.1	130
1100	31.7	93	1283	61.9	320
1113	65.2	360	1284	22.2	54
1114	46.7	180	1344	35.5	100
1131	60.7	300	1635	71.8	500

Cs^{137} sorption at various competing cation concentrations
M 1050 < 53 μ

Na^+ meq/ℓ	$\dfrac{K_d}{K_{d_o}}$ %	K^+ meq/ℓ	$\dfrac{K_d}{K_{d_o}}$ %	Ca^{++} meq/ℓ	$\dfrac{K_d}{K_{d_o}}$ %
0	100	0	100	0	100
0.44	90	0.26	89	1.0	98
2.2	85	1.3	56	3.0	87
4.4	80	2.6	43	5.0	83
22	50	13	13	25	63
44	35	26	7.3	50	59
218	15	128	1.4	250	35
435	9	256	0.07	500	26

Cs^{137} sorption versus competing cation concentration
M 1050   < 53 μ
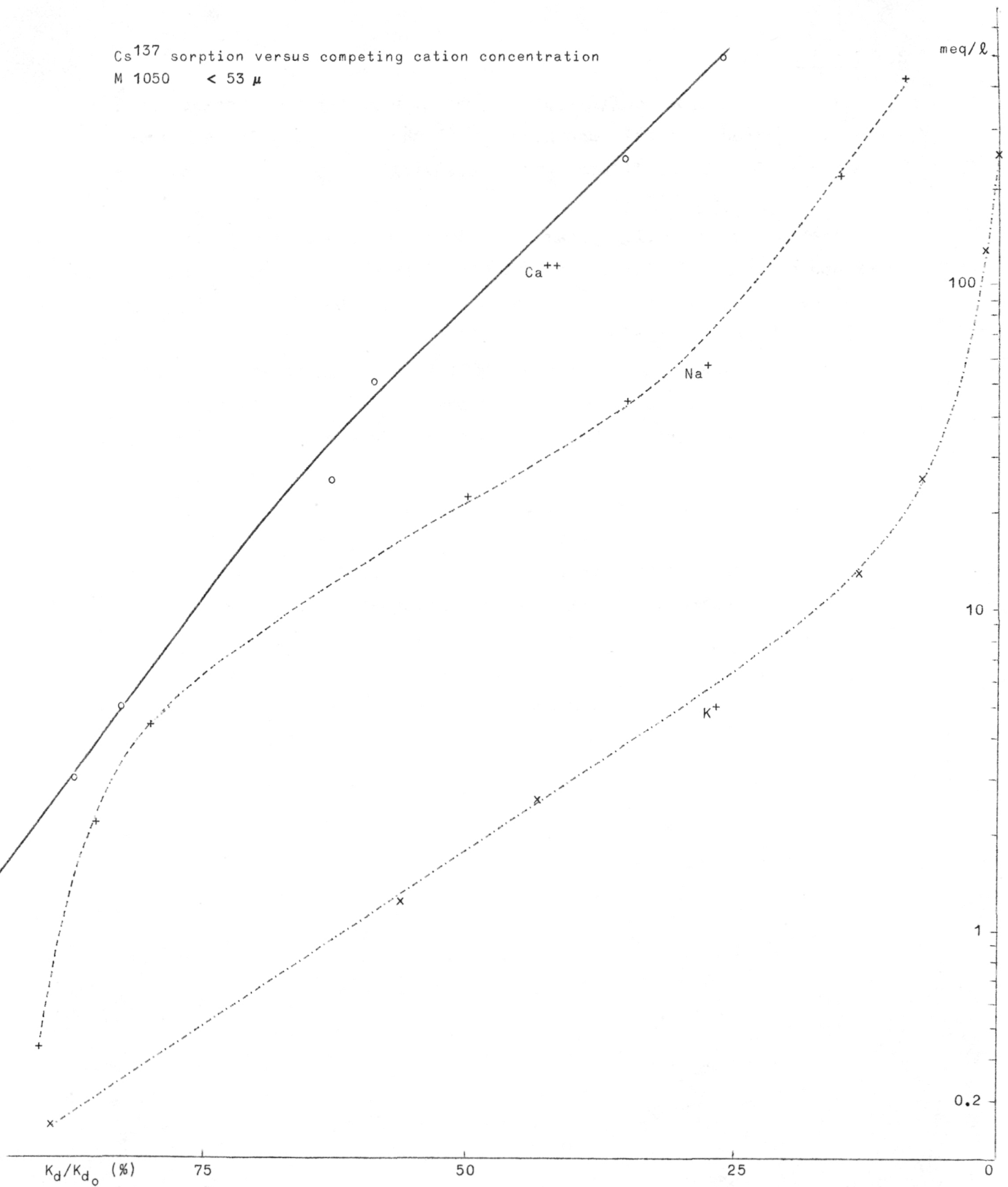
6.- Conclusions

The distribution coefficient for cesium will remain constant for a heavily varying sediment concentration in the sea water. In demineralized water, the K_d will rise with decreasing concentration of the sediment.

The K_d values will be maximum 830 for silty sediments in sea water and minimum 30 for sediments. The difference between fractionations less than 53 μ and less than 150 μ will be often strongly pronounced and depend on the granulometry of the sediment.

The capacities will be high for silt-rich sediments and low for sandy samples. The finer sand fractions may, however, contribute for a not insignificant share to the sediment's total capacity. For comparison's sake, we show the following values for quartz :

$$2-62 \text{ μ} : 0.006 \text{ meq/g} ,$$
$$< 2 \text{ μ} : 0.05 \text{ meq/g} .$$

The influence by foreign ions on the sorption of cesium. Particularly, K^+ will exert a heavily checking influence on the sorption of cesium. Since sea water comprises approximately 10,600 ppm of Na , 400 ppm of Ca and 380 ppm of K , these elements will certainly play an important part in preventing cesium sorption in sea water by sediments.