Mud transport studies using manganese as an accompanying element under temperate and tropical climatic conditions (Western Europe, Amazon area and Chao-Phya river area in Thailand)

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In many parts of the world the problems of origin and transport of alluvial sediments from the rivers to their delta areas and the adjacent coastal areas are very important. Geologists are interested in these problems in connexion with the genesis of soils derived from these sediments. Civil engineers build constructions to avoid siltation of channels to harbours and the harbours themselves. A detailed knowledge of the direction of movement of the sediments is necessary in this respect. Finally, the land reclamation expert needs information about quantities and texture of sediments he tries to gain in coastal areas for empoldering new land.

Sediments may consist of coarse- (sand) and fine-grained fractions. The method described in this paper is only appropriate for studying the origin and transport of fine-grained sediments. The transport of mud (fine-grained fraction < 16 microns) is investigated by the use of manganese as an accompanying element. The deposits from different rivers and locally from the sea bottom are distinguished by different Mn content.

METHODS OF INVESTIGATION

A main division of the Mn compounds in a sediment can be made into exchangeable Mn and higher oxides.

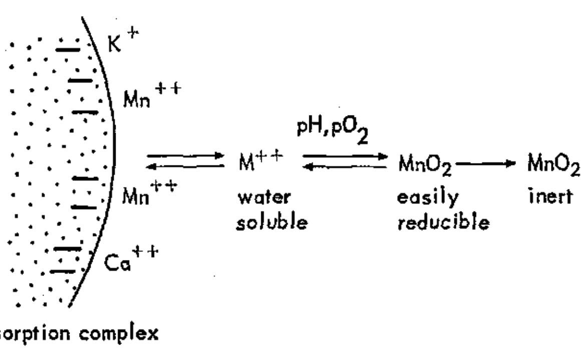

FIG. 1. Conversions between inorganic forms of manganese in a sediment.

The exchangeable Mn is bound as manganous ions to the adsorption complex (clay minerals and organic colloids) of the sediment and is the most mobile form apart from small amounts of Mn in the enclosed water. The higher oxides form a sequence of compounds with varying reactivity. They can be distinguished by their oxidizing power.

The conversions between the Mn forms are schematized in Figure 1.

The redox equilibrium between the mobile forms of Mn and easily reducible Mn is controlled by the pH and the oxygen concentration in the sediment.

The oxidation of bivalent Mn, as indicated in Figure 1, can take place by purely chemical processes, at pH values above 4.9, whereas microbiological oxidation may occur at pH values ranging from 4.8 to 8.9.

During transport in aerated river or sea water the mud cannot lose Mn, because the latter is almost exclusively present as insoluble higher oxides. Most of it is present in the grain-size fractions 0-35 microns. In connexion with this preferred occurrence in the fine fractions, a linear relationship is found between the contents of Mn (both total and reducible Mn) and the fraction < 16 microns (as a percentage of the $CaCO_3$-free mineral constituents), if the origin of the sediments is the same.

In Figure 2 these relationships are demonstrated for freshly deposited sediments of the River Ems and for sediments of the Flemish banks, the latter being mud deposits on the bottom of the North Sea before the shore of Belgium and the south-western Netherlands. The relationships between the Mn content and the fraction < 16 microns are extrapolated to 100 per cent of the fraction < 16 microns. An Ems deposit containing 35 per cent of the fraction < 16 microns, corresponds to the amount CE (= DF) of Mn in the fraction < 16 microns and the amount EF in the sand (fraction > 16 microns). Commonly the Mn composition of the fine fraction is represented by the line OA^1. The extrapolated Mn content is represented by O^1A^1.

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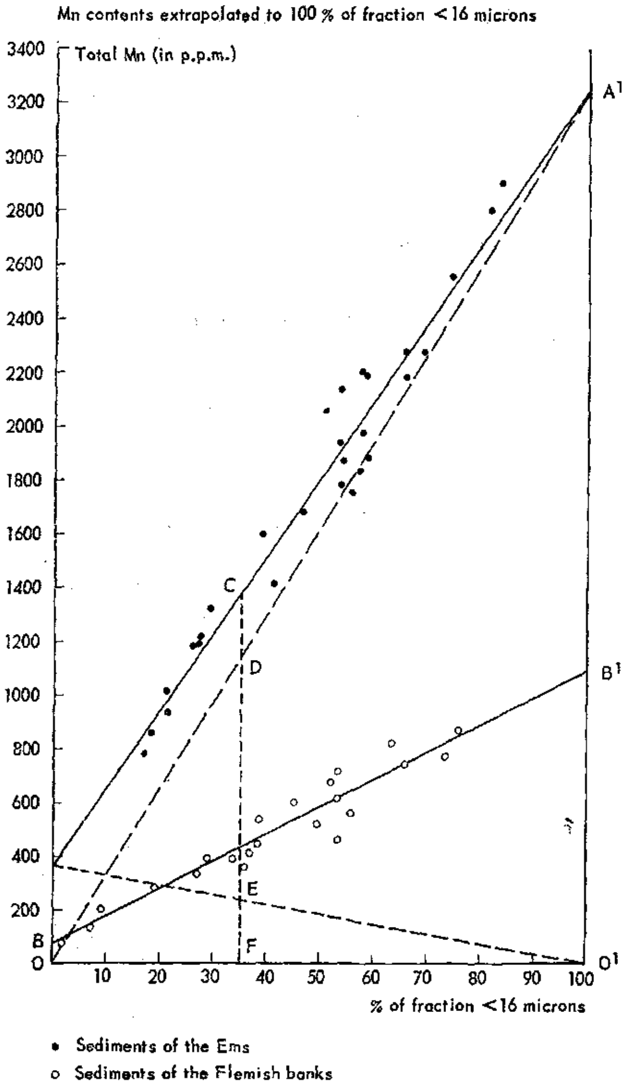

FIG. 2. Linear relationship between manganese content and percentage of fraction < 16 microns.

For mutual comparison of different kinds of mud the contents O^1A^1 are now used. Single values to characterize whole groups of CO-genetic sediments with different granulometric compositions are thus obtained.

The coefficients of the regression equation

$$y_l = \bar{a}x + \bar{b},$$

representing the relationship between the Mn content and the fraction < 16 microns, are computed as follows:

$$\bar{a} = \frac{n\Sigma xy - \Sigma x \Sigma y}{n\Sigma x^2 - (\Sigma x)^2} \qquad \bar{b} = \frac{1}{n}(\Sigma y - \bar{a}\Sigma x)$$

where n represents the number of analysed samples; x and y are, respectively, the contents of the fraction < 16 microns and the Mn contents of the samples concerned. Now the extrapolated Mn content O^1A^1 ($y_{l\,100}$) is derived from the regression equation by substitution of the value $x = 100$.

After deposition, reduction can take place, to a smaller or larger extent depending on the redox potential of the environment. At the moment of deposition of the sediment the redox potential is high, generally about 400 mV. If sedimentation occurs in stages on a low-lying surface such as the sea bottom or the lower parts of artificial settling beds (artificial systems of banks of brushwood and channels ensuring sedimentation) microbial attack of the sediment gives rise to a lowering of the redox potential (down to − 100 mV). Consequently the higher Mn oxides are reduced to the exchangeable form. Depending on the salt content of the surrounding water the Mn^{2+} ions can be more or less exchanged by the dissolved salt ions, leading to a lower Mn content of the sediment. However, in freshwater environments the Mn content decreases very slowly. Table 1 clearly demonstrates the contents of exchangeable Mn, calculated per 100 per cent of the fraction < 16 microns, of reduced sediments in relation to the salt content of the water.

TABLE 1. Contents of exchangeable Mn, calculated per 100 per cent of the fraction < 16 microns, of reduced sediments dependent on the salt content of the water

Locality	Exchangeable Mn (p.p.m.)	Cl (‰)
Settling beds, Uithuizerwadpolder	106	16
Submerged land of Saaftinge	407	8
Settling beds, Haringvliet	528	2
Sub-layers, eastern Biesbosch	618	0
Top layers, eastern Biesbosch	748	0

When mud is deposited on more elevated parts (higher than low-tide level) such as river forelands, reed marshes, willow coppices and marine forelands, no reduction of the deposits takes place. In consequence the sediments do not show an appreciable loss of Mn.

Irrespective of any loss of Mn, the relationship between Mn contents and percentages of the fraction < 16 microns remains approximately linear, so that the characteristic values (for 100 per cent of the fraction < 16 microns) can still be determined in the same way as for freshly deposited material.

ANALYTICAL METHODS

Total Mn

The amounts of total Mn are determined according to Kurmies (1953) by treating the air-dry sediment with NH_4NO_3, dissolving the ash in HNO_3, oxidation of the Mn to $HMnO_4$ and finally by measuring the colour in a spectrophotometer at 525 nm.

The above-mentioned method is rather elaborate. Recently a series of analyses were carried out with the

Philips Automatic X-Ray spectrometer. The sediments could be pressed to tablets with a pressure of 200 kg. per cm.[2] without further preparation. The tablets were analysed with a LiF crystal rotating in air. The total time for analysis of a sample is 240 seconds with an accuracy of 1-2 per cent.

$CaCO_3$

The fraction < 16 microns is expressed as a percentage of the $CaCO_3$-free mineral constituents, hence the content of $CaCO_3$ must be estimated. The content is determined according to the Scheibler method modified by Bruin (1937). The air-dry sediment is shaken with diluted hydrochloric acid (about 8 per cent), measuring the volume of the evolving CO_2 in comparison with the volumes of CO_2 liberated from a sequence of known amounts of pure $CaCO_3$.

Organic matter

Expressing the fraction < 16 microns as a percentage of the mineral $CaCO_3$-free constituents, the content of organic matter must also be estimated. The analyses are carried out according to Mebius (1960). The organic matter is oxidized by a solution of $K_2Cr_2O_7$, the excess $K_2Cr_2O_7$ titrated back with a solution of Mohr's salt, using N-phenylanthranilic acid as an indicator.

Redox potential

The redox potential is an important factor to distinguish recent sediments from older ones, the recent deposits with high redox potentials being most useful for studying the mud transport problems. The potential is measured in a suspension of the sediment under nitrogen atmosphere, using a platinum and a calomel-electrode. The details of the method have been described by the author (De Groot, 1963).

Fraction < 16 microns

The contents of the fraction < 16 microns are determined with the pipette method according to Hooghoudt (1945).

GENERAL RESULTS IN WESTERN EUROPE

There are distinct differences in the Mn contents of the different sources of mud along the coasts of England, Belgium, the Netherlands and Western Germany. If the Mn content of the fine-grained sediments of the River Thames is taken as 1, the mud entering the North Sea through the Straits of Dover contains twice the amount, the rivers Scheldt, Meuse and Rhine 4 times, the River Ems 5 ½ times and the River Elbe even 7 times the amount of Mn of the River Thames (Fig. 3). Very low Mn contents (one-third) are found in the old alluvial clay layers on the sea bottom off the coast of Schleswig Holstein, resulting from the reduction of the sediments

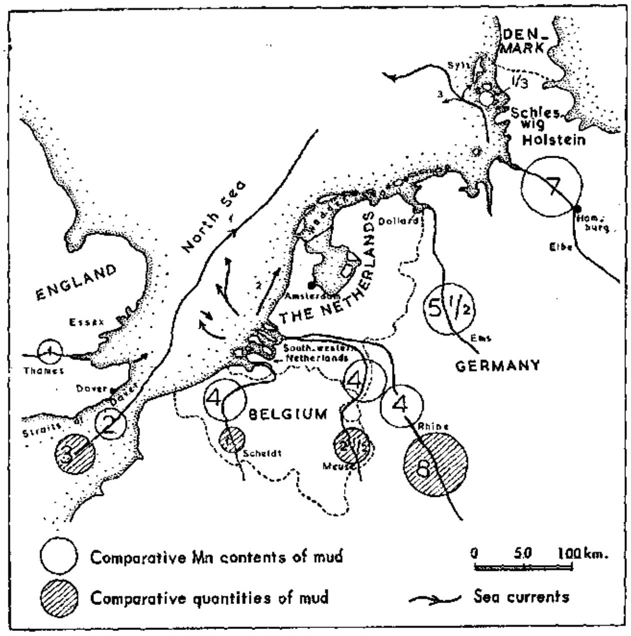

FIG. 3. Sources of mud and water movements in the North Sea area.

and exchange of the Mn^{2+} ions by the salt ions of the sea-water which has been going on for many centuries already.

By examining several thousands of samples from the above-mentioned area, a detailed insight was obtained into the origin and transport of mud from the rivers and locally from the sea and shallow floor to the areas outside the dikes along the various coasts. The great differences in contents of Mn in the deposits examined were very helpful in this respect.

Apart from one detail, only a few main details as regards these investigations will be given in this paper. For full details the reader is referred to the author's papers (De Groot, 1963, 1964).

Sedimentation along the continental coast is not effected by the mud of the River Thames. This is obvious, for example, from the fact that water from the Thames is separated from the water along the coast of the continent by the ocean water penetrating via the Straits of Dover (sea current 1 in Fig. 3). Therefore, the distribution of mud from the Thames is restricted to the Essex coast in England.

The supply of mud to the south-western Netherlands occurs both from the south (via the Straits of Dover) and from the River Scheldt.

The Meuse and the Rhine transport their fine-grained sediments (mainly originating from the Rhine) in a northerly direction into the western part of the Dutch Wadden Sea (sea current 2 in Fig. 3). The mud is partly deposited temporarily in the western Wadden Sea (with partial loss of its Mn content as a consequence of reduction and exchange), from where it is further transported in an easterly direction over the Wadden Sea flats, and partly enters into the Ems-Dollard estuary.

The mud transported by the River Ems is deposited in a limited area of the Dollard, as will be further outlined in the next section.

The Elbe mud is carried by the sea currents (3 in Fig. 3) in a north-westerly direction and has primarily only a limited influence on the sedimentation along the western shore of Schleswig Holstein. Thus in the middle of this coast the Elbe mud, containing more Mn than any other mud investigated, is mixed to a considerable extent with the old alluvial clay (very low Mn contents) off the coast. Farther to the north the sea current branches off towards the southern point of the island of Sylt in a north-easterly direction (see Fig. 3), giving rise to a more important influence of the River Elbe on the sedimentation with high Mn contents just south of the Danish frontier.

DETAIL OF THE INVESTIGATIONS IN WESTERN EUROPE

A detail is given here from the investigations along the continental coast, especially relating to the River Ems. The Dollard area, being a part of the estuary of the Ems (Fig. 4), receives fine-grained sediments from the Dutch Wadden Sea, originating from the Rhine and Meuse, and from the Ems. As described in the preceding section, the Mn content of the Ems mud is higher than the contents of the Rhine and Meuse material. Moreover the Rhine and Meuse material entering the Dollard lost part of its Mn during temporary sedimentation in the Dutch Wadden Sea. In Figure 4 the Rhine and Meuse material enters the Dollard area by tidal currents from the left side, the Ems sediments coming from the right.

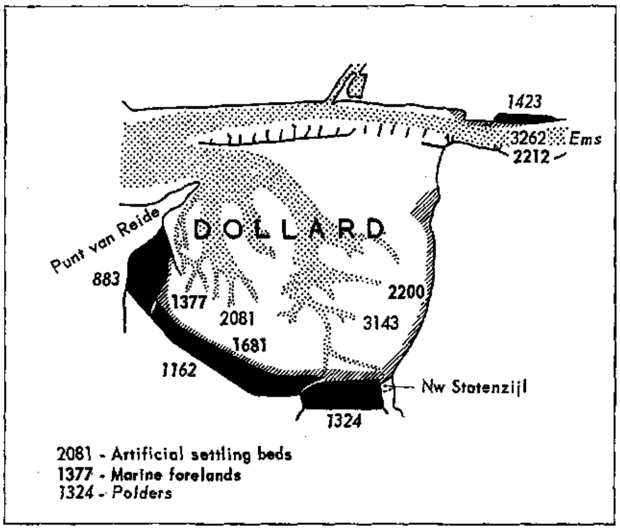

FIG. 4. Influence of the Ems on sedimentation in the Dollard.

In this figure the Mn contents relative to the fraction < 16 microns (= 100 per cent) are given of freshly deposited sediments on the artificial settling beds, the contents of marine forelands and of the polders embanked from forelands. Passing along the Ems and farther along the Dollard from the Ems mouth via Nieuw Statenzijl to the Punt van Reide, the high Mn contents of the original Ems muds decrease constantly in the muds, marine forelands and polders. In this way the significance of the Ems in the sedimentation of the Dollard is clearly shown.

The marine forelands have lower Mn contents than the freshly deposited muds, because the forelands are partly composed of reduced material eroded from deeper layers of the artificial settling beds. The polders lost part of their Mn after embankment from the marine forelands.

RESULTS IN TROPICAL AREAS

River Amazon, South America

In recent times more serious attention has been paid to the origin of the fine-grained sediments deposited along the Guiana coast in South America. The general opinion is that these sediments are carried to the sea by the Amazon and transported by the Caribbean sea current to the Guiana coast (Fig. 5).

Bakker (1963), however, believes that the sediments in the shallow area of Guiana are partly of a more eastern origin. He bases his conclusion on the fact that the mineral compositions of the Amazon sediments (kaolinite and halloysite) and the shallow deposits (illite, montmorillonite and kaolinite) off the Guiana coast differ. The illite and montmorillonite of the recent coastal sediments of Guiana would at least partly come from the western coast of Africa. The sea

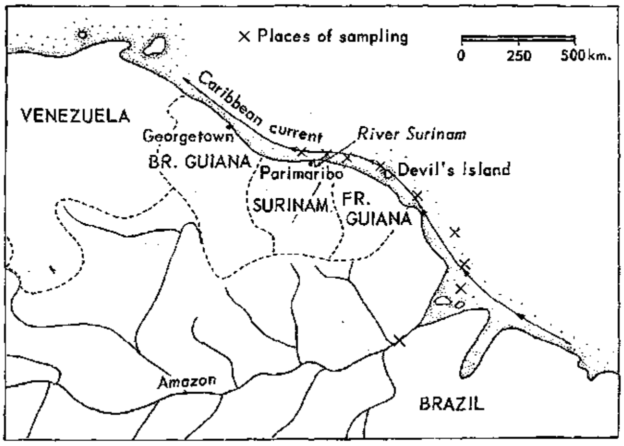

FIG. 5. Sampling area of Amazon sediments.

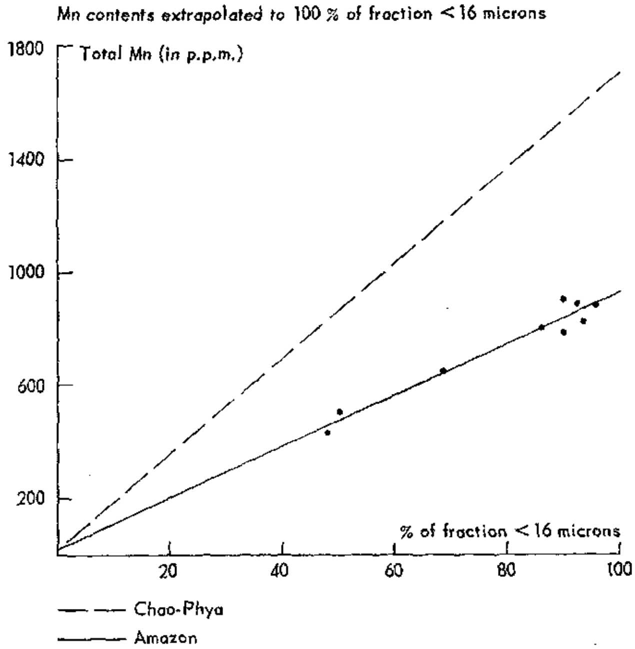

FIG. 6. Manganese content of sediments of the Amazon area.

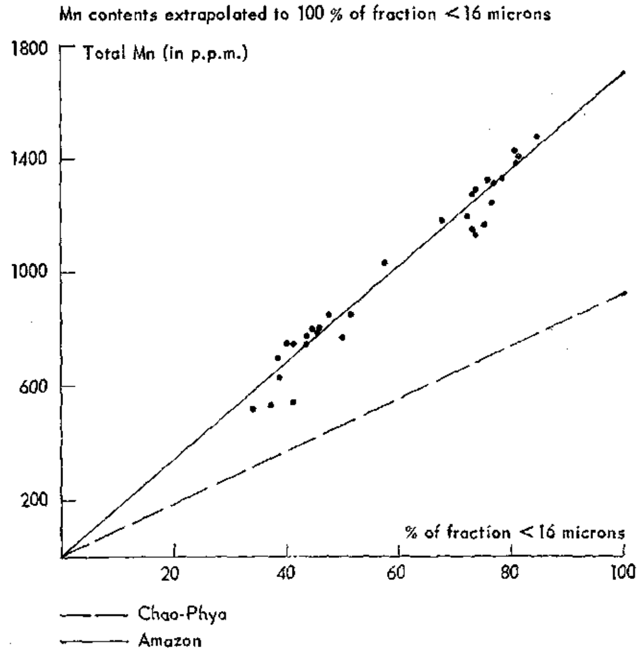

FIG. 7. Manganese content of sediments from the Chao-Phya.

currents of the Atlantic Ocean would be responsible for the transport to the Guiana coast.

In collaboration with L. J. Pons (at present with the Department of Soil Survey in Paramaribo), a very limited investigation has been carried out in the Amazon area. A set of samples has been taken from the River Surinam via Devil's Island into the estuary of the Amazon, as indicated in Figure 5. The Mn contents of these samples have been plotted against the fraction < 16 microns in Figure 6. There is a linear correlation between the dots, having its beginning in the origin of the graph, pointing to a uniform composition of the sediments examined. Taking into account the small amount of samples, no clearer indication could have been obtained for a direct transport of Amazon mud to the coast of Guiana.

The investigations in the Amazon area will be amplified by the examination of the mineralogical composition of the sediments and with analyses of sediments of the interior of the Amazon area.

River Chao-Phya, Thailand

Instructed by the Thailand office of the Netherlands Engineering Consultants (NEDECO), investigations are in progress in which the Mn method is used for studying the movement of mud from the Chao-Phya to the bar of the river in the Bay of Thailand and vice versa. These investigations are carried out in connexion with siltation problems of the harbour of Bangkok. It is impossible, however, to give full details of these investigations in this paper, because a report to the Thailand authorities has not yet been made available. Only the principles of the investigations will be given here.

The Mn contents of the fine-grained sediments deposited by the Chao-Phya are given in Figure 7. Here again a linear relationship exists between Mn contents and percentages of fine-grained fractions. In the same figure the line for the Amazon deposits has been given, just as the Chao-Phya line has been plotted in Figure 6. The Mn contents of the Amazon and of the Chao-Phya are not very high compared with the contents of European rivers.

The mud load of the Chao-Phya depends greatly on the time of the year, as may be seen from Figure 8. During certain months there is even a reverse movement of mud from the bar to the river.

To get an insight into the movements of mud from the river mouth to the bar, over the bar and from the

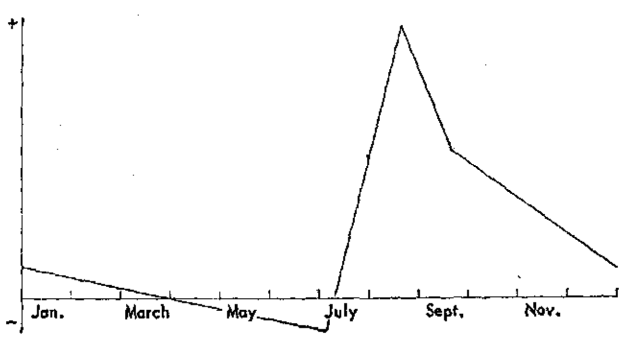

FIG. 8. Mud discharge of the Chao-Phya.

bar to the river, samples have been taken periodically from a network of sites. A simplified example of the results of the Mn analyses in a series of samples at a certain time has been given in Figure 9.

The Mn contents in this figure are relative amounts, expressed as percentages of the Mn contents of fresh mud deposited by the river (at equal contents of the fraction < 16 microns).

In this way a survey is obtained from the freshness of the mud in different places on the bar. A lower Mn content points to less recent sedimentation or to sedimentation material eroded at an earlier date. By making several of these Mn maps in the course of a year and comparing them with each other, conclusions can be drawn concerning the movement and sedimentation of mud on the bar and in the river-mouth area.

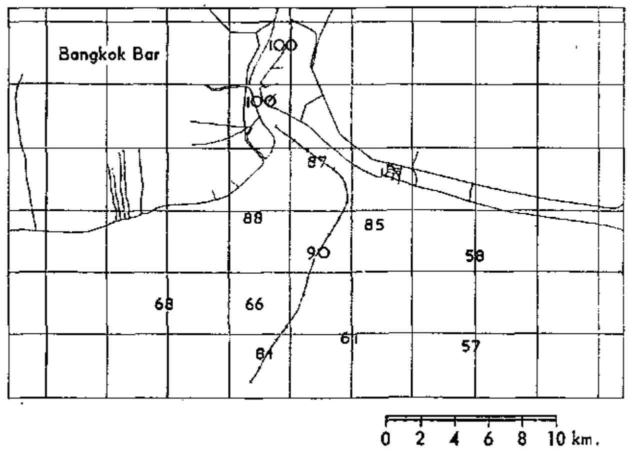

FIG. 9. Relative manganese content of sediments from the Bangkok bar.

Résumé

Le manganèse indicateur de transport de limon en climats tempérés et tropicaux (A. J. de Groot)

Le manganèse peut contribuer à déterminer l'origine du limon (fraction inférieure à 16 microns) ainsi que la direction vers laquelle il est transporté le long des côtes de régions tempérées et tropicales.

L'auteur décrit en détail les méthodes physiques et chimiques. Ensuite il donne un aperçu des résultats obtenus en étudiant l'origine et le mouvement des sédiments fins dans les eaux côtières de la mer du Nord, en Europe occidentale. En outre, il discute des possibilités d'appliquer cette méthode aux régions tropicales (Amazonie et Thaïlande).

Discussion

A. Q. M. B. KARIM. In which forms and in which fractions do the insoluble manganese oxides in the sediment occur? Does any relation exist between the amount of manganese and the type of clay minerals in the sediments?

A. J. DE GROOT. In very young soil in which pedogenesis has not yet taken place, the manganese is mainly present in the granulometric fractions < 50 microns as coatings around the clay particles. The amount of manganese per unit of weight of the fractions is quickly diminishing with the increase of the dimension of the fraction.

After pedogenesis, however, there is to a certain extent a shift of the manganese from the finer to the coarser fractions (solution and recrystallisation of the manganese in the form of concretions).

No relationship between the amount of manganese and type of clay minerals is known.

J. HERVIEU. (1) How many samples must be taken to study the sediment transport of a river to its bar and in reverse? (2) How much time does the estimation of manganese content take?

A. J. DE GROOT. (1) Studying the transport of the fine-grained fractions in the course of a year with a total of 500 samples will give a sufficient insight into the problem. (2) During an eight-hour working day about fifteen analyses of total manganese, by using a colorimetric method, can be done. By using the Röntgen fluorescent method the capacity can be speeded up to 100 samples a day.

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