# III

# Mass transfer in disturbed sediments

by

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## Introduction

The knowledge of the properties of the water-sediment interface, as well as the kinetics of the chemical reactions taking place in the sediments, are essential for the description and understanding of the mass transfer processes between sea-water and marine deposits.

It must be recognized that the boundary conditions at this interface are often poorly known; in some cases, its exact position is not even well defined.

One of the most important reasons for this situation is the difficulty of collecting cores without disturbing the water-sediment interface.

With the classical gravity or piston corer, and to a lesser extent the box corer, the turbulence caused by the instrument itself is able to resuspend the poorly compacted top sediments.

The removal of the supernatant water of the core may possibly carry away another fraction of the surface layer of the sediments.

It is thus necessary to use an adequate coring technique and to perform a careful treatment of the core in order to avoid any loss of information.

The properties of the surface layer of the sediments generally differ very much from those of the deeper layers, and may considerably affect the mass transport across the water-sediment interface.

The degree of compaction in the surface layer is low, especially in the case of muds.

The shear stresses produced by the overflowing water induce perturbations of this uncompacted layer, and increase the mass transfer coefficient of dissolved species within the layer.

Also, the high porosity favours the diffusion process in the interstitial waters.

Furthermore, the biological activity of various benthic organisms is generally more intense in the surface layer.

This activity affects not only the chemistry of the whole environment, but produces mechanical transports known as bioturbation.

This paper is an attempt to describe the properties of the upper sediments of the North Sea along the Belgian coast.

These sediments are essentially constituted by organic rich muds (up to 5 % of organic C) deposited in shallow waters, at a mean depth of about 20 meters. The surface currents are high and the storms frequent, inducing important shear stresses on the water-sediment interface and favouring the existence of a disturbed boundary layer.

At the opposite, the activity of the benthic macro- and meio-fauna is extremely low in these sediments [De Coninck (1972)]. The existence of this layer has been demonstrated by careful coring techniques and chemical analysis performed on very closed vertical spacings. The analytical results were interpreted by kinetic models describing the vertical concentration profiles of various dissolved species in the porewater.

In a first part, special attention has been given to the influence of the disturbed layer on the vertical profiles and mass transfer coefficients have been computed through a kinetic model for dissolved silica.

A comprehensive model for sulfate, nitrate and ammonia will be presented in a second part.

We will present here as an example the results obtained on two cores taken in the North Sea at the position 51°19'45" N ; 3°04'44" E . These cores are representative of a large muddy zone along the Belgian and Dutch coast and display the typical pattern of the disturbed upper layer. It must be pointed out, however, that sandy sediments, which can also be found in the same region, do not show this pattern.

The results reported here may only be considered as representative of the behaviour of poorly consolidated sediments in shallow waters.

## 1.- Experimental

The cores were collected by divers of the Belgian Navy in 6.35 cm PVC core-liner tubes. The inner part of the tubes was covered with a thin polyethylene shield which allowed an easy removal of the sediments from the core barrel. The penetration of the core-liner tube was restricted to the first 25 cm . The tube was then sealed *in situ* with two rubber corks and brought aboard the ship in a vertical position. Two cores were collected at each site. The first one was immediately treated by discarding the supernatant water and cutting the sediment in short segments 1 to 4 cm long. These samples were then immediately centrifugated and the Eh , pH and alcalinity were measured on the interstitial water. The remaining part of the sample was deep frozen for subsequent chemical analysis.

The second core was immediately deep frozen. Segmentation was performed in the laboratory where the fractions were centrifugated. The chemical analysis included the determination of ammonia, nitrate, nitrite, silica and sulfate. It became apparent by comparison of the results of the chemical analysis performed on the interstitial water of the two cores that the 3 upper centimeters of the first core were lost when discarding the supernatant water. Only the second procedure did not disturb the structure of the water-sediment interface.

## 2.- Results

### 2.1.- Porosity

The vertical profile of porosity is given in figure 1. The porosity decreases rapidly from 100 % to about 65 % in the first 4 cm and remains practically constant at a greater depth.

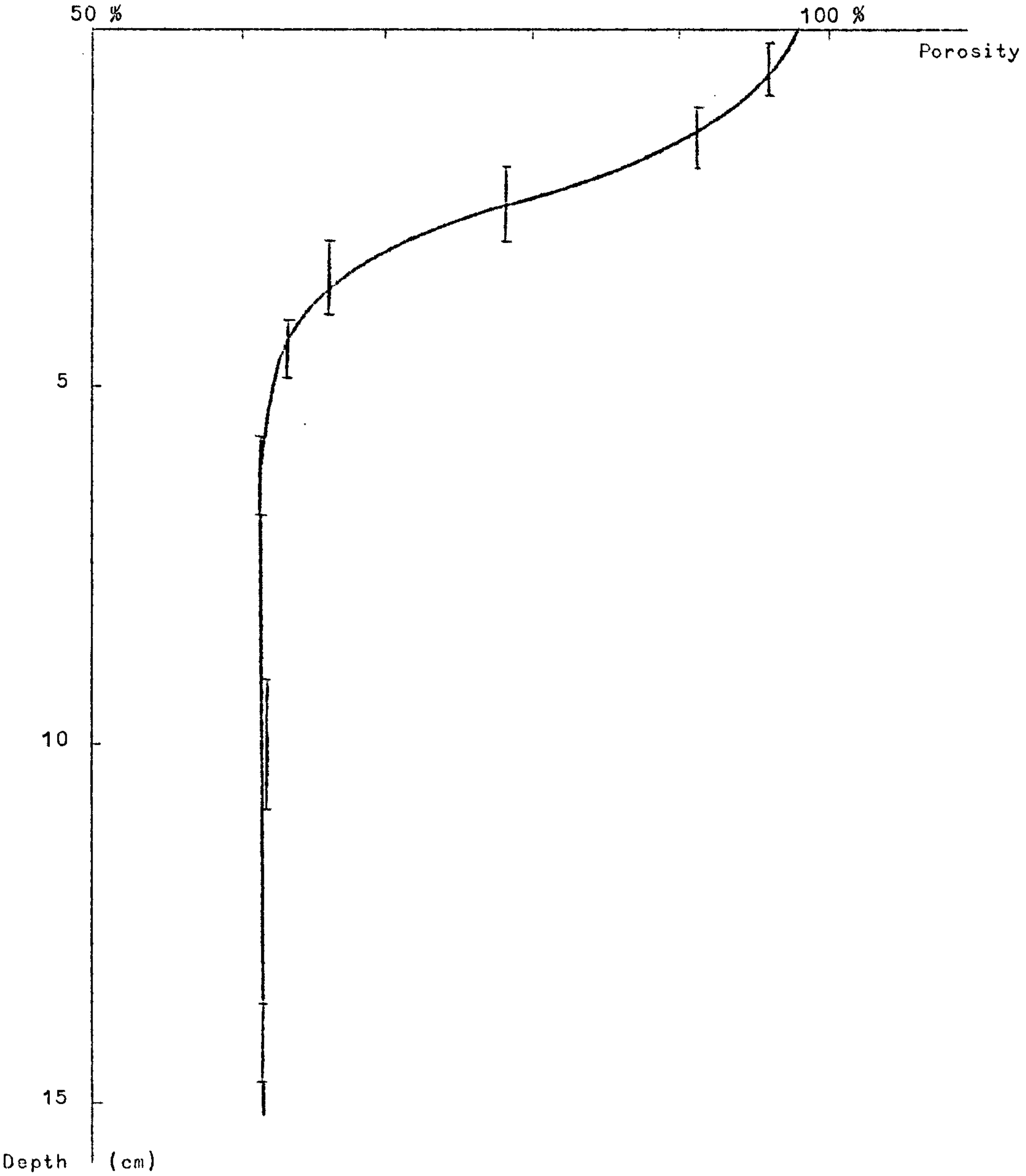


fig. 1.

## 2.2.- Redox potential

The existence of a sharp transition at a depth of 3.5 cm between a brown colored oxidized layer and a black reduced layer indicates that, in spite of the high amount of organic matter present, oxidizing conditions prevail in the upper part of the sediments. On the other hand, redox potentials as low as - 150 mV were measured in the lower part. This situation is in contrast with the Eh profiles of cores taken in a small lagoon near the Belgian coast [Vanderborght and Billen (1975)] where similar sediments are deposited but are not submitted to high shear stresses as in the open sea. In this case, reducing conditions are encountered at less than a few millimeters from the water-sediment interface.

## 2.3.- Dissolved silica

Figure 2 shows the vertical profile of dissolved silica obtained on the core. A sharp gradient discontinuity is observed at a depth of about 4 cm , with a very low gradient of concentration in the upper part of the sediment. This profile differs from those usually described [Anikouchine (1967), Hurd (1973), Fanning (1974)], where high gradients of dissolved silica are observed at the interface.

## 2.4.- Sulfate

The classically described anaerobic reduction of sulfate can be observed in the deeper part of the North Sea sediments (fig. 3), where sulfate is completely depleted at a 25 cm depth. As may be expected, the reduction of sulfate does not occur in the upper oxidizing layer.

## 2.5.- Nitrate

Nitrate profiles in the North Sea cores display a maximum value in the upper layer at a depth of about 2 cm (fig. 4). It is interesting to compare these results with those obtained for muddy and sandy deposits taken from a lagoon near the Belgian coast. It has been shown [Vanderborght and Billen (1975)] that in the muddy organic rich sediments, the nitrate concentration is always lower in the interstitial water than in

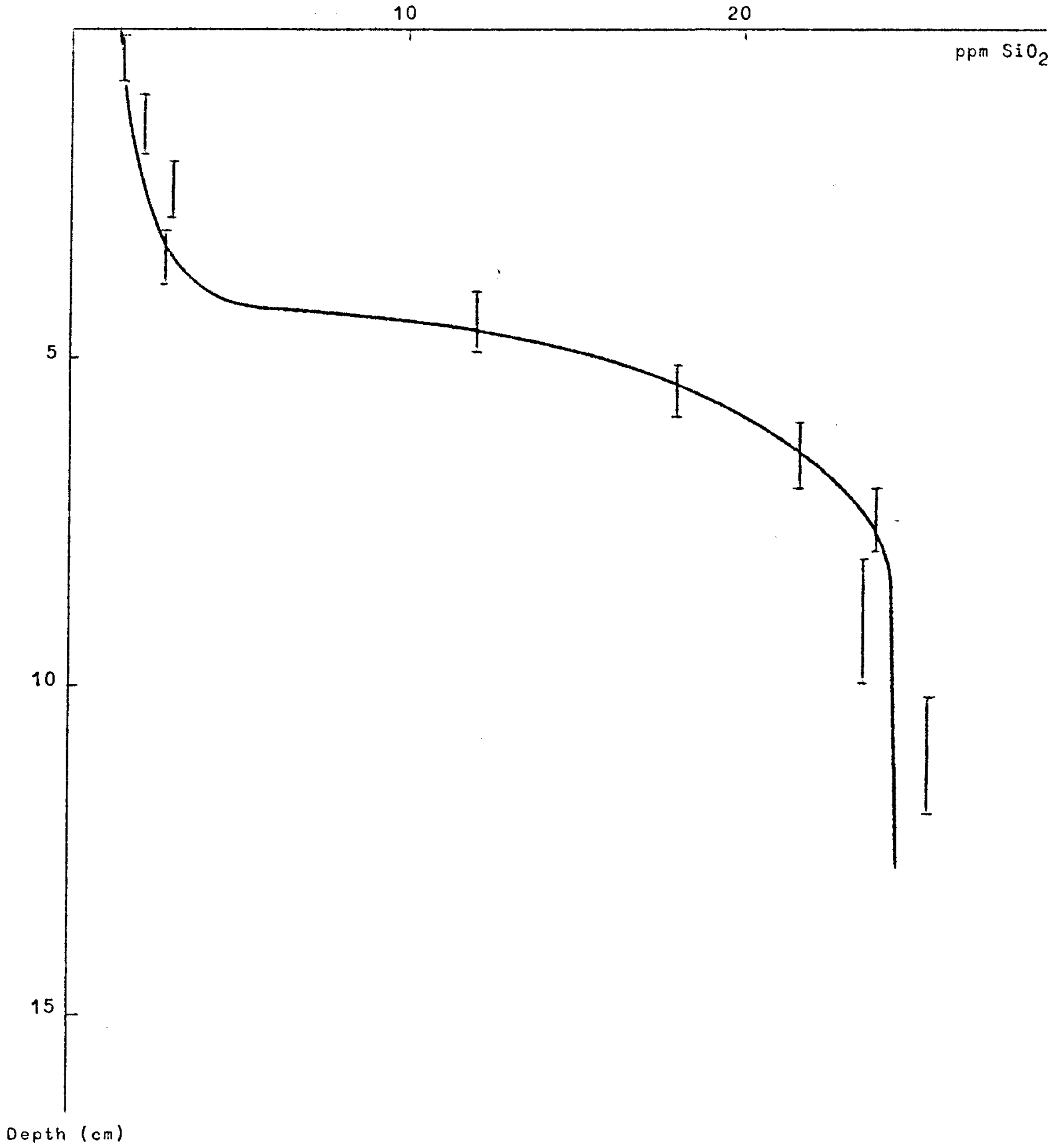


fig. 2.

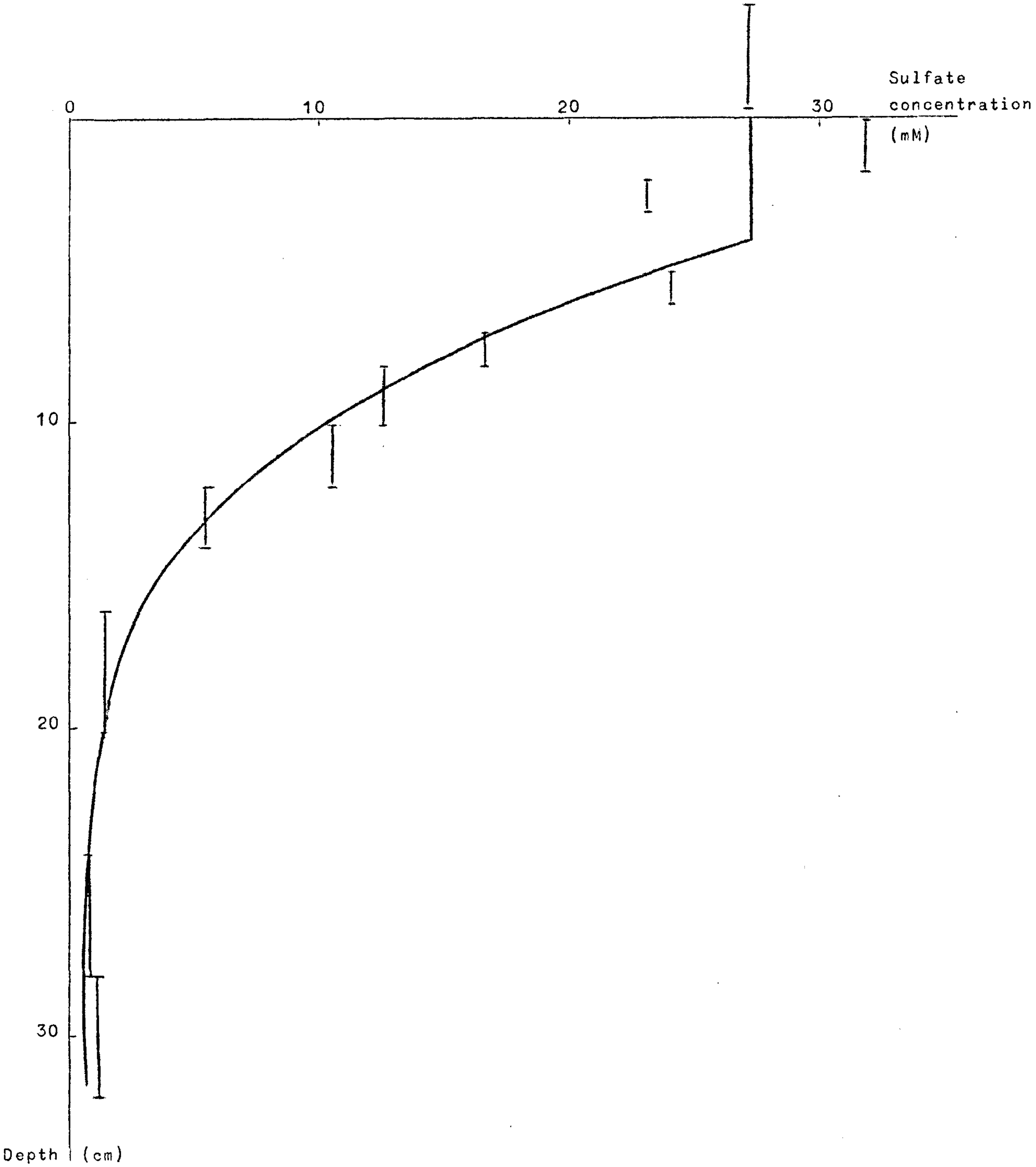


fig. 3.

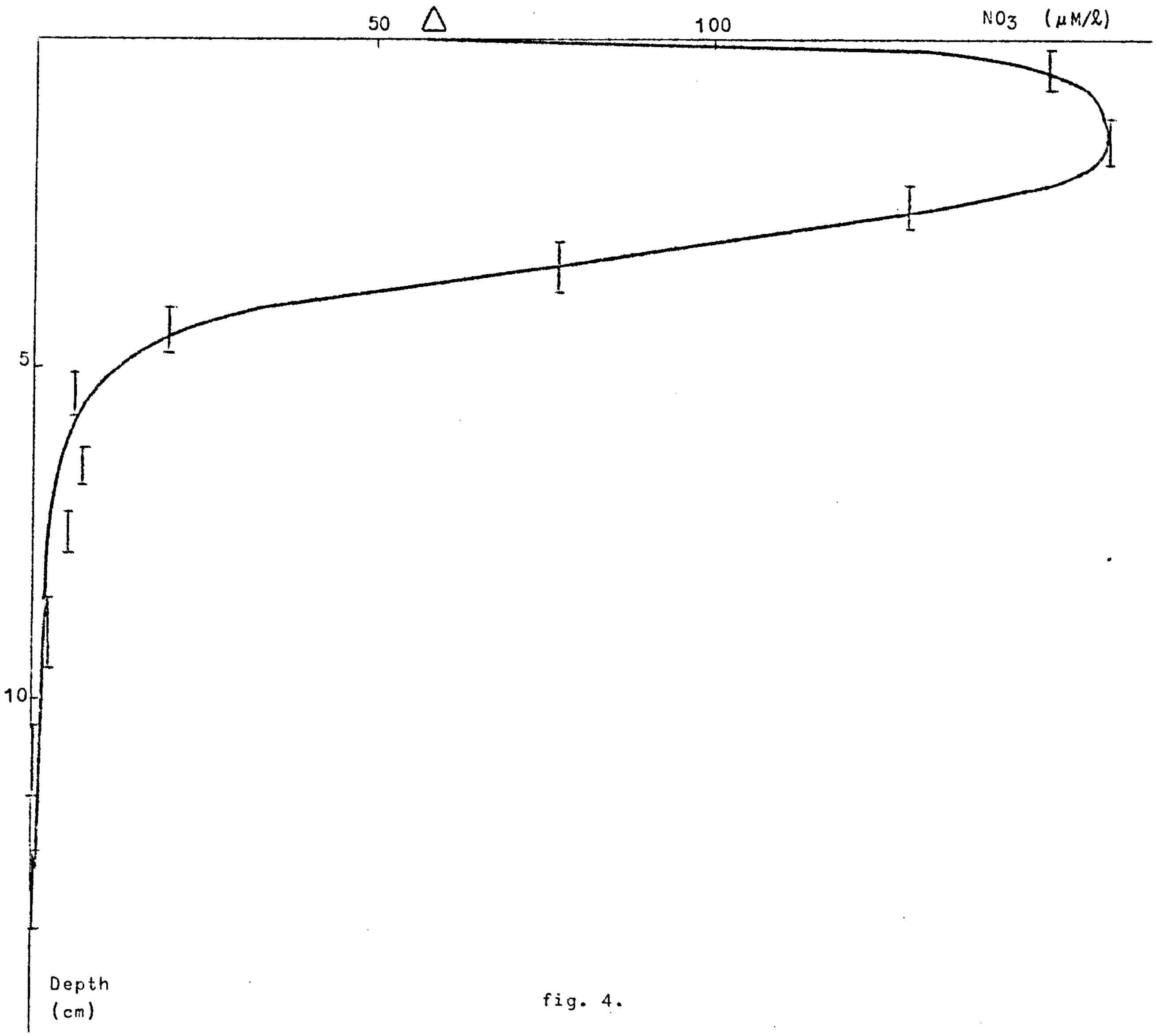


fig. 4.

overlying water, and decreases rapidly with depth. In sandy sediments, which are poor in organic matter, profiles commonly show a maximum in nitrate concentration at a depth of a few centimeters. It has also been demonstrated by these authors that this maximum can be related to the activity of autotrophic nitrifying bacteria in the bulk of the sediments, which itself strongly depends on the local redox potential value. This nitrification may also occur in the disturbed layer of muddy sediments because of the oxidizing conditions prevailing there.

## 2.6.- Ammonia

The increase of the ammonia concentration in pore water due to decomposition of organic material is also observed in the North Sea cores (fig. 5). However, in contrast with the usual profiles obtained in deep-sea cores, a sharp discontinuity of the concentration gradient occurs at a depth of about 4 cm .

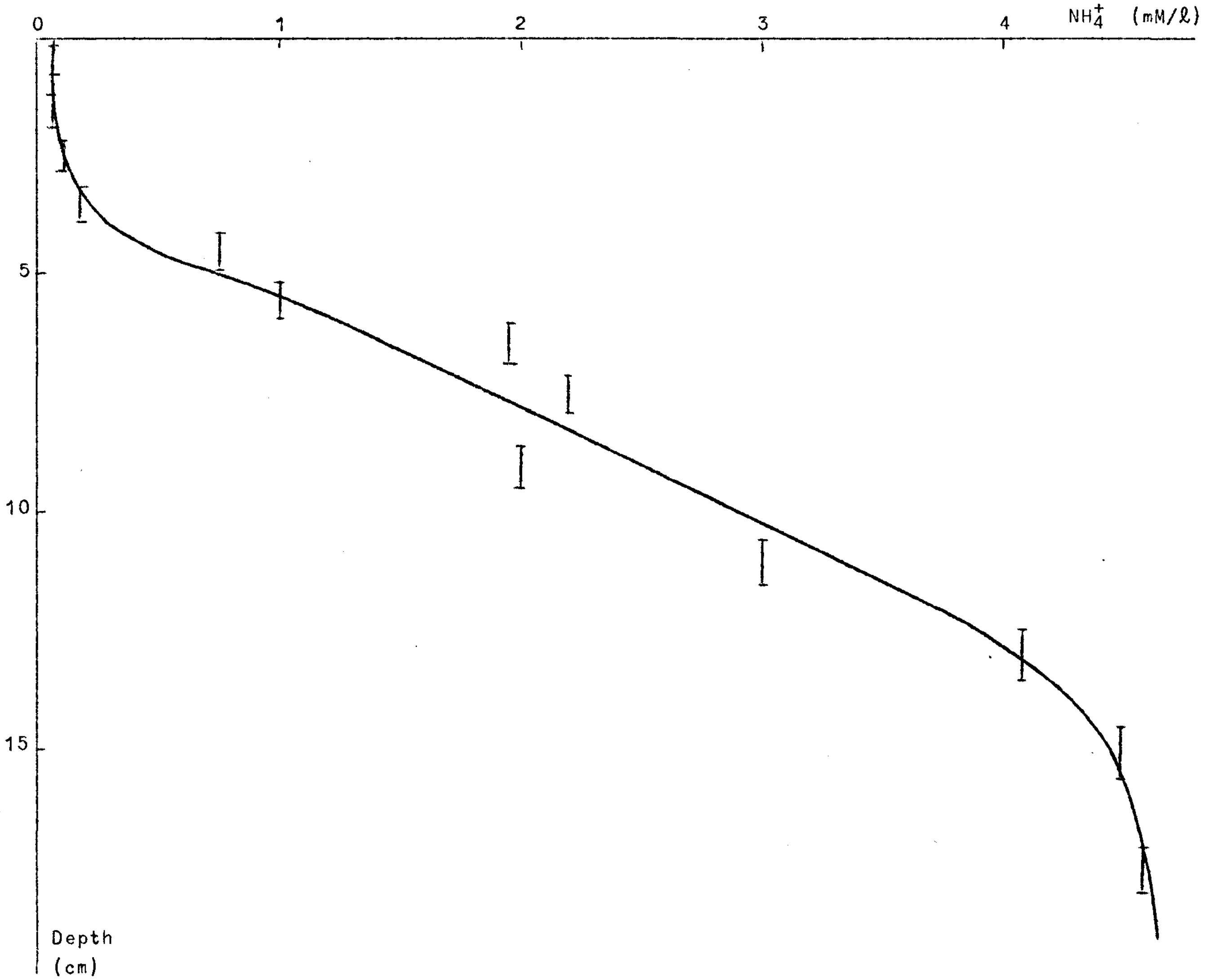


fig. 5.

## 3.- Kinetic model for dissolved silica

To analyse more quantitatively the importance of the upper layer of the sediments in the exchange with surface waters, we have tried to describe the vertical concentration profile of the dissolved silica in pore water by considering the various physical and chemical processes taking place in the sediments. The general approach of the proposed kinetic model has been extensively described by Berner (1971), (1974) for homogeneous sediments. However, simple models for homogeneous deposits are not able to describe the existence of discontinuities in the concentration gradient, as observed in the profiles of the North Sea cores. These profiles strongly suggest that one distinguishes a thin disturbed layer near the water-sediment interface from a rather consolidated underlying sediment.

The continuous decrease of porosity and of mechanical perturbations with depth imply that the mass transfer coefficient be a continuous function of depth. However, a simplification of the mathematical treatment has been made by considering a two-layer sediment system, where each layer is characterized by a constant mass transfer coefficient. Furthermore only a steady-state model will be considered here, implying that all the parameters appearing in the kinetic equation are time independant. This hypothesis has been mathematically justified for a similar case [Vanderborght and Billen (1975)].

In the kinetic equation describing the vertical concentration profile of silica, we will consider the contribution of the following processes :

- diffusion in the pore water of the dissolved substance under its concentration gradient;
- advection related to the deposition of fresh sediments;
- chemical reactions affecting the concentration by production or consumption of silica.

The net rate of dissolved silica production results from a competition between dissolution of highly reactive opal and reprecipitation processes. These are not well understood, but it is generally admitted that, in the presence of clay minerals, reprecipitation of dissolved silica due to reactions with solids in the sedimentary column must be considered. It can be shown [Hurd (1973), Berner (1974), Fanning and Pilson (1974), Wollast (1974)] that the net rate of reaction may be simply described by the kinetic relation :

$$r_{Si} = k_{Si} \; ([Si]_\infty - [Si])$$

where $k_{Si}$ is an apparent kinetic constant, $[Si]$ is the concentration of dissolved silica and $[Si]_\infty$ is either an equilibrium concentration of dissolved silica or a steady state value of this concentration which is reached at high depth.

The equation describing the behaviour of dissolved silica in the upper and lower layers can be written :

$$(1) \qquad D_i \frac{d^2[Si]}{dz^2} - \omega \frac{d[Si]}{dz} + k_{Si} \; ([Si]_\infty - [Si]) = 0$$

where $D_i$ represents the global mass transfer coefficient in the considered layer.

The following boundary conditions are imposed to solve the system :

- at $z = 0$ , the concentration is equal to the concentration $[Si]_0$ in the overlying sea-water;
- at large z-values, the concentration tends towards a finite value;
- at the interface between the upper and lower layer $(z = z_n)$ , there is no discontinuity in the concentration profile, on the other hand, the fluxes across this interface are conservative :

$$(2) \qquad \Phi_n = - D_1 \frac{d[Si]}{dz}\Big|_1 = - D_2 \frac{d[Si]}{dz}\Big|_2 \qquad \text{at} \qquad z = z_n \; .$$

The solution to equation (1) is, for the upper layer :

$$(3) \quad [Si]_1 = [Si]_\infty - ([Si]_\infty - [Si]_0) \left\{\frac{ch[\alpha_1(z_n - z)] - \beta \; sh[\alpha_1(z_n - z)]}{ch(\alpha_1 z_n) + \beta \; sh(\alpha_1 z_n)}\right\} e^{\frac{\omega}{2D_1} z}$$

for the lower layer :

$$(4) \quad [Si]_2 = [Si]_\infty - ([Si]_\infty - [Si]_0) \left[\frac{e^{\frac{\omega}{2D_1} z_n}}{ch(\alpha_1 z_n) + \beta \; sh(\alpha_1 z_n)}\right] e^{(\frac{\omega}{2D_2} - \alpha_2)(z - z_n)}$$

with $$\alpha_1 = \left(\frac{\omega^2}{4 D_1^2} + \frac{k_{Si}}{D_1}\right)^{\frac{1}{2}} ,$$

$$\alpha_2 = \left(\frac{\omega^2}{4\ D_2^2} + \frac{k_{Si}}{D_2}\right)^{\frac{1}{2}} ,$$

$$\beta = \frac{D_2\ \alpha_2}{D_1\ \alpha_1} .$$

The depth $z_n$ is estimated from the porosity profiles. A value of 3.5 cm, which also corresponds to the color transition in the cores, was used throughout the calculations. Many estimations have been made on the deposition rate $\omega$ for the southern part of the North Sea and a mean

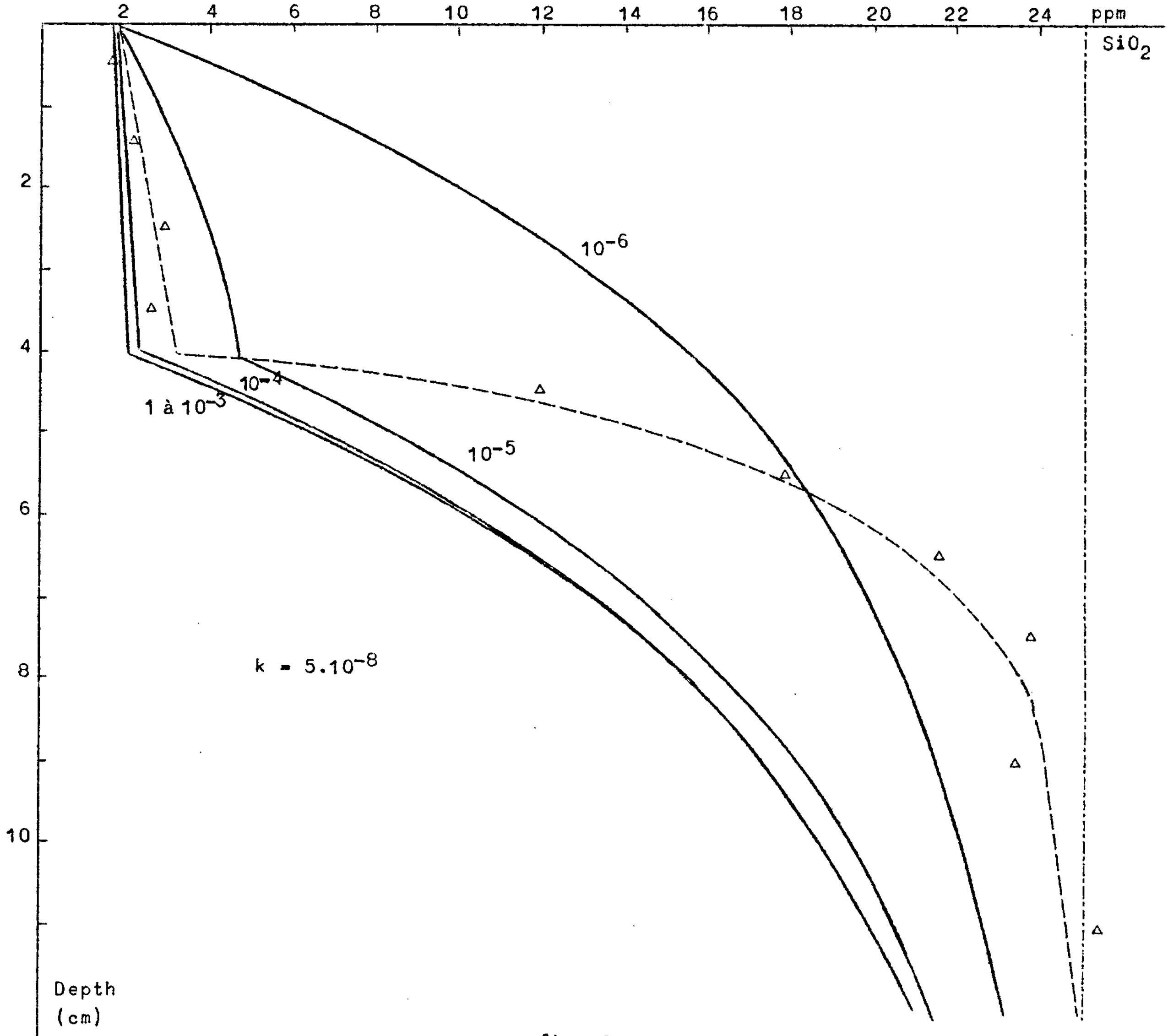


fig. 6.

value of 3 cm per 100 years seems to be the best approximation [MacCave (1971)]. Deposition rates one or two orders of magnitude higher can be locally observed. The mass transfer for the lower part may be considered as only due to molecular diffusion. At the mean temperature of the system 11 °C and taking into consideration the porosity and an estimation of the tortuosity of this layer, the diffusion coefficient for the lower layer approximately equals $10^{-6}$ $cm^2.s^{-1}$ [Anikouchine (1967), Wollast, Garrels (1971), Hurd (1973), Berner (1974), Fanning (1974)]. The asymptotic value of the dissolved silica concentration $[Si]_\infty$ can be deduced from the experimental profiles (fig. 2) : a value of 400 µmoles.

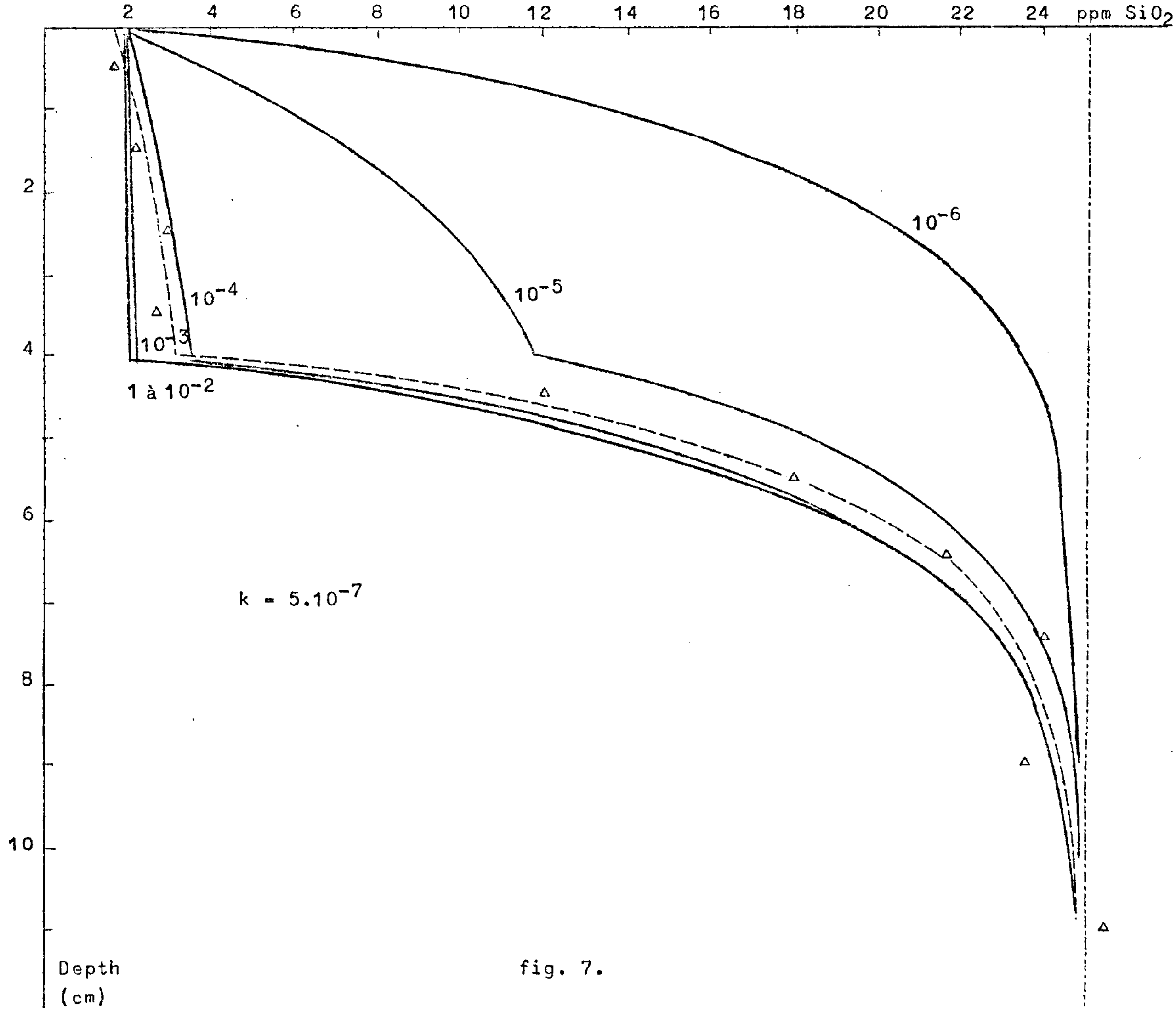


fig. 7.

$\ell^{-1}$ has been selected. The only unknown parameters are $D_1$ and $k_{Si}$. A set of curves has been drawn for various values of $k_{Si}$ and $D_1$ (fig. 6 and 7). The distribution of dissolved silica in the lower part of the sediments is very sensitive to the values of $k_{Si}$ which allows one to select the value

$$k_{Si} = 5 \times 10^{-7}\ s^{-1} .$$

The best fit for the surface layer is then obtained for

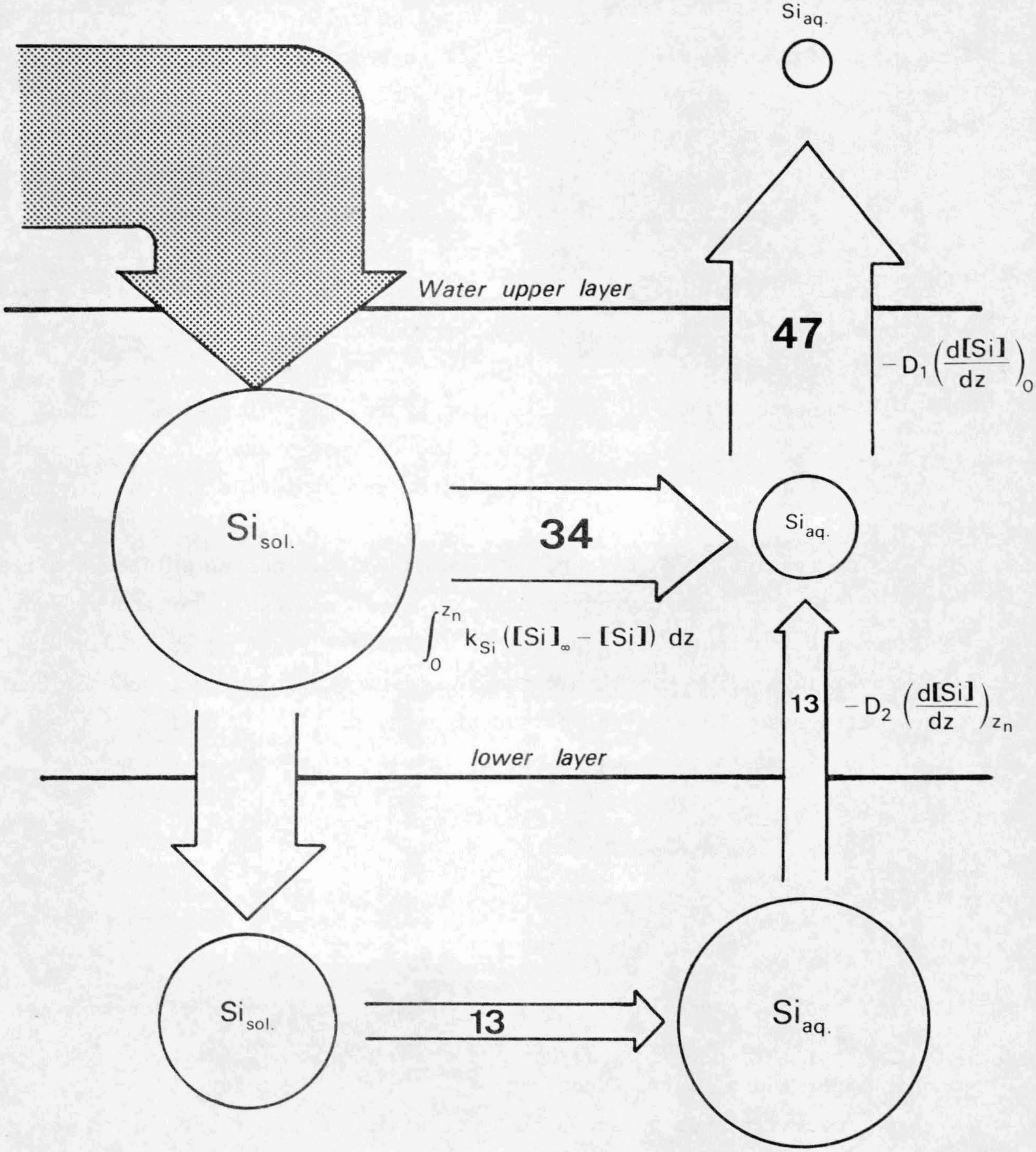
$$D_1 = 10^{-4}\ m^2.s^{-1} .$$

Our value for $k_{Si}$ is in agreement with the value calculated from the laboratory experiments of Grill and Richards (1964) on diatoms, and Hurd (1972) on radiotarians. The rate constant deduced from these experiments are respectively equal to $2 \times 10^{-7}$ and $7 \times 10^{-7}\ s^{-1}$. It should be noticed that the sedimentation rate $\omega$ can be neglected as long as it is less than 10 cm/year and has not to be known with a great precision. The value of the mass transfer coefficient $D_1$ for the upper layer is 100 times greater than the apparent diffusion coefficient in the compacted layer. This large increase is partially due to the change of porosity and tortuosity (approximately a factor of 2), but mainly to the advective processes induced by the movement of overlying water.

The model allows to calculate the flux across the boundary between layer 1 and layer 2, across the water-sediment interface and the net dissolution rate of silica (fig. 8). The contribution of the upper layer represents 75 % of the total flux of silica out of the sediments. As a consequence, the fluxes may be underestimated by a factor of 4 if this layer is discarded during sampling or handling of the core.

## 4.- Kinetic model of nitrogen diagenesis

The preceeding discussion, and the purely physico-chemical model build up for silica, has shown that the mass transfer mechanisms in the muddy sediments of the coastal region of the North Sea could be described by considering two distinct layers with two different mass transfer



mg $Si/m^2$.day

fig. 8.

coefficients. The application of the same model to other nutrients like nitrogen, for which microbiological action is of importance, requires not only to consider different mass transfer mechanisms for the dissolved species, but also fundamental changes of the biological processes occuring in the two layers. In an organic rich sediment, the most important factor controlling microbiological activity is probably the availability of oxidants. As far as the overlying water is a major source of these oxidants their availability will be strongly influenced by the mass transfer properties of the two layers. The most important oxidants for biological activity are oxygen and sulfate.

Manganese oxide, nitrate and iron hydroxide utilization, although it can account for a part of the oxidation of the organic matter in sediments, will not be taken explicitely into account in the present simplified model.

The results of Eh measurements and the experimental sulfate profile (fig. 3) suggest that oxygen is available in the upper layer and prevents sulfate utilization, while sulfate is extensively used as an oxidant in the lower layer. The microbiological decomposition of organic matter can thus be represented by coupling equation (a) with equation (b) in the disturbed layer and with equation (c) in the lower compacted layer :

$$CH_2O + 2H_2O \rightarrow HCO_3^- + 5H^+ + 4e^- \tag{a}$$

$$4e^- + O_2 + 4H^+ \rightarrow 2H_2O \tag{b}$$

$$4e^- + \frac{1}{2} SO_4^{--} + \frac{9}{2} H^+ \rightarrow \frac{1}{2} HS^- + 2H_2O \ . \tag{c}$$

Ammonification, a result of the heterotrophic utilization of organic matter will thus be under the control of oxygen concentration in the upper layer and of sulfate concentration in the lower layer. For the same reason, nitrification is supposed to occur in the upper oxygenated layer while denitrification is only possible in the lower layer.

The behaviour of $O_2$ , $SO_4^{--}$, $NH_4^+$ and $NO_3^-$ in the pore water of the sediment can be described by the following general equation :

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - \omega \frac{\partial C}{\partial z} + r \tag{5}$$

where $C$ is the concentration of the dissolved substance ($\text{mole}.\ell^{-1}$) and $r$ the rate of production ($r > 0$) or consumption ($r < 0$) ($\text{mole}.\ell^{-1}.\text{s}^{-1}$), $z$, $D$ and $\omega$ as above. Under the assumption of steady state

$$\frac{\partial C}{\partial t} = 0 \ .$$

The expression of the rates of reaction will now be discussed briefly for each constituent.

## 4.1.- Oxygen

A Michaelis-Menten function would be the best way of expressing the oxygen consumption rate. However, for reasons of mathematical simplification, this Michaelis-Menten kinetics has been approximated by a zero order kinetics at oxygen concentration higher than some critical value (around 1 % saturation) and a first order kinetics at lower concentration. It is also assumed that this critical oxygen concentration is reached at the boundary between the upper and the lower layer, so that

$$r_{O_2} = \begin{cases} -\,k_{O_2} & \text{for} \quad z < z_n \\ -\,k'_{O_2}\ [O_2] & \text{for} \quad z > z_n \ . \end{cases}$$

## 4.2.- Sulfate

As stated above, sulfate reduction does not occur in the well aerated part of the sediment, but only in the lower layer. In his kinetic model of sulfate distribution in sediments, Berner (1964), (1974), postulated that the rate of bacterial sulfate reduction was first order with respect to the concentration of a particular fraction of organic material used by sulfate reducing bacteria. In the case of these organic rich sediments, however, the organic content (measured both as total organic carbon and as aminoacids) was found to be degraded only to a small extent (15 to 20 %) at a depth of 25 cm whereas sulfate is completely depleted. This suggests that the rate of organic decomposition is limited by the availability of oxidants rather than by the concentration of organic matter. Sulfate reduction rate will then be first order with respect to sulfate concentration :

$$r_{SO_4} = \begin{cases} 0 & \text{for} \quad z < z_n \\ - k_{SO_4} \, [SO_4] & \text{for} \quad z > z_n \end{cases}$$

### 4.3.- Nitrate

The modelling of nitrification and denitrification in sediments has been extensively discussed in a previous paper [Vanderborght and Billen (1975)]. The same model will be used here : a constant nitrification term will be assumed in the upper layer :

(d) $$NH_4^+ + 2\,O_2 + 2\,H^+ \rightarrow NO_3^- + H_2O \; .$$

A first order denitrification rate will be postulated in the lower one :

$$r_{NO_3} = \begin{cases} + k_{NO_3} & \text{for} \quad z < z_n \\ - k'_{NO_3} \, [NO_3] & \text{for} \quad z > z_n \; . \end{cases}$$

### 4.4.- Ammonium

As ammonium production is related to heterotrophic activity, its rate is proportional to the rate of oxygen consumption in the upper layer and to the rate of sulfate reduction in the lower layer. A consumption term due to nitrification must further be taken into account in the upper layer. Several works show that denitrification in natural water and sediments produces essentially nitrogen and no ammonium [Chen *et al.* (1972), Wheatland *et al.* (1959), Chan and Campbell (1973)]. There is thus no additional production term in the lower layer :

$$r_{NH_4} = \begin{cases} - k_{NO_3} + k_{NH_4} & \text{for} \quad z < z_n \\ + \alpha \, k_{SO_4} & \text{for} \quad z > z_n \; . \end{cases}$$

The equations of table 1 can then be solved analytically; the solutions are summarized.

## Table 1

| | Upper layer $(z < z_n)$ | Lower layer $(z > z_n)$ |
|---|---|---|
| Oxygen | $D_1 \frac{d^2[O_2]}{dz^2} - \omega \frac{d[O_2]}{dz} - k_{O_2} = 0$ | $D_2 \frac{d^2[O_2]}{dz^2} - \omega \frac{d[O_2]}{dz} - k'_{O_2} [O_2] = 0$ |
| Sulfate | $D_1 \frac{d^2[SO_4]}{dz^2} - \omega \frac{d[SO_4]}{dz} = 0$ | $D_2 \frac{d^2[SO_4]}{dz^2} - \omega \frac{d[SO_4]}{dz} - k_{SO_4} [SO_4] = 0$ |
| Nitrate | $D_1 \frac{d^2[NO_3]}{dz^2} - \omega \frac{d[NO_3]}{dz} + k_{NO_3} = 0$ | $D_2 \frac{d^2[NO_3]}{dz^2} - \omega \frac{d[NO_3]}{dz} - k'_{NO_3} [NO_3] = 0$ |
| Ammonium | $D_1 \frac{d^2[NH_4]}{dz^2} - \omega \frac{d[NH_4]}{dz} - k_{NO_3} + k_{NH_4} = 0$ | $D_2 \frac{d^2[NH_4]}{dz^2} - \omega \frac{d[NH_4]}{dz} + a\, k_{SO_4} [SO_4] = 0$ |

### Solution of the differential equations of table 1

Oxygen Upper layer

$$[O_2]_1 = \frac{k_{O_2}}{2\,D_1} z^2 + Az + [O_2]_0$$

Lower layer

$$[O_2]_2 = B \quad e^{-\left(\frac{k'_{O_2}}{D_2}\right)^{\frac{1}{2}} (z - z_n)}$$

with

$$A = \frac{-\frac{k_{O_2}}{D_1} \left\{\frac{z_n^2}{2} + z_n\left(\frac{D_2}{k'_{O_2}}\right) \right\} - [O_2]_0}{\left(\frac{D_2}{k'_{O_2}}\right)^{\frac{1}{2}} + z_n}$$

$$B = \frac{k_{O_2}}{2\,D_1} z_n^2 + Az_n + [O_2]_0$$

Sulfate Upper layer

$$[SO_4]_1 = [SO_4]_0 \quad e^{\frac{\omega}{2D_1} z} \quad \frac{\omega\ \mathrm{ch}\ \{\frac{\omega}{2D_1} (z - z_n)\} - \beta\ \mathrm{sh}\ \{\frac{\omega}{2D_1} (z - z_n)\}}{\omega\ \mathrm{ch}\ (\frac{\omega}{2D_1} z_n) + \beta\ \mathrm{sh}\ (\frac{\omega}{2D_1} z_n)}$$

Lower layer

$$[SO_4]_2 = [SO_4]_0 \quad e^{\frac{\omega}{2D_1} z_n} \quad \frac{\omega \; e^{\frac{\gamma}{2D_2}(z - z_n)}}{\omega \; ch\,(\frac{\omega}{2D_1} z_n) + \beta \; sh\,(\frac{\omega}{2D_1} z_n)}$$

with

$$\beta = (\omega^2 + 4\, k_{SO_4} \; D_2)^{\frac{1}{2}}$$

$$\gamma = \omega - \beta$$

Nitrate Upper layer

$$[NO_3]_1 = - \frac{k_{NO_3}}{2\; D_1} z^2 + Az + [NO_3]_0$$

Lower layer

$$[NO_3]_2 = B \quad e^{-(\frac{k'_{NO_3}}{D_2})^{\frac{1}{2}} (z - z_n)}$$

with

$$A = \frac{\frac{k_{NO_3}}{D_1} \{\frac{z_n^2}{2} + z_n \; (\frac{D_2}{k'_{NO_3}})^{\frac{1}{2}}\} - [NO_3]_0}{(\frac{D_2}{k'_{NO_3}})^{\frac{1}{2}} + z_n}$$

$$B = - \frac{k_{NO_3}}{2\; D_1} z_n^2 + Az_n + [NO_3]_0$$

Ammonium Upper layer

$$[NH_4]_1 = [NH_4]_0 - \alpha \; [SO_4]_0 \left[ e^{\frac{\omega}{2D_1} z} \quad \frac{\omega \; ch\{\frac{\omega}{2D_1}(z - z_n)\} - \beta \; sh\{\frac{\omega}{2D_1}(z - z_n)\}}{\omega \; ch(\frac{\omega}{2D_1} z_n) + \beta \; sh(\frac{\omega}{2D_1} z_n)} - 1 \right]$$

$$+ \frac{h}{\omega^2} \quad e^{-\frac{\omega}{D_1} z} \; (1 - e^{\frac{\omega}{D_1} z}) + \frac{h}{\omega} z$$

Lower layer

$$[NH_4]_2 = [NH_4]_0 - \alpha \; [SO_4]_0 \left[ e^{\frac{\omega}{2D_1} z_n} \quad \frac{\omega \; e^{\frac{\gamma}{2D_2}(z - z_n)}}{\omega \; ch(\frac{\omega}{2D_1} z_n) + \beta \; sh(\frac{\omega}{2D_1} z_n)} - 1 \right]$$

$$+ \frac{h}{\omega^2} \quad e^{-\frac{\omega}{D_1} z_n} (1 - e^{\frac{\omega}{D_1} z_n}) + \frac{h}{\omega} z_n$$

with

$h = k_{NH_4} - k_{NO_3}$

$\beta$ , $\gamma$ as above

Eleven parameters ($z_n$ , $\omega$ , $D_1$ , $D_2$ , $k_{O_2}$ , $k'_{O_2}$ , $k_{SO_4}$ , $k_{NO_3}$ , $k'_{NO_3}$ , $k_{NH_4}$ , $\alpha$) have to be fixed for the calculation of the concentration profiles from these theoretical solutions. Of these, four ($z_n$ , $\omega$ , $D_1$ , $D_2$) have been determined by the aid of the silica model discussed above. A further parameter, $\alpha$ , can be easily estimated. The results of the determination of alcalinity and ammonium in the pore water of the lower layer (fig. 9) show that one mole of ammonium is produced for each 11 moles of organic carbon oxidized. Considering the stoechiometry of reaction (a) and (c), the value of $\alpha$ is then

$$\frac{2}{11} \simeq 0.18 \ .$$

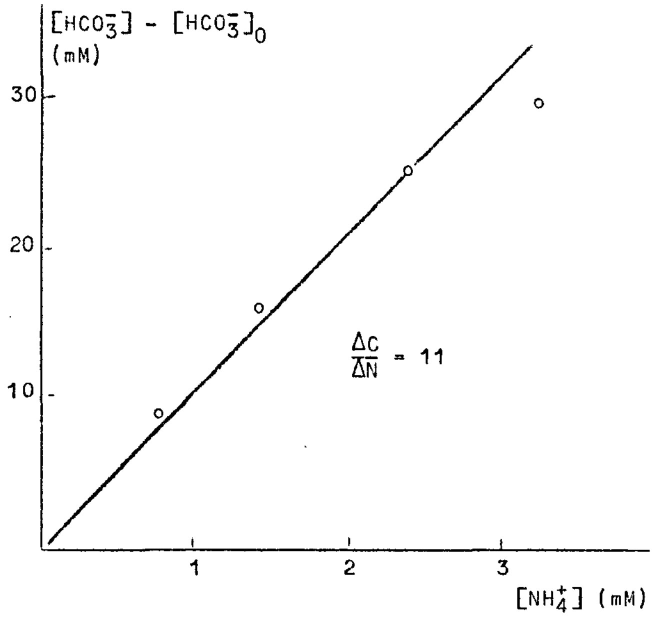


fig. 9.

Furthermore, a relation must exist between three other parameters, $k_{O_2}$ , $k_{NO_3}$ and $k_{NH_4}$ : the oxygen consumption is indeed the result of both aerobic heterotrophic activity and nitrification. Considering a $\frac{\Delta C}{\Delta N}$ ratio equal to 8 for this upper layer, the stoechiometry of reactions (a) and (b), and of reaction (d), the value of $k_{O_2}$ can be expressed by

(6) $$k_{O_2} = 8\ k_{NH_4} + 2\ k_{NO_3} \ .$$

The remaining parameters must now be chosen in order to fit simultaneously the three experimental profiles $SO_4^{--}$, $NO_3^-$, $NH_4^+$. As far as oxygen is concerned, no experimental profile is available. However, some constraints can be formulated : oxygen concentration at the water-sediment interface is supposed to be 100 % saturation, *i.e.* 340 μM . Oxygen concentration must be higher than about 1 % saturation (3.4 μM) all over the upper layer and lower than this value in the lower layer, for the upper layer has been assumed aerobic and the lower layer anaerobic.

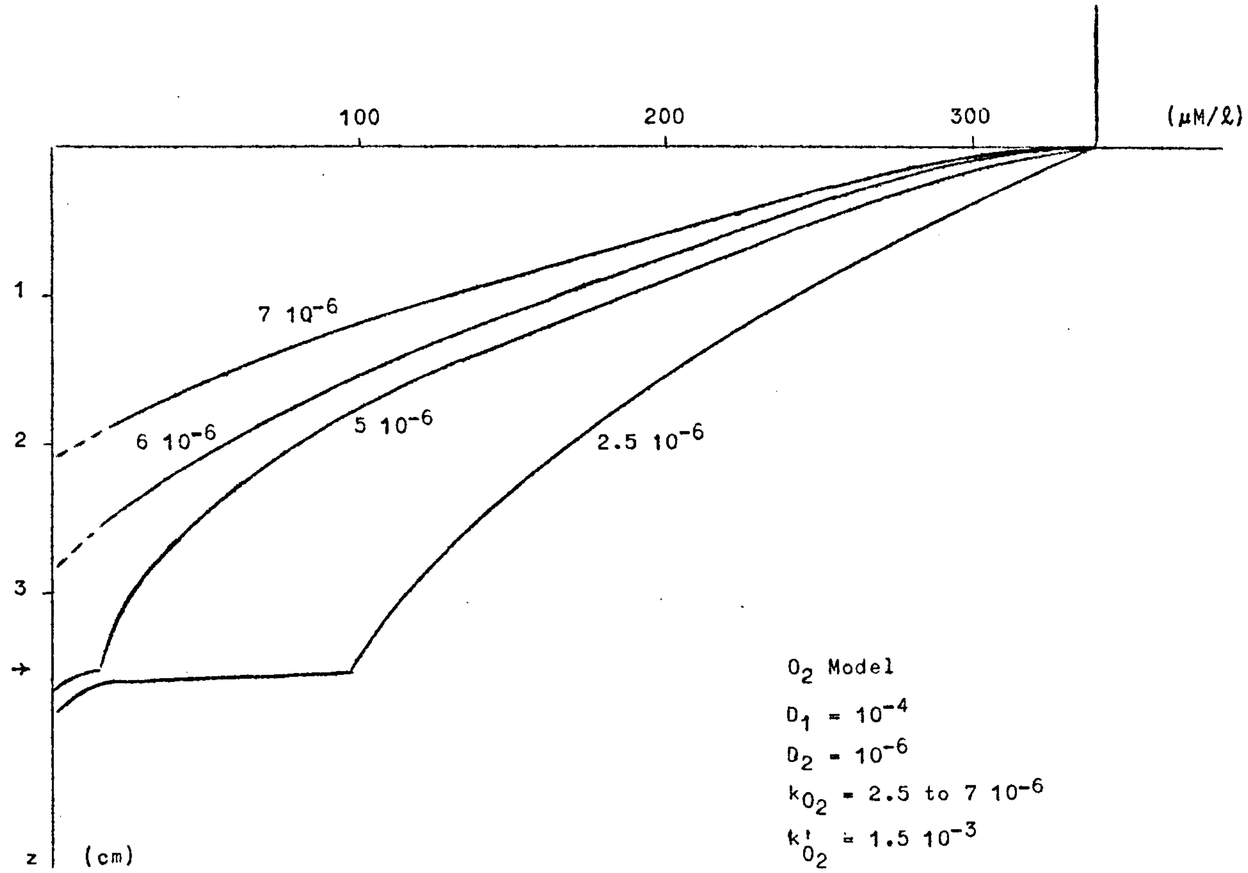


fig. 10.

Figures 10, 11, 12 and 13 show the solution of the equations of table 1 for selected values of the parameters. It can be seen that the theoretical curves are very sensitive to small variations of the parameters. The permitted range of values for the parameters is thus very narrow. The best fit is obtained for the following values :

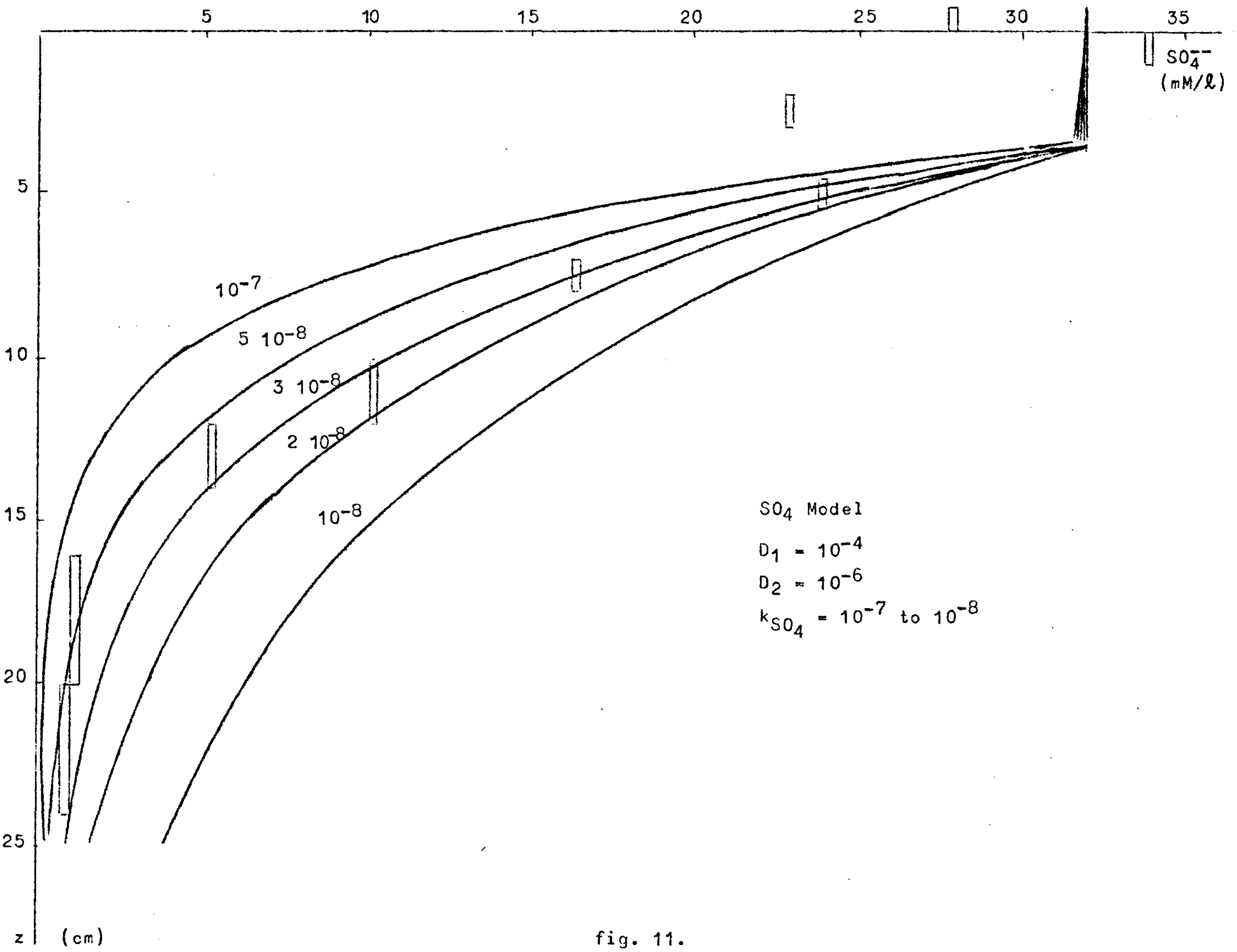


fig. 11.

$k_{O_2} = 5 \times 10^{-6}$ μmoles cm$^{-3}$ s$^{-1}$

$k'_{O_2} = 1.5 \times 10^{-3}$ s$^{-1}$

$k_{SO_4} = 2.5 \times 10^{-8}$ s$^{-1}$

$k_{NO_3} = 1.5 \times 10^{-6}$ μmoles cm$^{-3}$ s$^{-1}$

$k'_{NO_3} = 5 \times 10^{-6}$ s$^{-1}$

$k_{NH_4} = 2 \times 10^{-6}$ μmoles cm$^{-3}$ s$^{-1}$

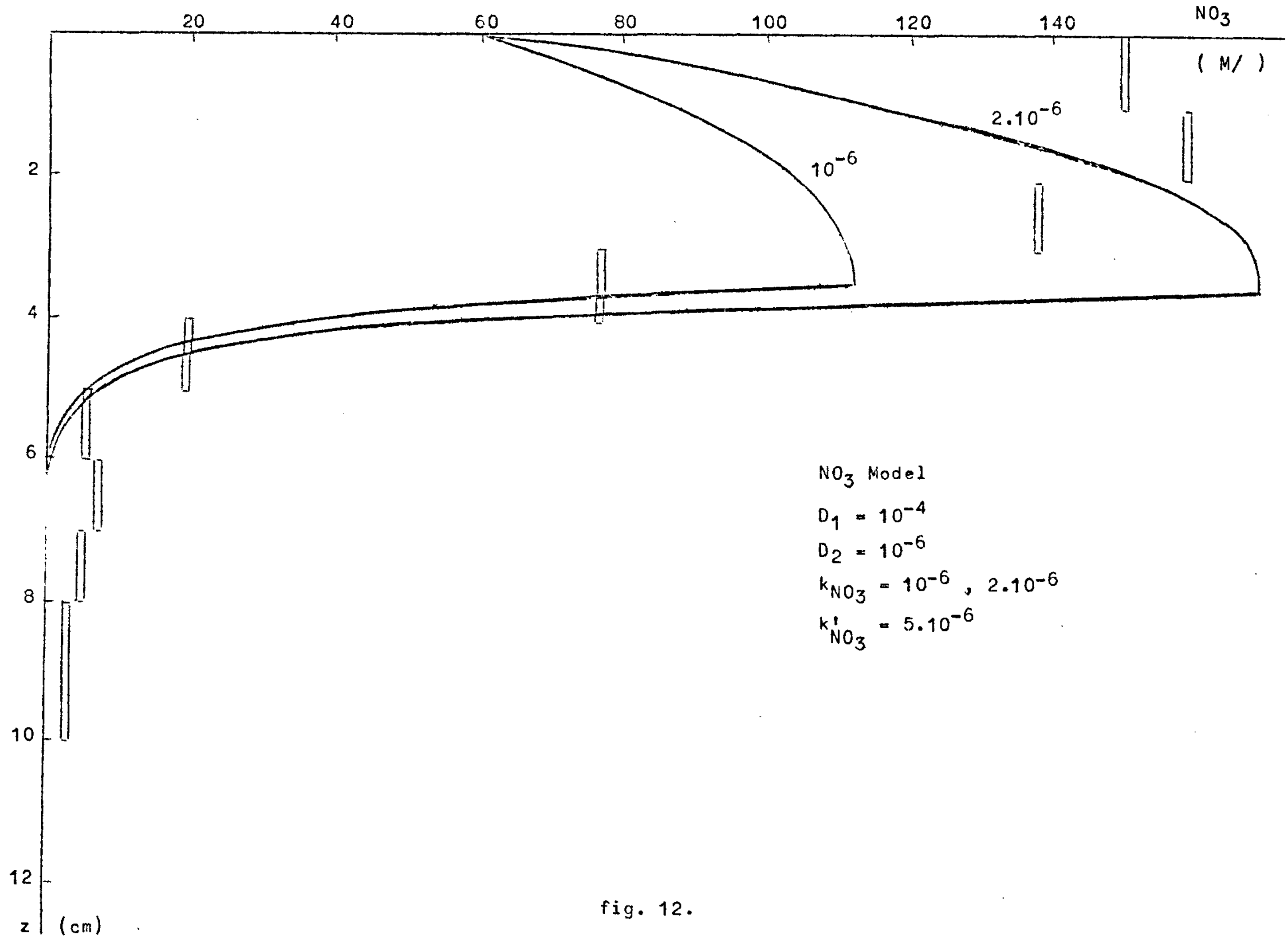


fig. 12.

$\alpha = 0.18$ .

All these values appear realistic when compared with direct measurements of microbiological activities in sediments published in the literature [Sorokin (1962), Billen (1975)].

It should be noticed that the value of $k_{O_2}$ is too low by a factor of 3.5 to satisfy relation (6). This is probably due to the fact that other oxidants can be used in the upper layer, [$MnO_2$ , $NO_3^-$ , $Fe(OH)_3$], and have not been taken into account by the model. If these oxidants are used successively as in the Scheldt estuary [Billen and Smitz (1975)], a multilayer model would be necessary to describe the phenomena. However, experimental results are not yet sufficient to allow such a model to be elaborated.

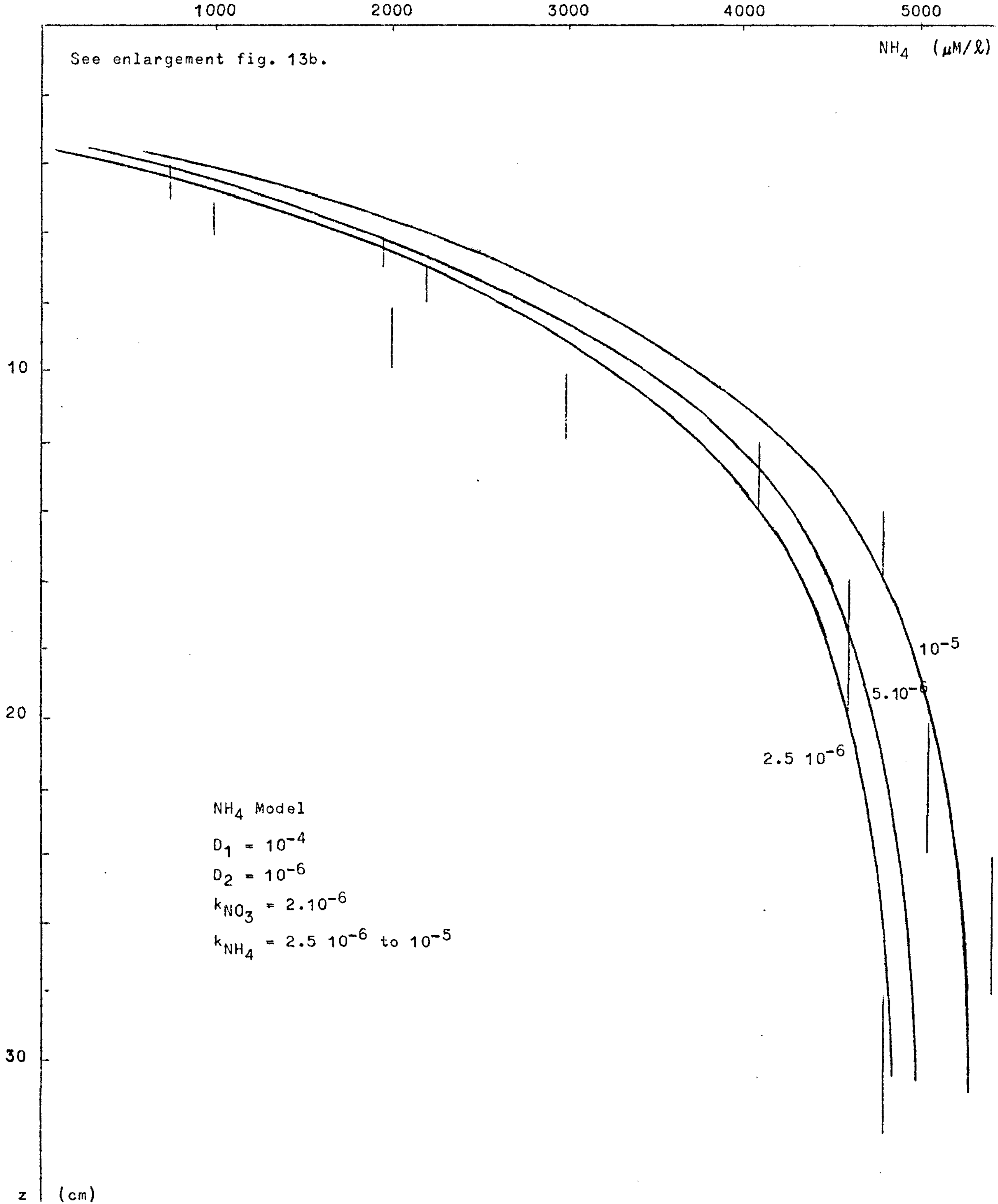

1000
2000
3000
4000
5000
NH$_4$ (μM/ℓ)
See enlargement fig. 13b.
10
20
30
z (cm)
$10^{-5}$
$5.10^{-6}$
$2.5\ 10^{-6}$
NH$_4$ Model
$D_1 = 10^{-4}$
$D_2 = 10^{-6}$
$k_{NO_3} = 2.10^{-6}$
$k_{NH_4} = 2.5\ 10^{-6}$ to $10^{-5}$

fig. 13a.

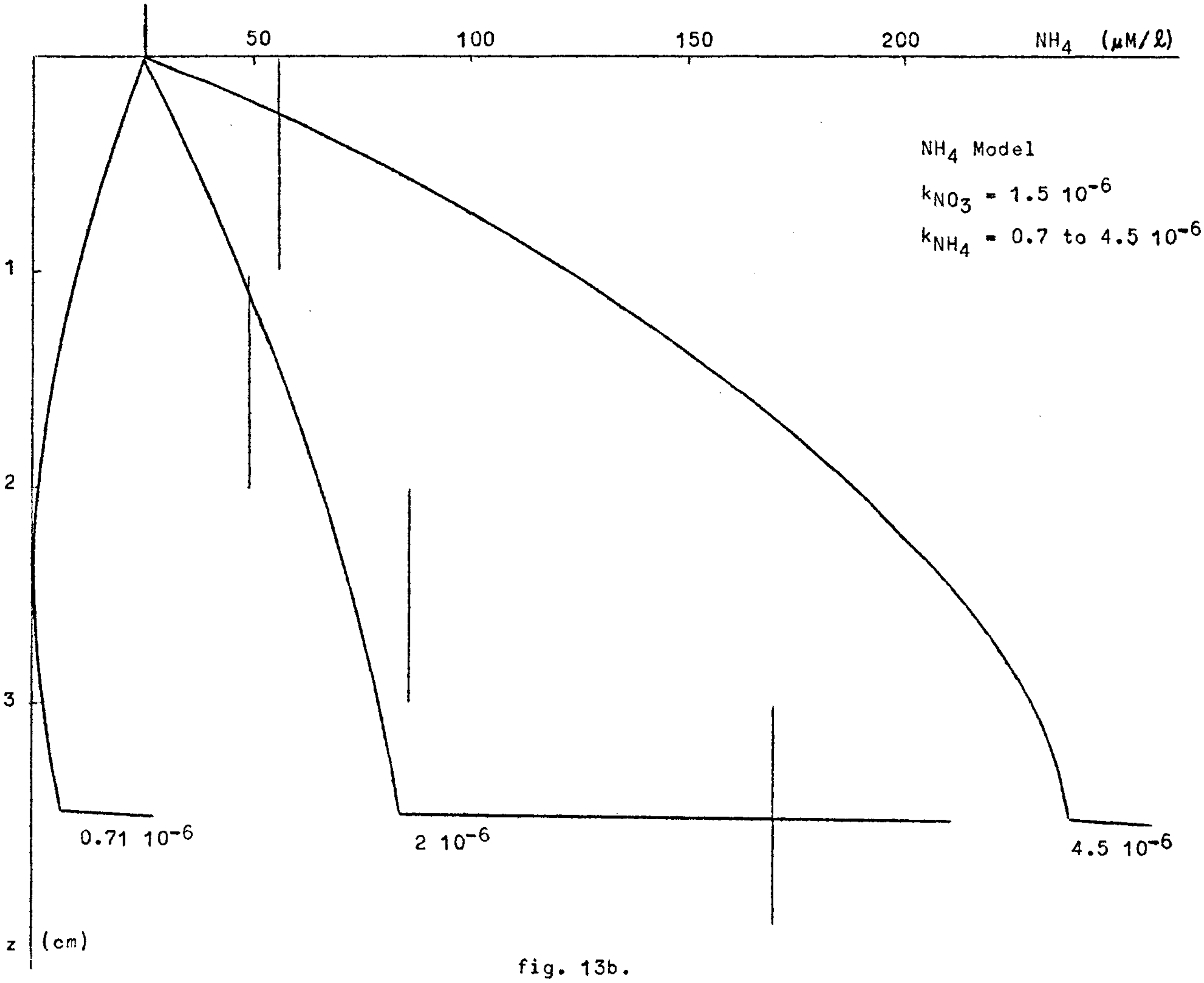


fig. 13b.

The value of the different mass transfers were calculated from the equations of table 1 and the results are represented in fig. 14. As in the case of silica, the contribution of the upper layer is much more important than the one of the underlying sediment. It is probable that the thickness and the influence of the disturbed layer is more important in coastal regions than in the deep ocean, because the existence of this layer is related to appreciable shear stresses or intense biological activity. However, many estimations of fluxes from the pore waters of the sediments are probably underestimated because of the difficulty to recover this layer during the coring. Also, this layer may play an important role in the early diagenetic processes and especially for organic

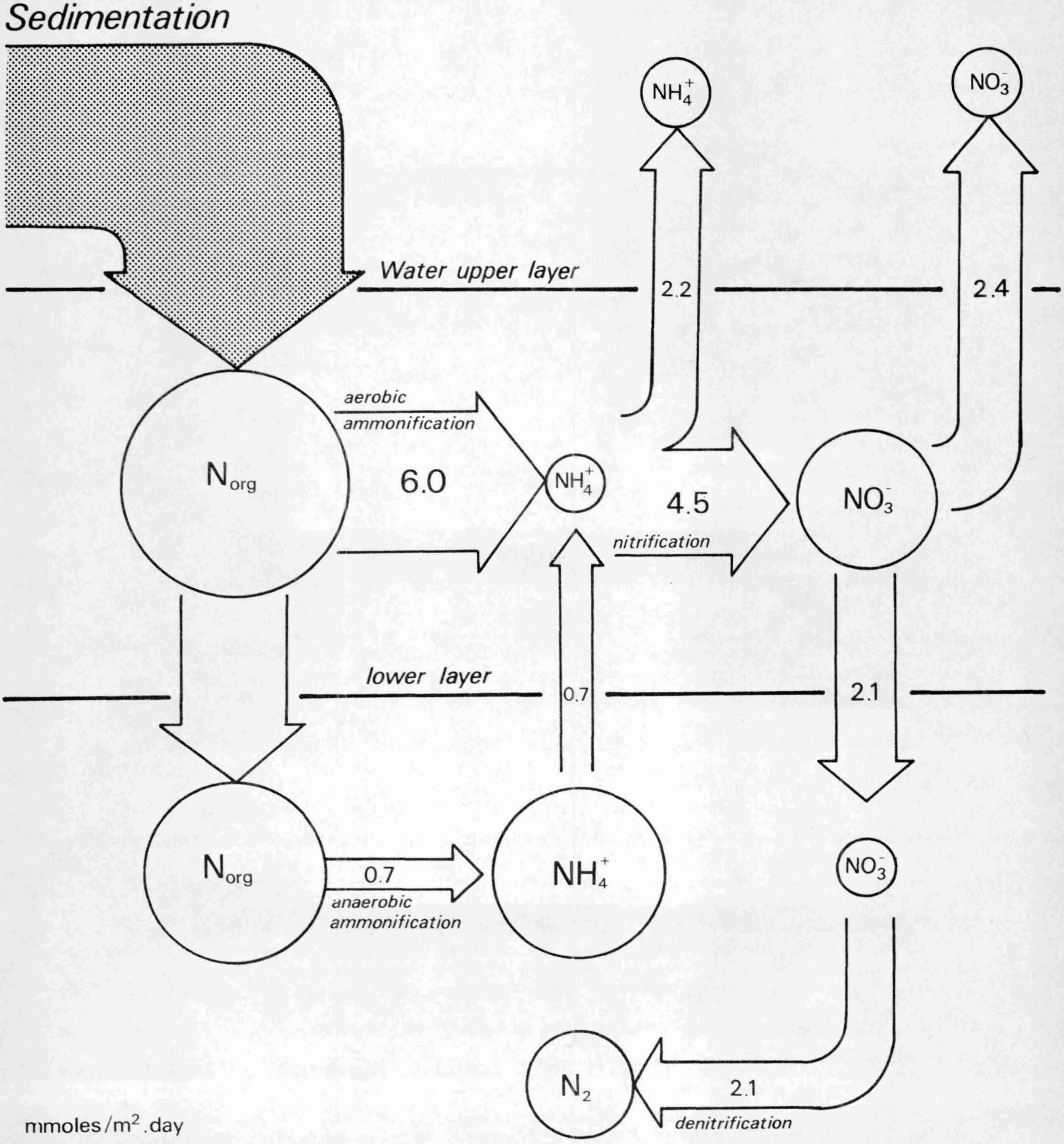

Sedimentation
NH4+
NO3-
Water upper layer
2.2
2.4
aerobic
ammonification
Norg
6.0
NH4+
4.5
nitrification
NO3-
lower layer
0.7
2.1
Norg
0.7
anaerobic
ammonification
NH4+
NO3-
N2
2.1
denitrification
mmoles/m2.day

fig. 14.

matter. It may be assumed that most of the decomposition of the organic matter takes place in this well aerated layer.

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# IV

# Sorption by some North Sea sediments

by

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The sorption properties of about seventy soil samples of the thousand points system were investigated up to now by means of four radioisotopes, namely $Cs^{137}$ , $(Cs^{134})$ , $Co^{60}$ , $Mn^{54}$ and $Cd^{109}$ . Similar tests with $Zn^{65}$ are now being conducted actively. The methods and measuring systems used have been described in previous reports. Special attention was devoted to non-sandy samples which explains why most of the samples investigated derive from the South of the survey network and toward to coast. Figure 1 shows the specimens examined and their place within the thousand points system. About thirty new samples are being investigated in order to obtain a better spread over the entire area under survey. To note that further toward the sea, the samples become increasingly sandy and the values for capacities and coefficients of distribution decrease significantly. As already premised in previous reports, the sediments rich in clay and silt are actually the only ones featuring high values for sorption. However, the contribution of sandy samples to sorption may not be neglected considering that these soils cover much larger surfaces.

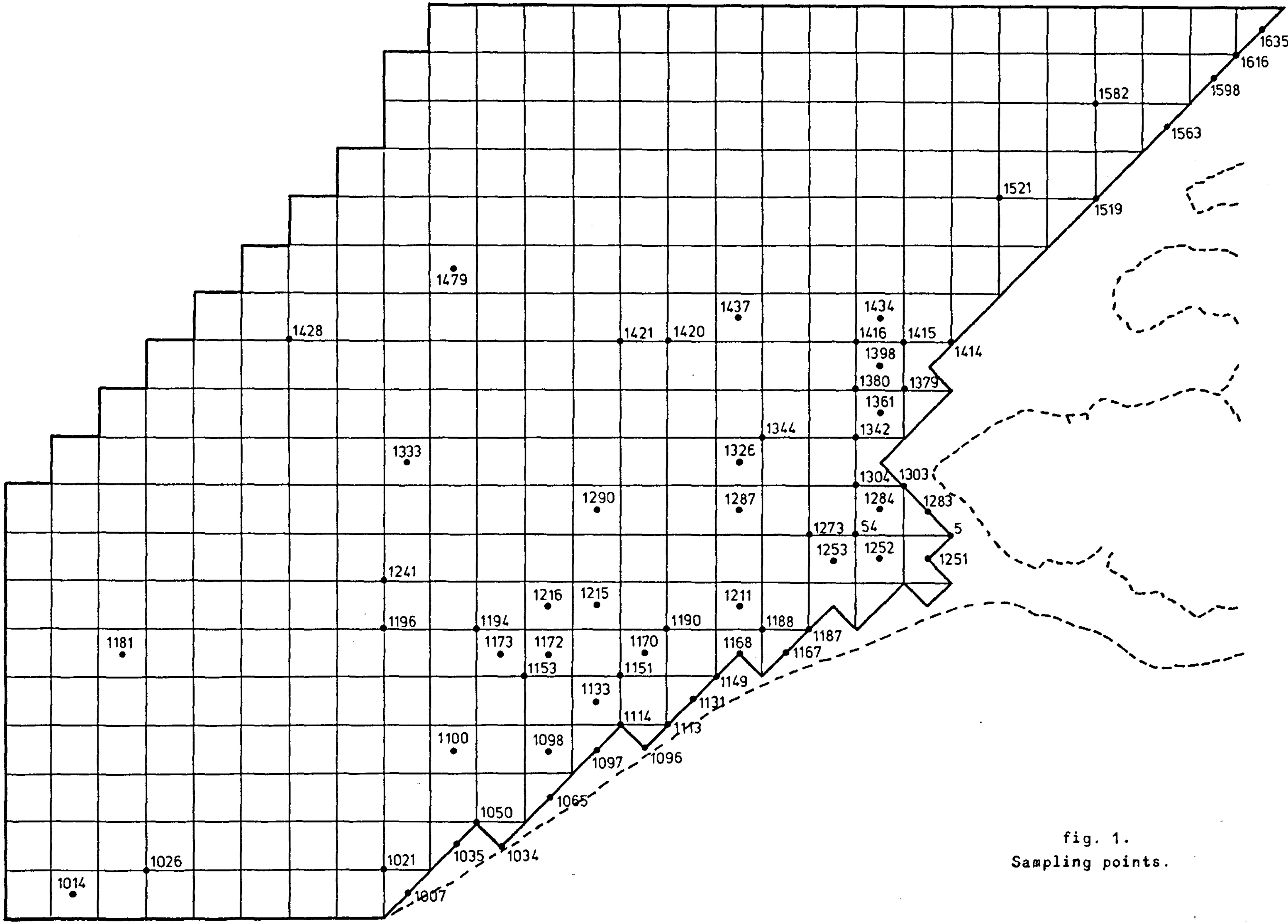

fig. 1.
Sampling points.

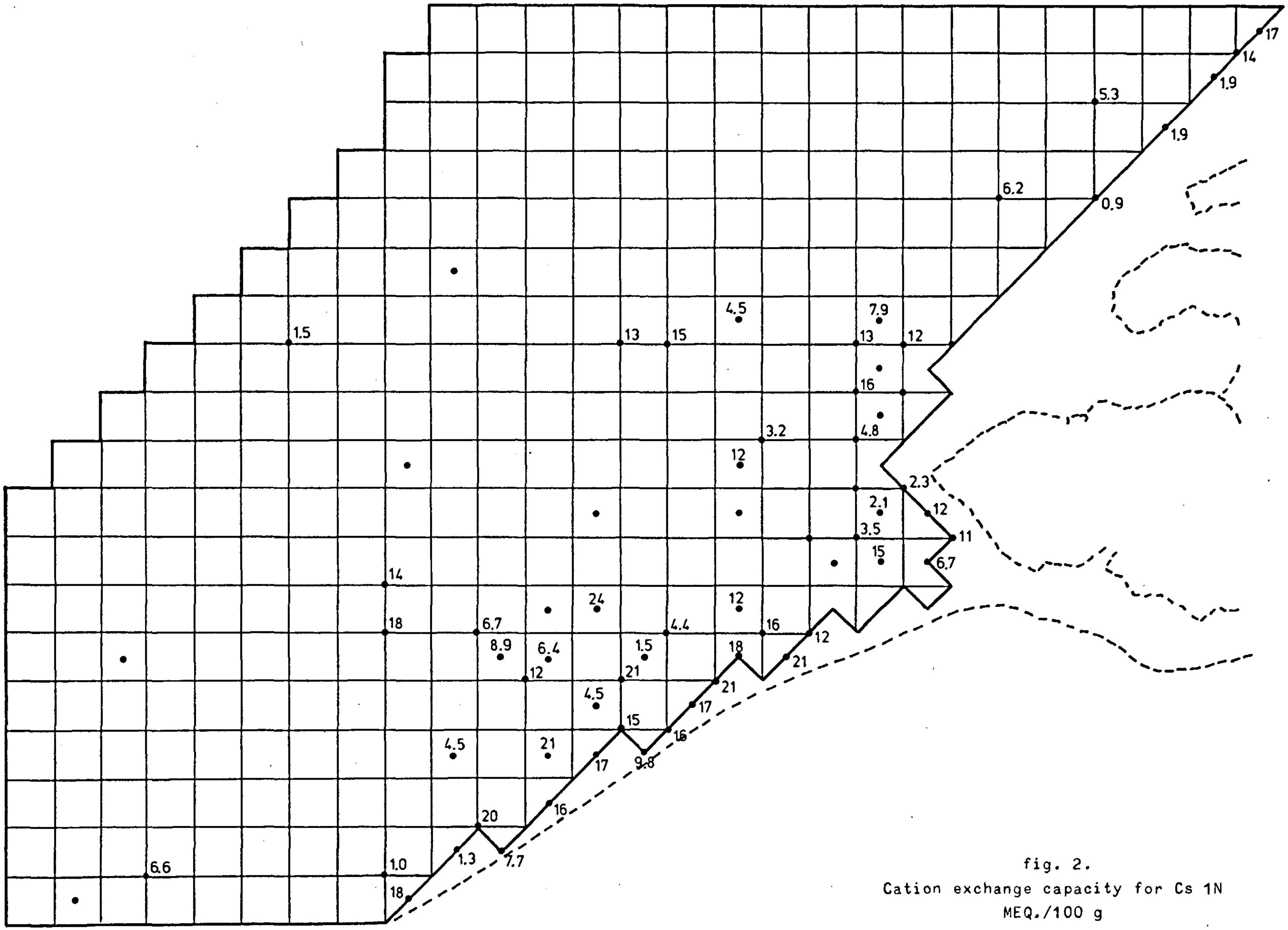

fig. 2.
Cation exchange capacity for Cs 1N
MEQ./100 g

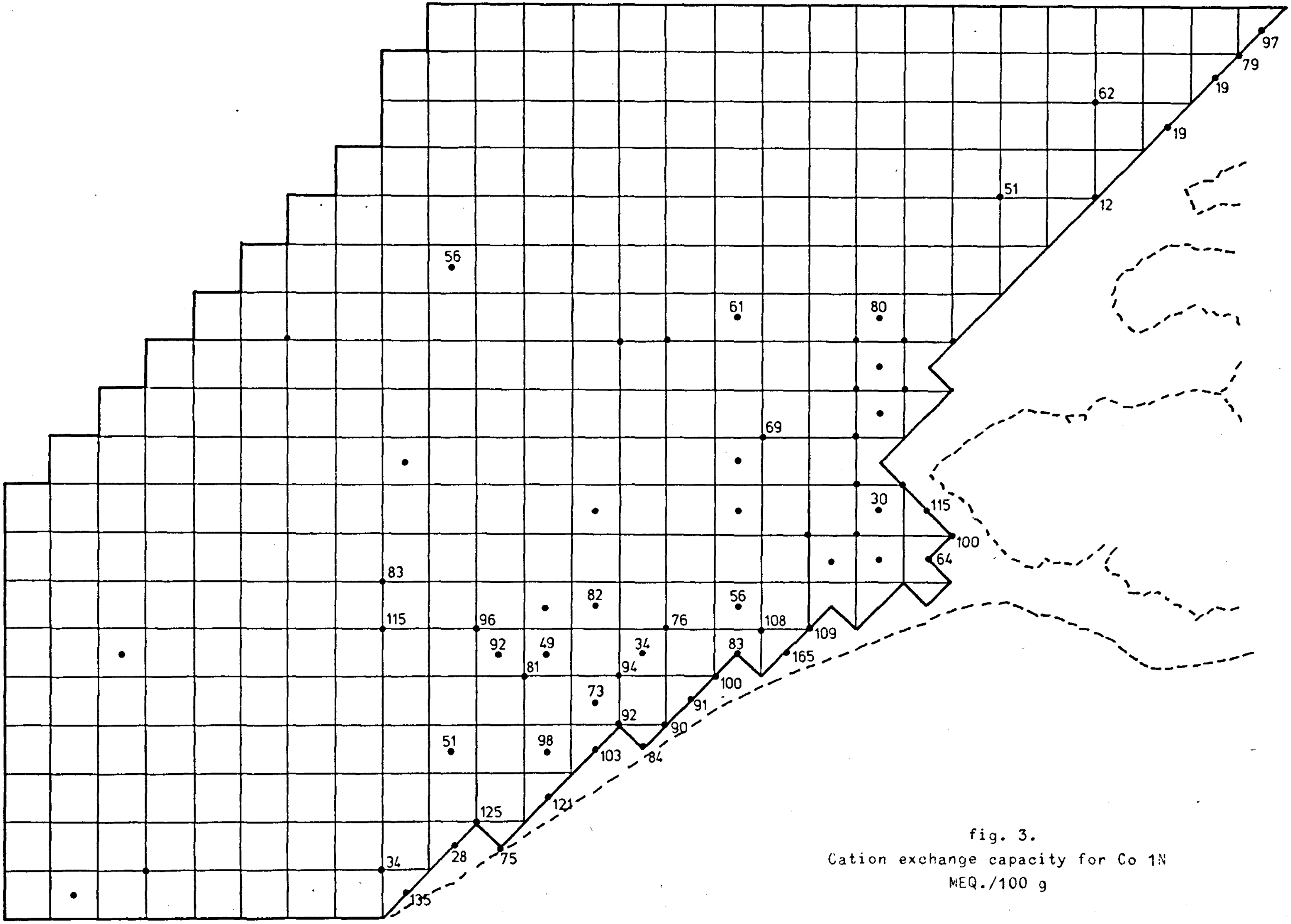

fig. 3.
Cation exchange capacity for Co 1N
MEQ./100 g

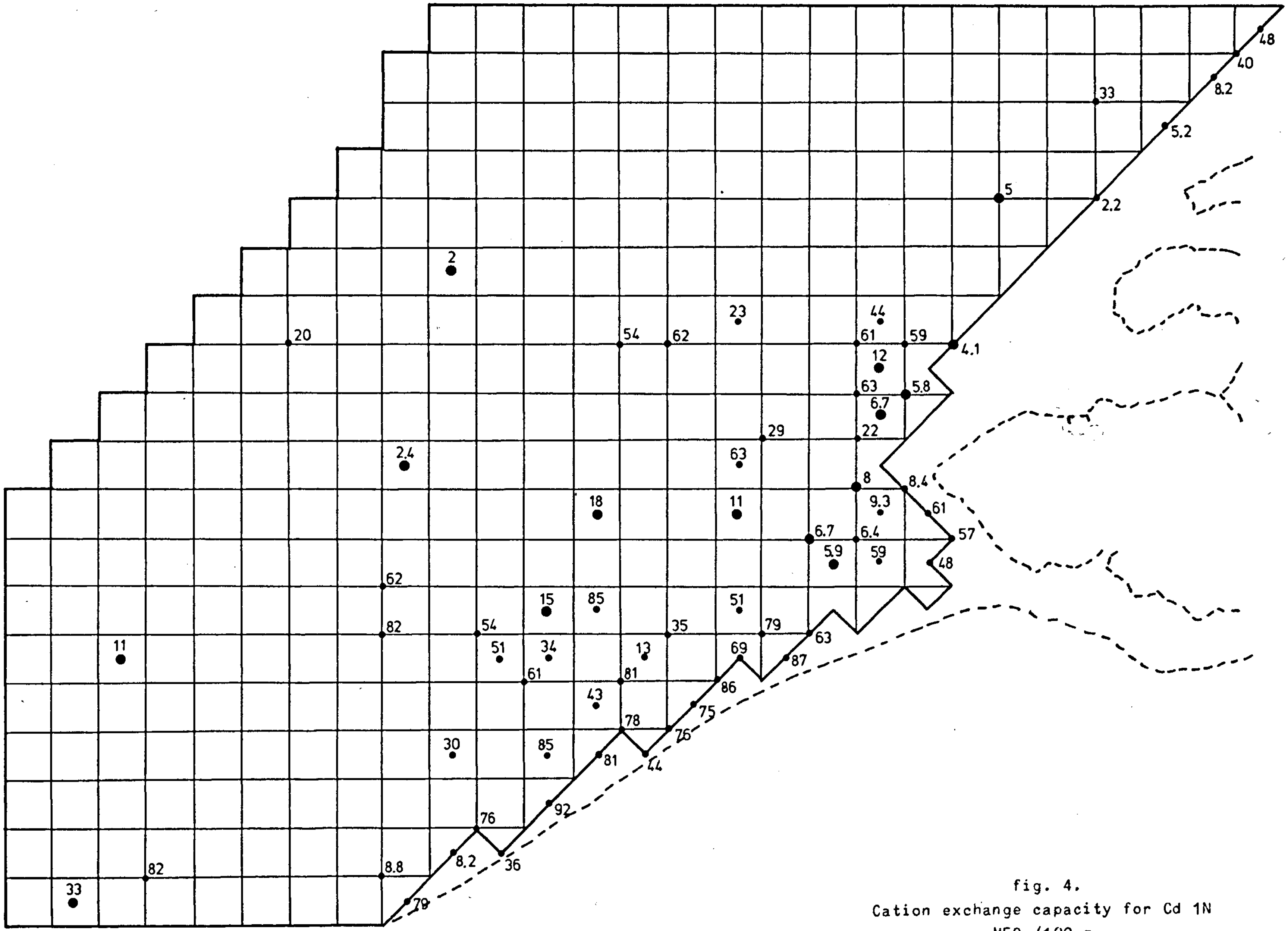

fig. 4.
Cation exchange capacity for Cd 1N
MEQ./100 g

Figures 2, 3 and 4 show the capacity Q of the specimens with respect to the various elements. The capacity of most specimens has been determined by means of the fraction $< 150\ \mu$ . For some sand-containing specimens we were forced to apply fraction $< 300\ \mu$ because, otherwise, we would have had no material left. These latter mostly present much lower capacity values.

A comparison of the capacity between the various elements has taught us that we may classify the elements in the following order of decreasing capacity with respect to soil specimens :

$$\mathrm{Mn} \gg \mathrm{Co} > \mathrm{Cd} \gg \mathrm{Cs}\ .$$

There is a definite difference between monovalent and bivalent radio-isotopes where their capacities are concerned. While with Cs , Co and Cd the capacities of sandy samples are small ($< 0.1$ meq/g) , they remain for all samples with $\mathrm{Mn} > 0.6$ meq/g . This shows that with Mn there is surely another phenomenon than the exchange of ions. With Co we determine the largest relative dispersion of the capacity values and with Cs we find the smallest differences.

These capacity values do not offer an accurate picture of what may actually take place on the ocean bottom. They only offer the possibility to fix specific elements under extreme conditions (1 N solution!) from the sediment.

Figures 5, 6, 7 and 8 show distribution constants $K_d$ . The following indications have been used : (∘) fraction $< 150\ \mu$ and (o) fraction $< 300\ \mu$ of the specimen.

These distribution constants offer a truer picture of what may occur in seawater upon contact with sediments. They have been determined in seawater and with respect to the element in tracer quantities. They show the distribution of the element concerned between the solid and the fluid phase.

The coefficients of distribution determined in sea-water show the following picture for the various radio-isotopes :

$$\mathrm{Co} \geq \mathrm{Cs} \gg \mathrm{Cd} \geq \mathrm{Mn}\ .$$

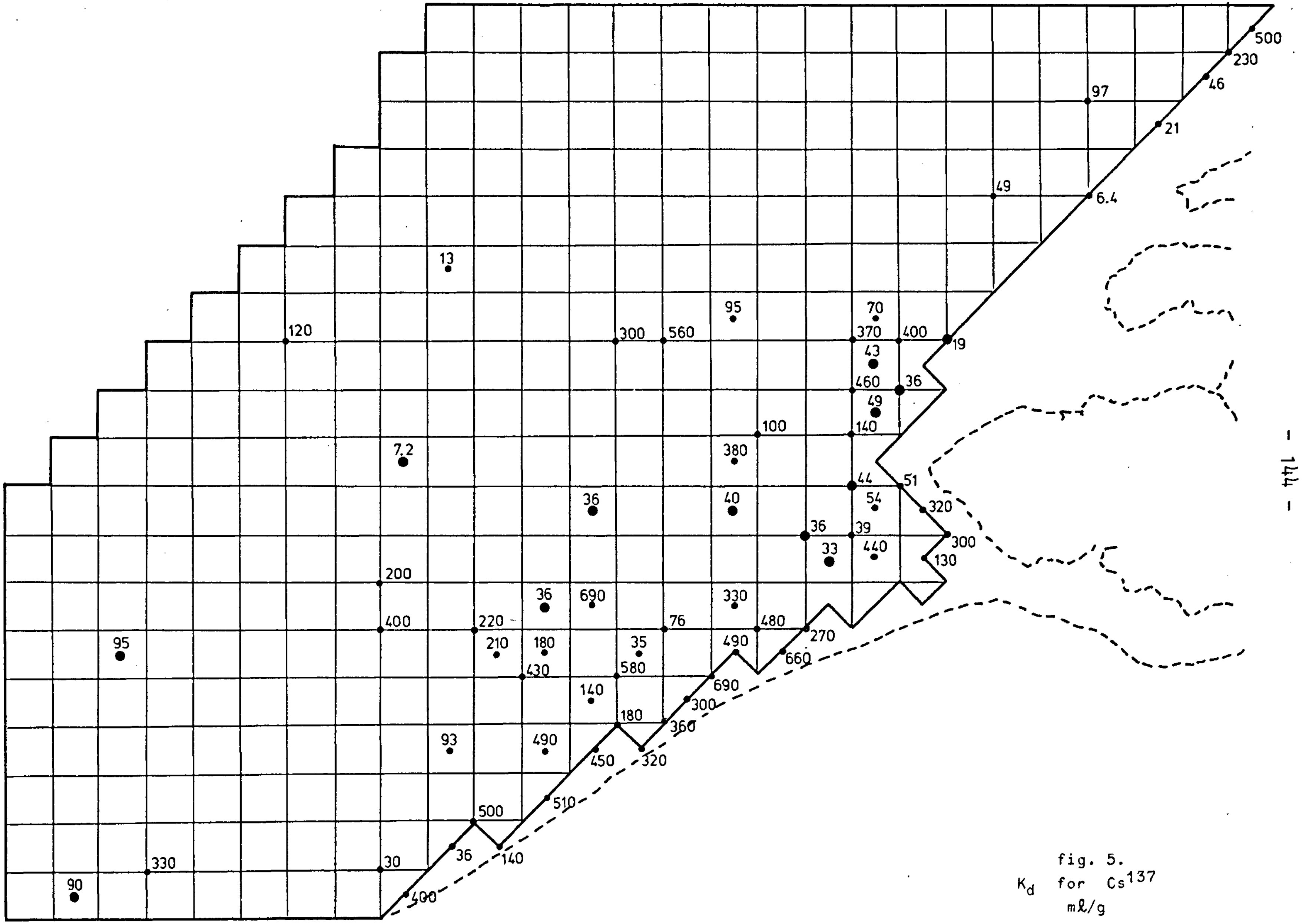

fig. 5.
$K_d$ for $Cs^{137}$
mℓ/g

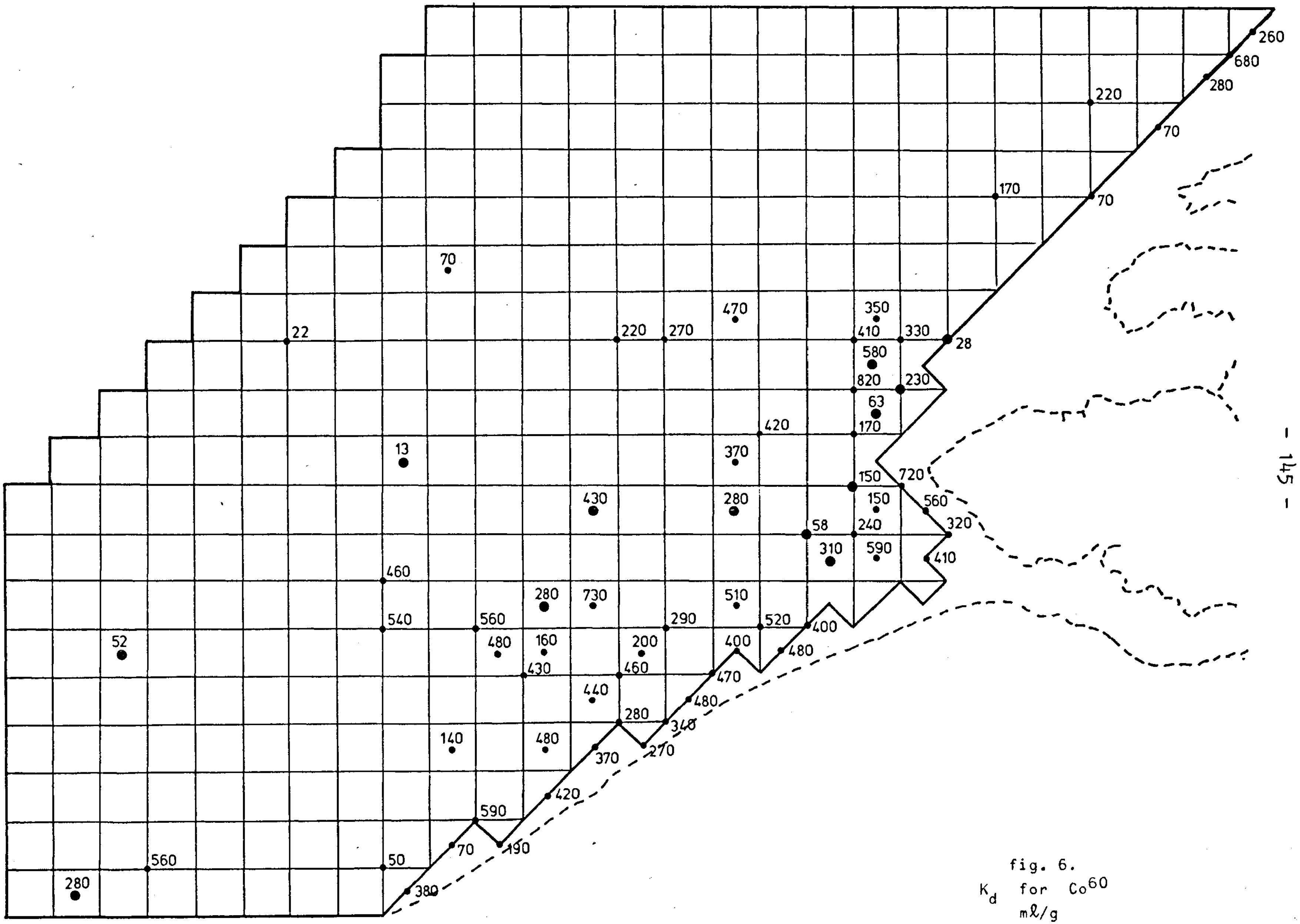

fig. 6.
$K_d$ for $Co^{60}$
mℓ/g

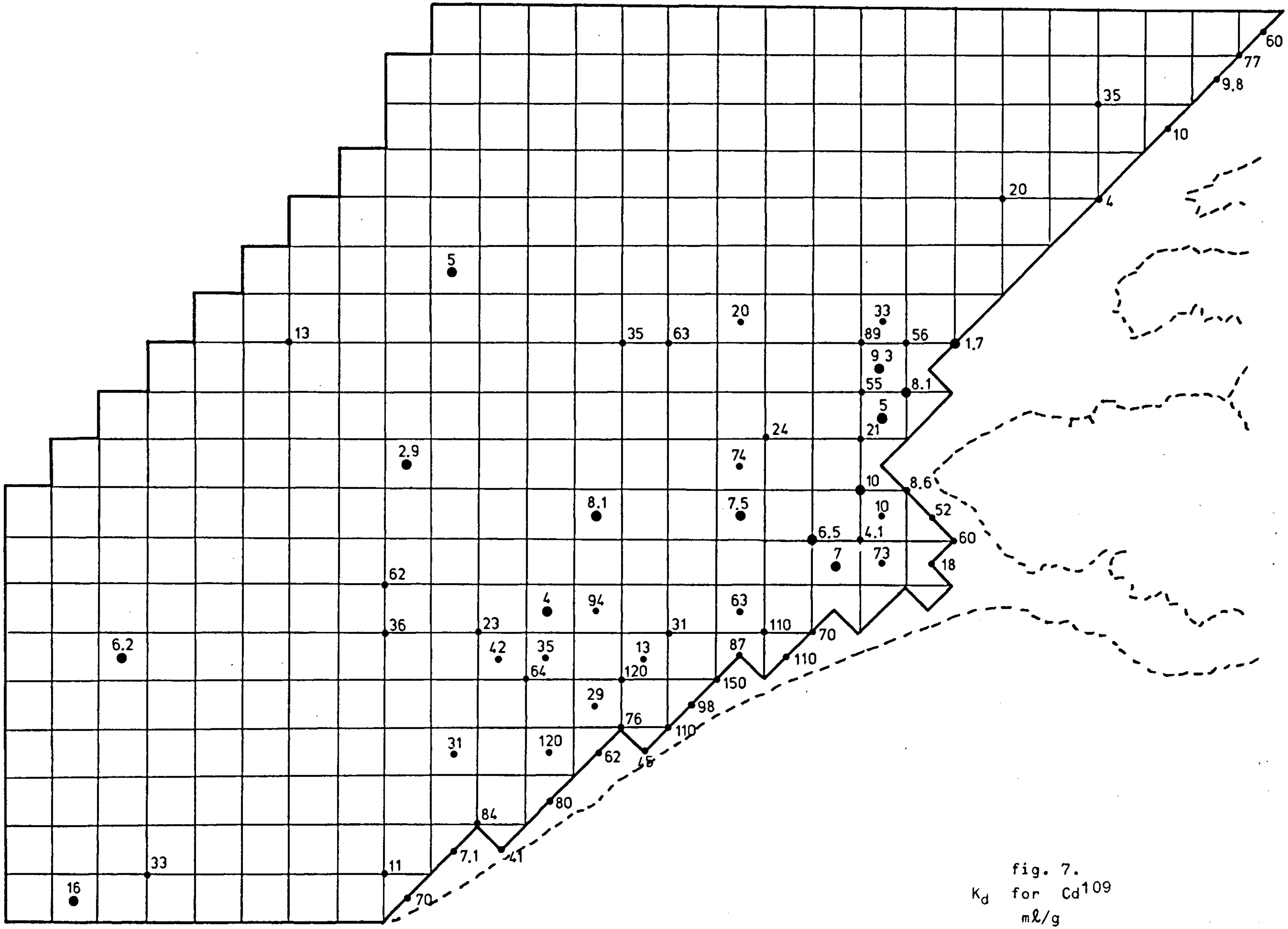

fig. 7.
$K_d$ for $Cd^{109}$
mℓ/g

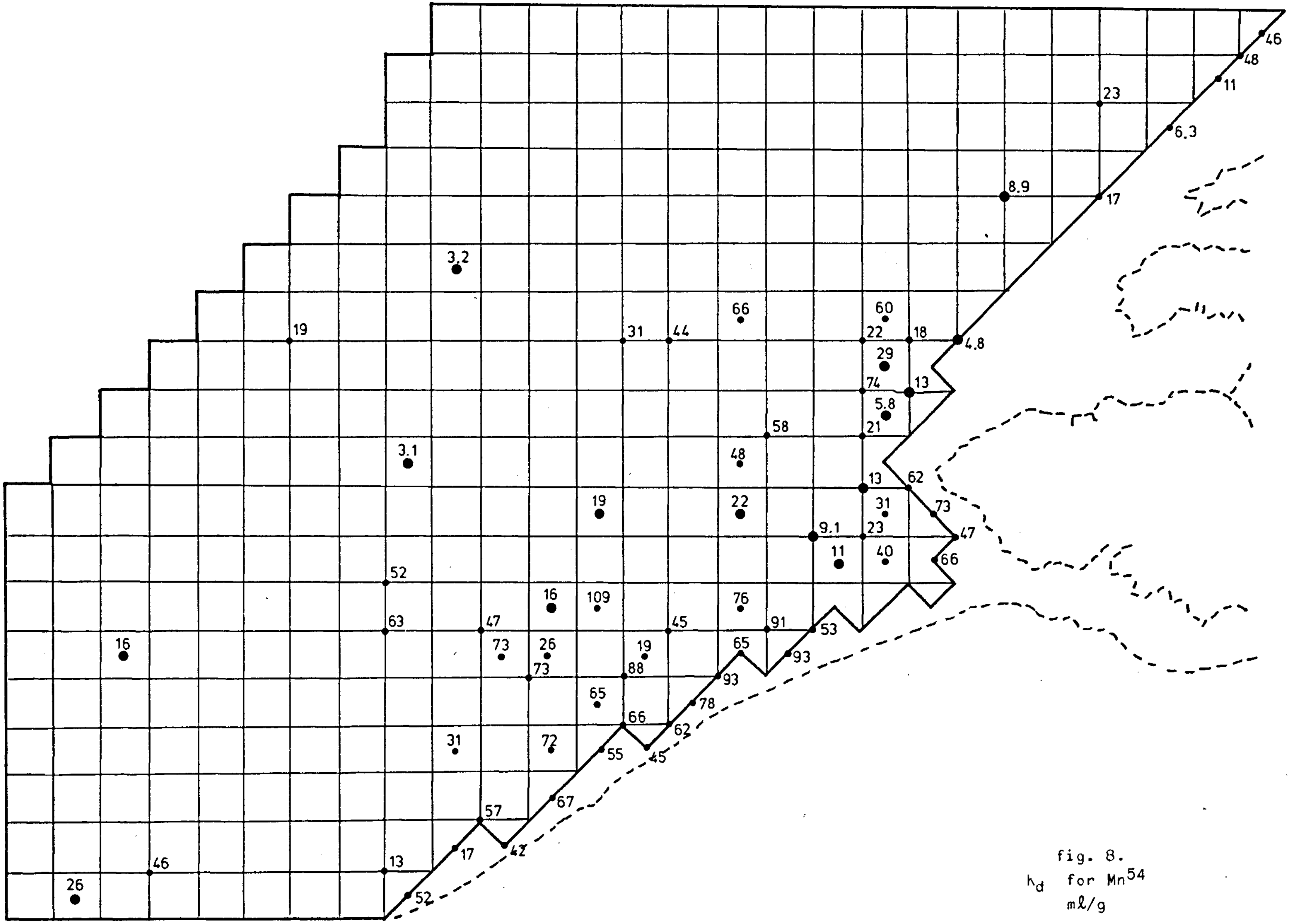

fig. 8.
$h_d$ for $Mn^{54}$
$m\ell/g$

With all ions we determine for definitely sandy samples small $K_d$ values ($K_d < 50$) , while for samples rich in clay and silt these values increase to 100 with Mn and Cd , and to 600 with Co and Cs . Considering the number of specimens examined and the considerable differences in soil structure, it will remain impossible, however, to indicate areas on the maps. This explains why the maps show but the value determined at that specific point.

When we compare the values measured with regard to capacity and $K_d$ for one and the same ion, we note a certain connection determined

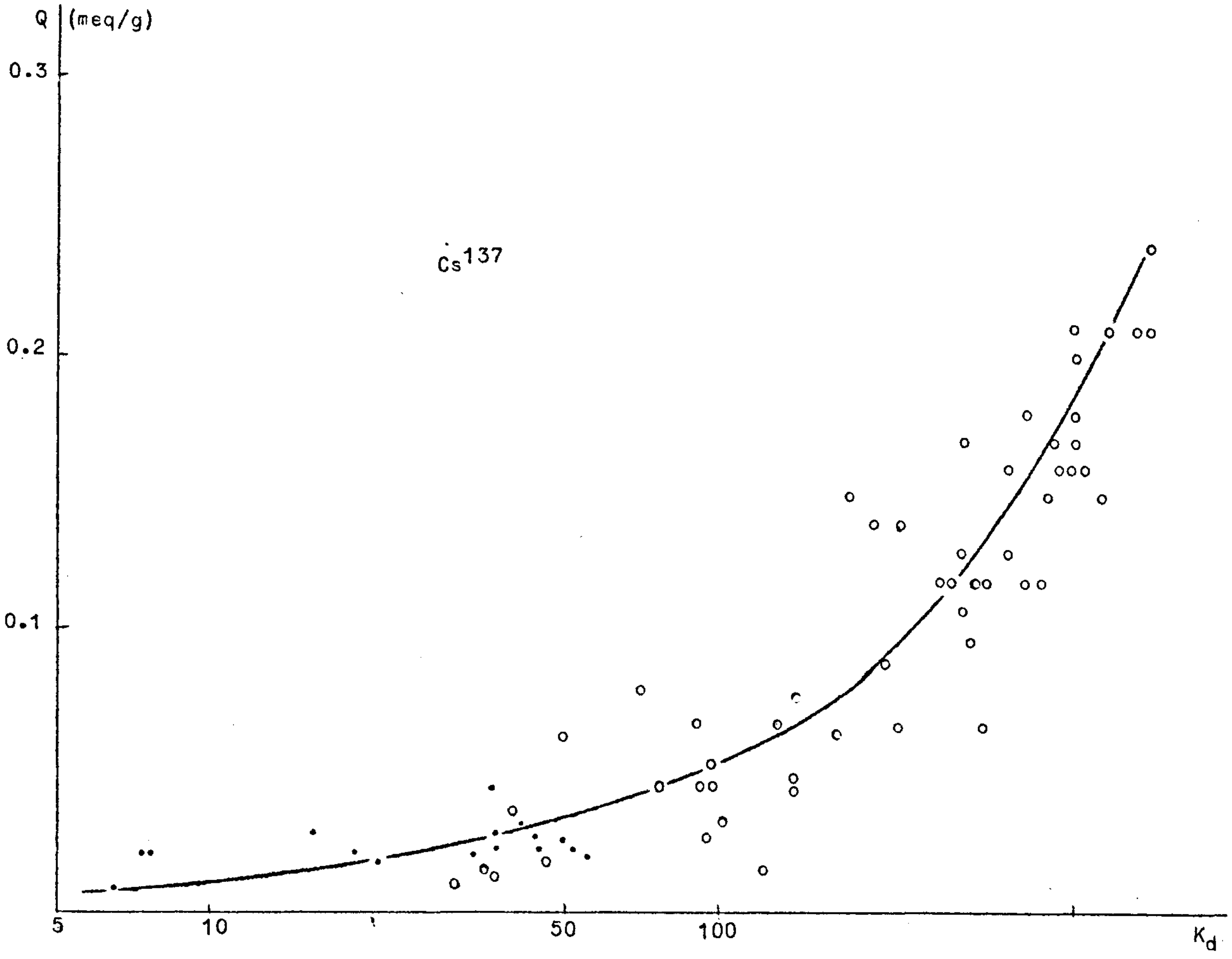

fig. 9.

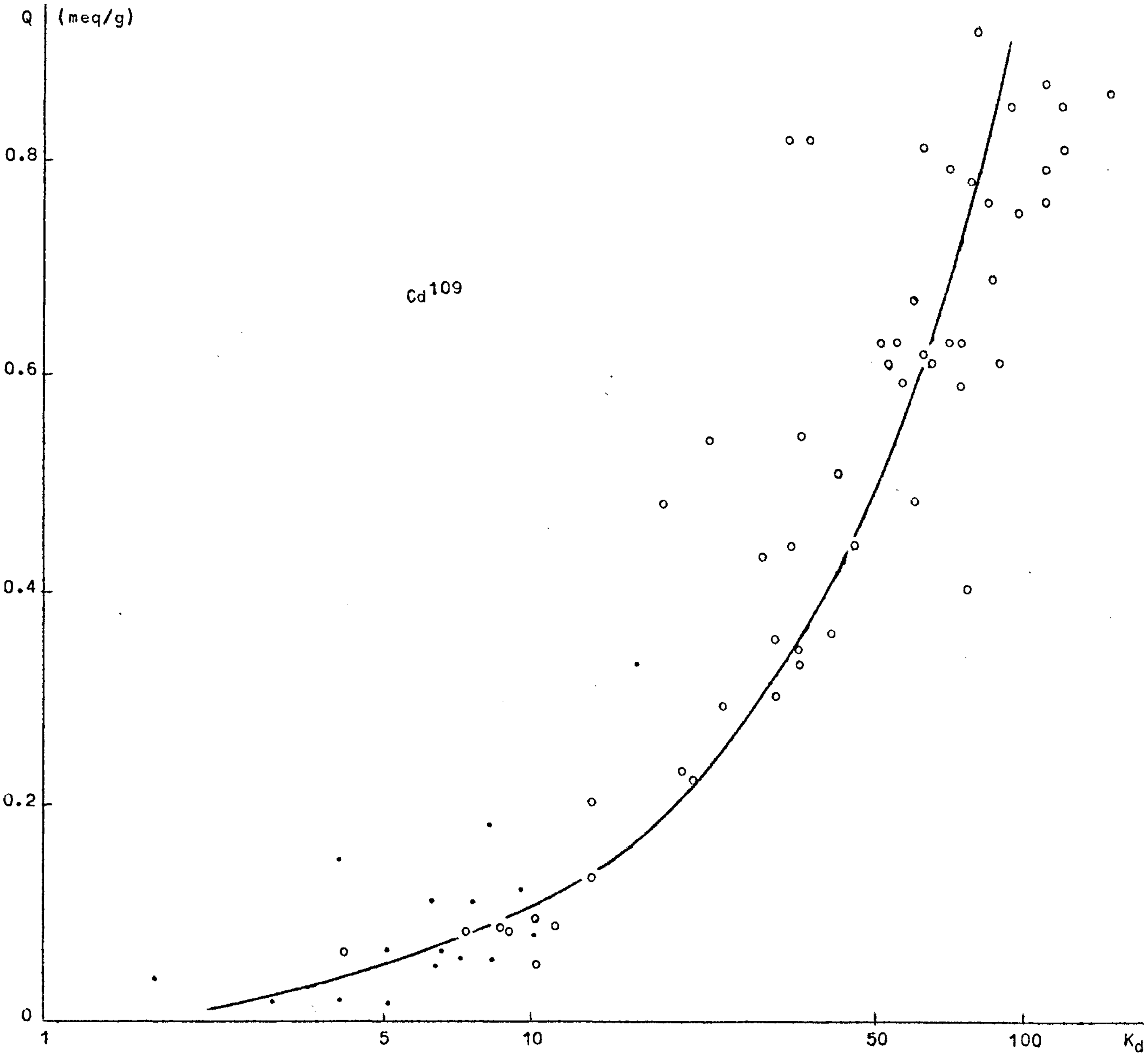

fig. 10.

between both quantities only with Cs and Cd (fig. 9, 10). With Co and Mn there actually seems to be no connection (fig. 11, 12). Investigations conducted by Duursma (1973) on soil samples from all over the

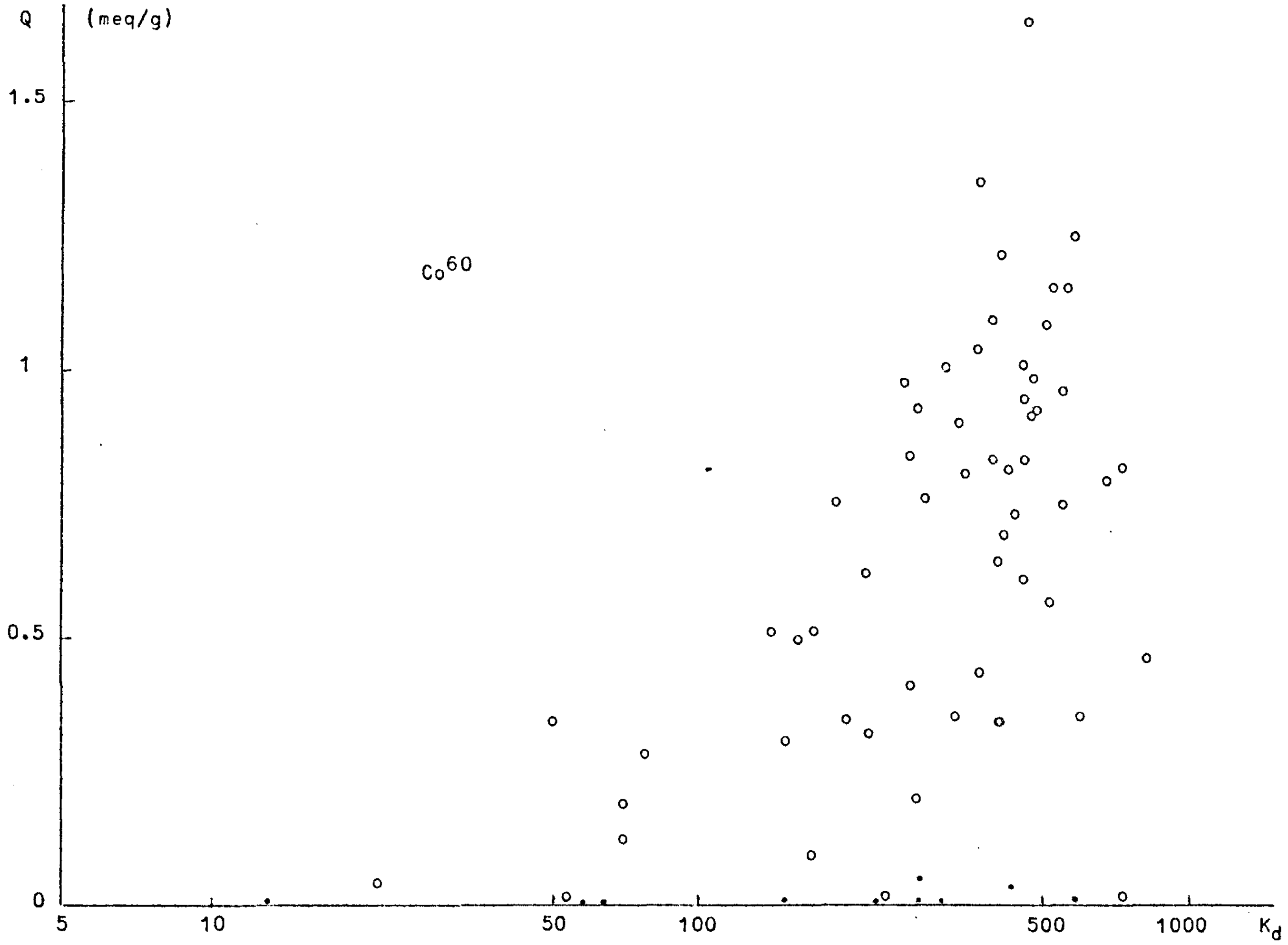

fig. 11.

world lead to the same result where Cs is concerned. They determine a connection with Zn too.

Our determinations with $Zn^{65}$ are still being conducted but already they point in this direction too. He did not investigate $Cd^{109}$ . We also find a certain correlation to exist between the capacity and the $K_d$ determined with Cd and Cs for one and the same sample. Duursma, too, determines no connection between $K_d$ and Q with Co and Mn . For this reason and based on sorption reaction speed determinations he concludes that there can be an exchange of ions only with Cs

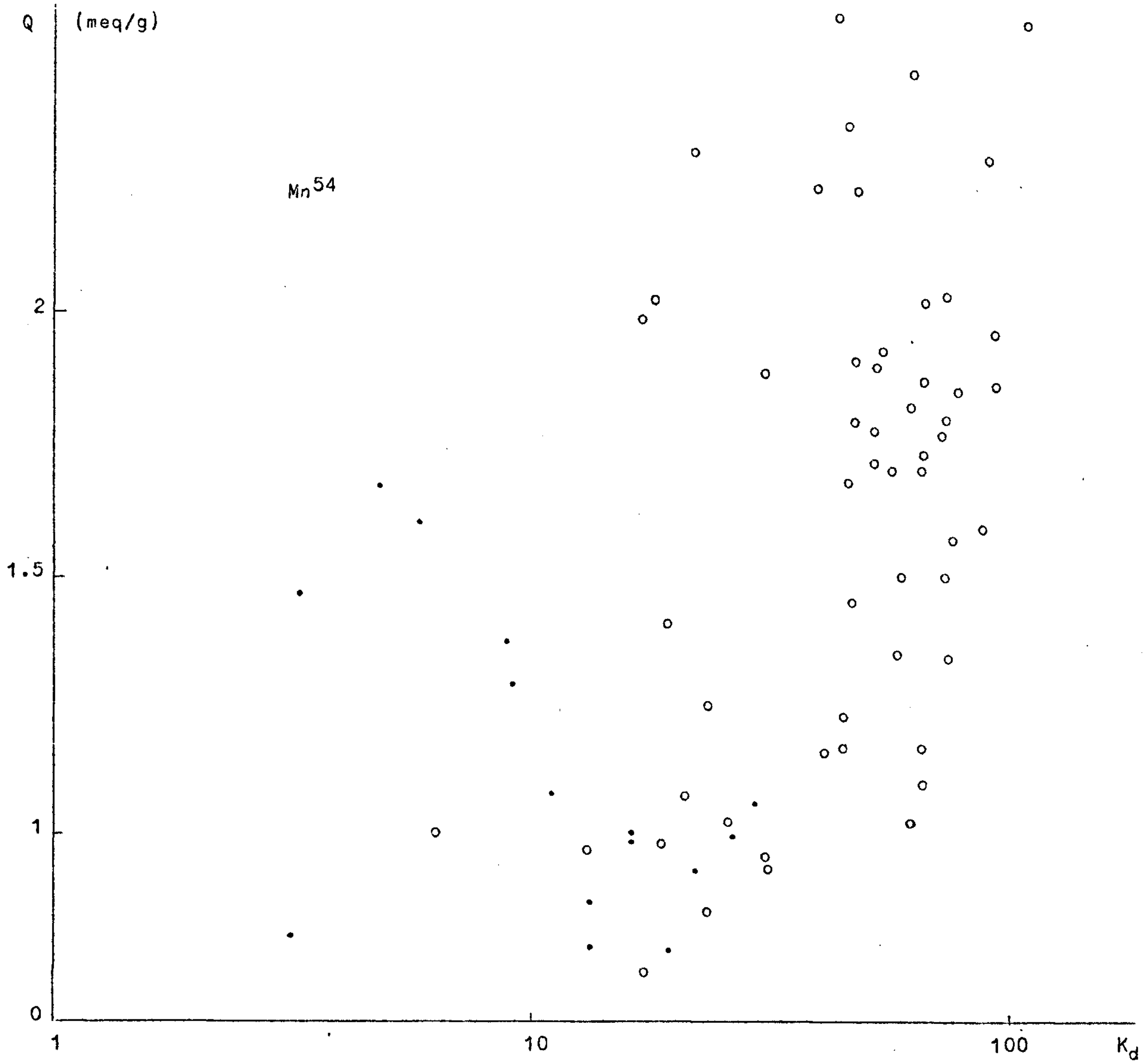

fig. 12.

and Zn while different mechanisms play a more important part for the other radio-isotopes (precipitation, isotopic exchange, complex formation, ...). The speed of the sorption reaction which supplies an indication for the sorption mechanism will be further investigated in order to check the possibilities proposed by Duursma.

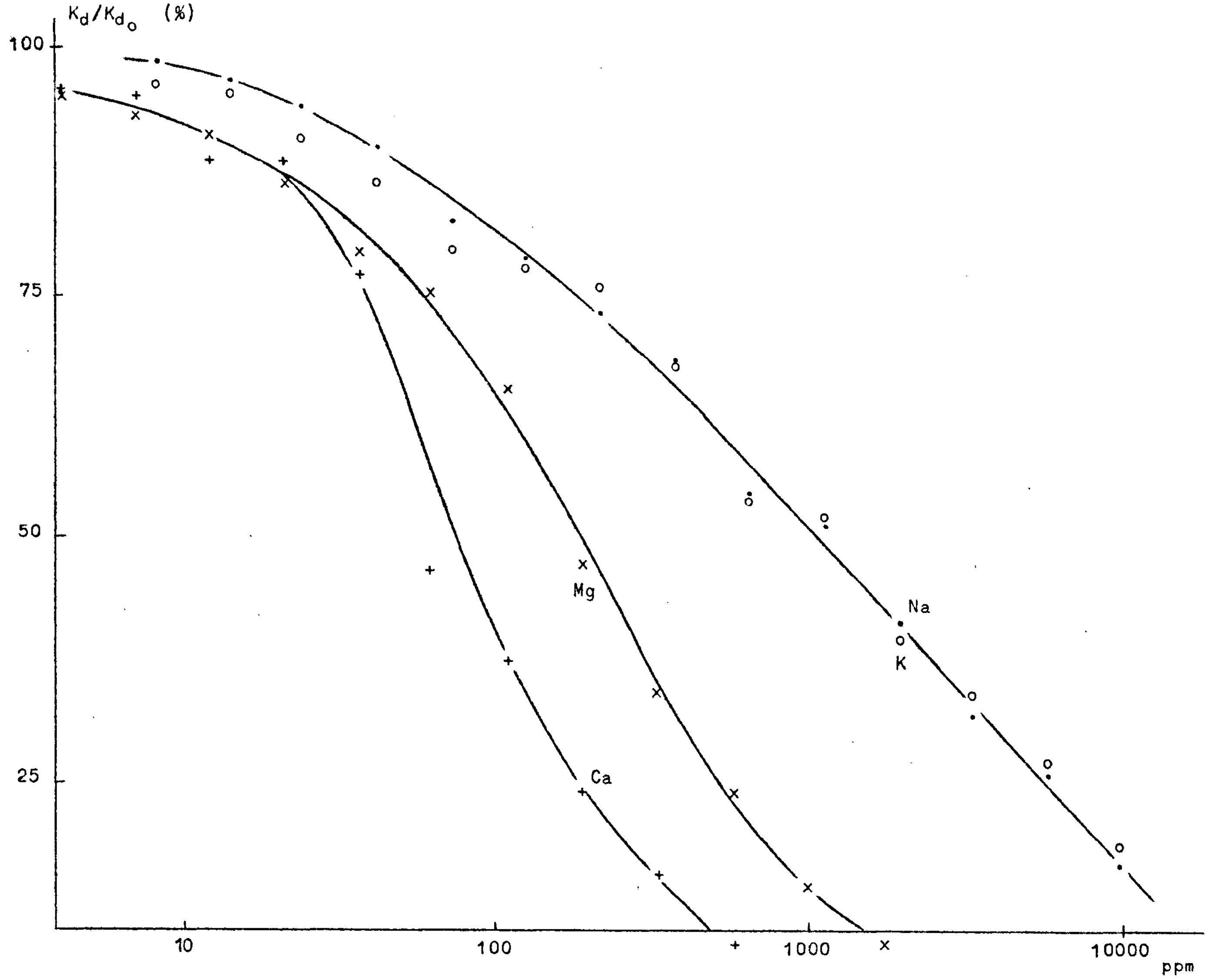

fig. 13.
$Cd^{109}$ Sorption versus competing cation concentration.

The influence of other ions (Na , K , Ca and Mg) on the sorption of Cd , Co and Mn was investigated. While with Cs (*cf.* 1973/Sed.-Synthesis 01) it was mostly Na and K that caused a significant decrease of $K_d$ whereas Ca and Mg had lesser influence, conditions are different where bivalent radio-isotopes are concerned. With $Cd^{109}$ the differences between monovalent and bivalent ions are much less pronounced. Ca and Mg have a greater influence here as

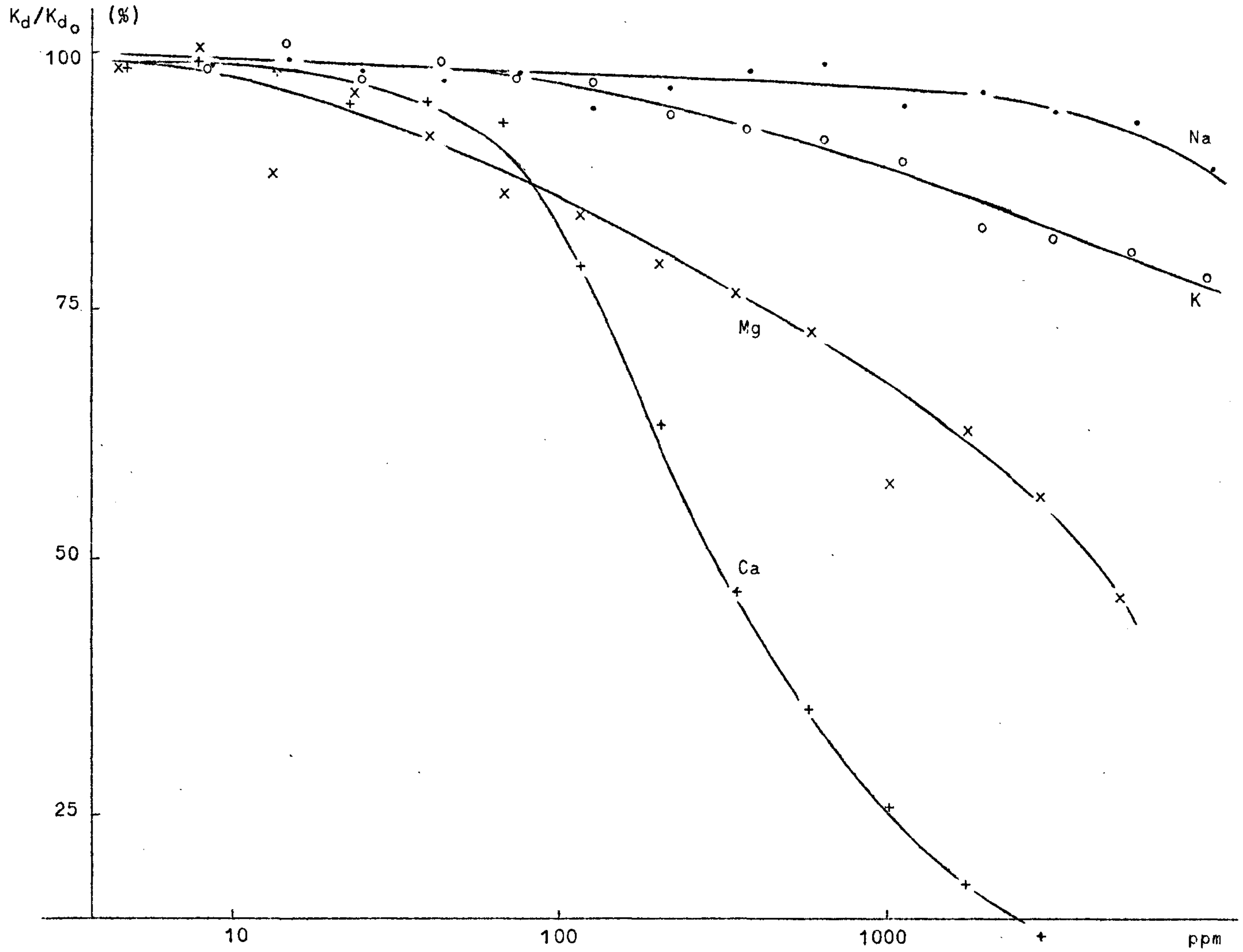

fig. 14.
$Co^{60}$ Sorption versus competing cation concentration.

compared to Na and K . We have the same picture again with the sorption of $Mn^{54}$ and $Co^{60}$ where the influence of Na and K is considerably decreased (fig. 13, 14, 15).

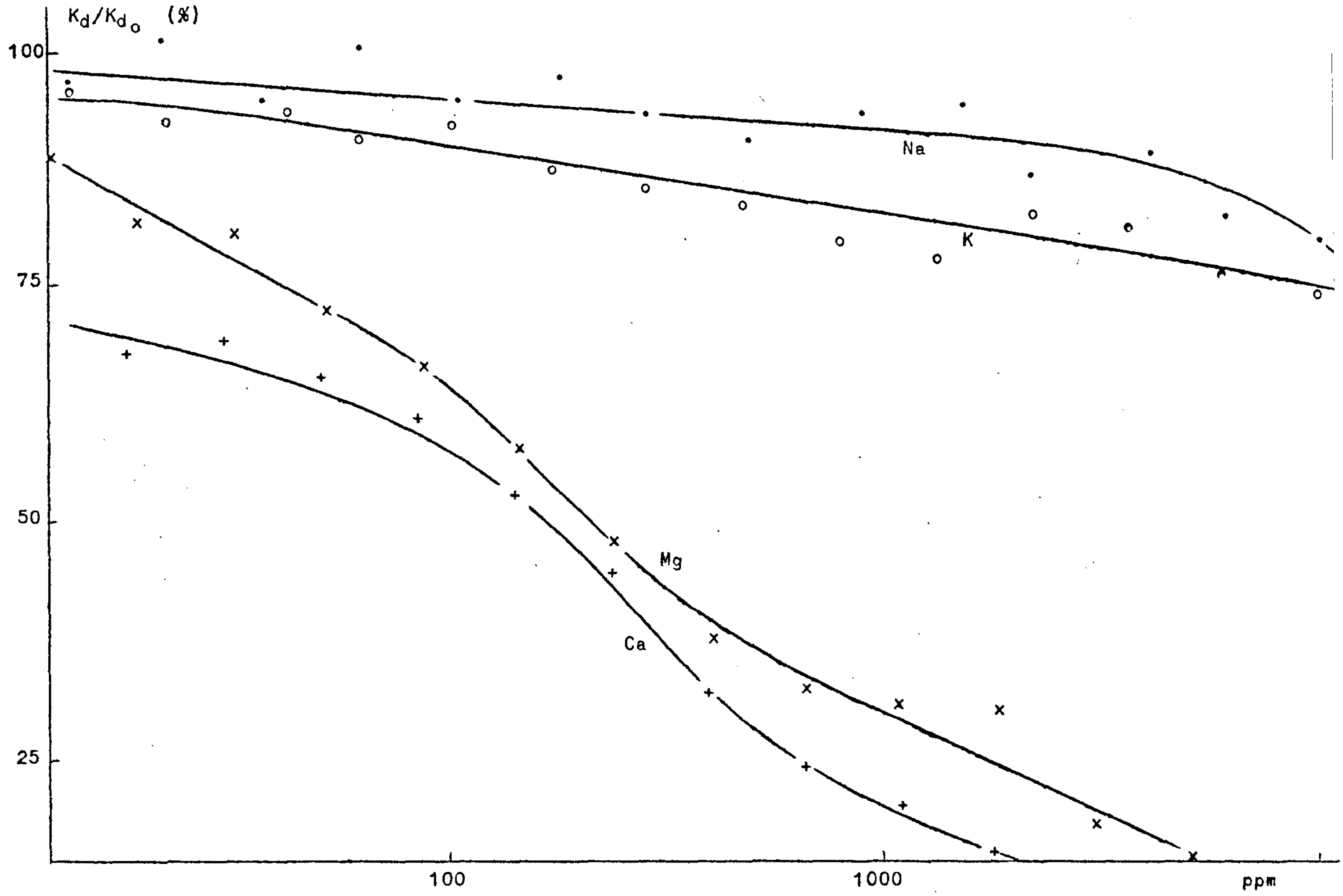

fig. 15.
$Mn^{54}$ sorption versus competing cation concentration.

In order to bridge the gap existing between capacities determined by 1N solution and distribution constants determined by tracer quantities, we determined in seawater the $K_d$ for five specimens with an increasing concentration of the same ion. With $Mn^{54}$ , $Co^{60}$ and $Cd^{109}$ this influence is much smaller than with $Cs^{137}$ which also points to other reaction mechanism than a pure exchange of ions (fig. 16, 17, 18, 19).

There will be further investigation to determine a possible connection with the granulometric data of the soil samples as collected by

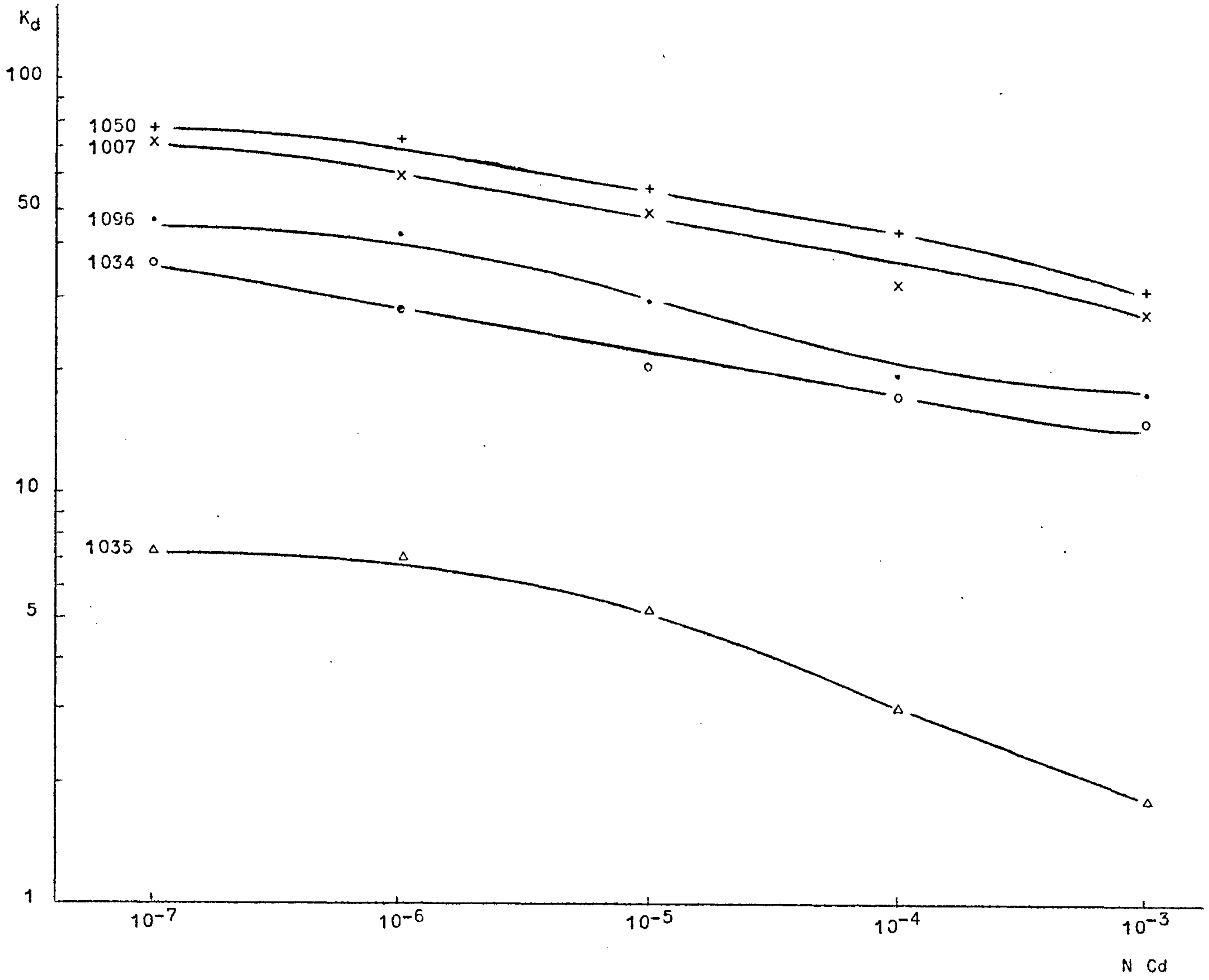

fig. 16.
$Cd^{109}$ sorption versus Cd concentration.

Prof. Gullentops' research team. The average diameter as well as the quantity of clay and silt in the samples appear to be the most appropriate parameters for this purpose. Other investigations will determine possible influence by the lime contents and by the organic material.

The tests proposed and worked out by Duursma for the purpose of determining the cleaning effect produced by suspensions on the radioactive solutions and the pertaining values of Kd will also be conducted

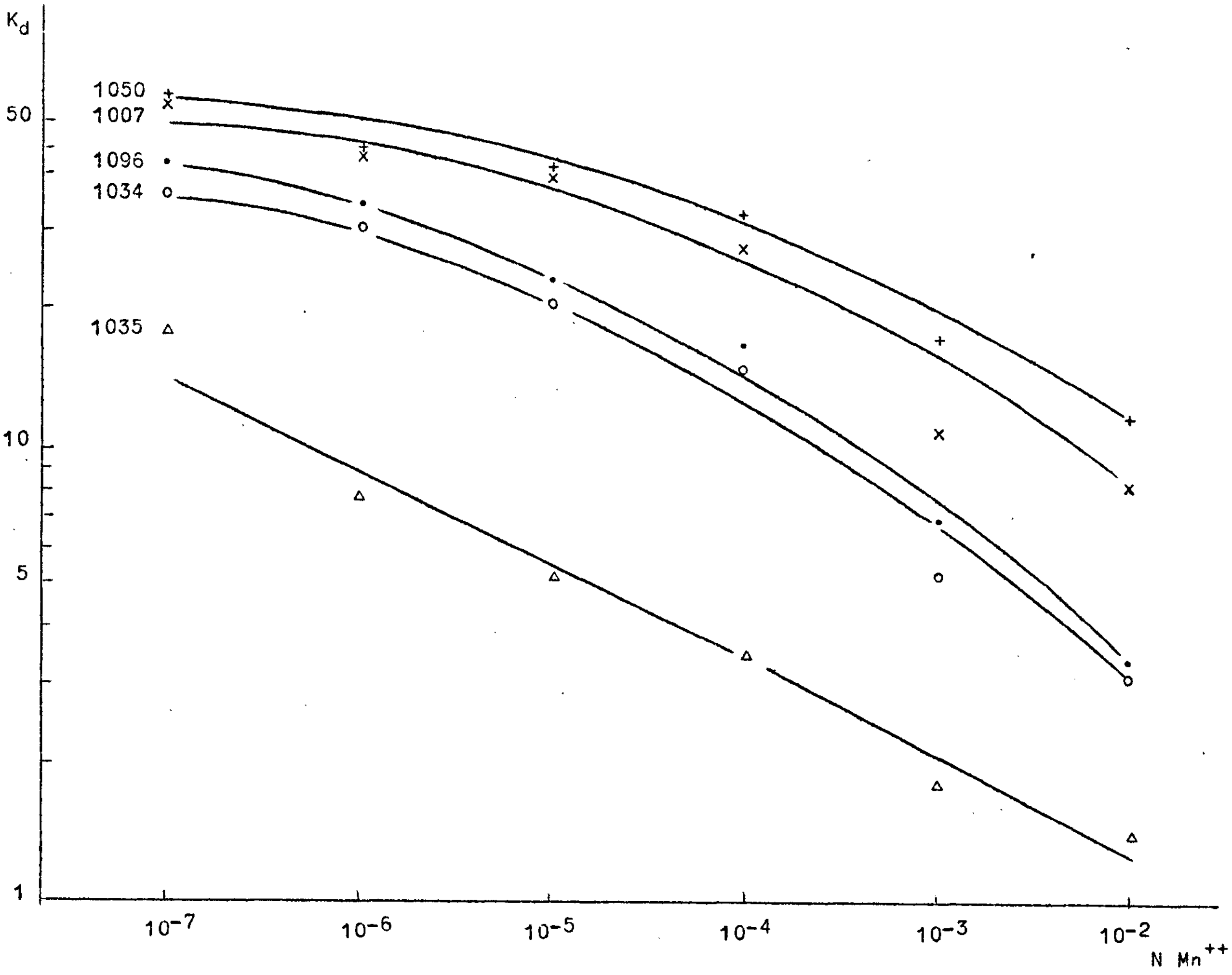

fig. 17.
$Mn^{54}$ sorption versus Mn concentration.

in the future where samples rich in clay and silt are concerned. He draws, however, attention to the fact that $K_d$ values obtained by means of different methods may mutually vary to a greater extent as compared to those obtained with one and the same method applied to different samples. He suggests, consequently, to use $K_d$ values of these tests that best agree with what occurs in nature. Thus the results obtained with the precipitation will be more appropriate for describing the absorption of ions by soil material which has been brought again into

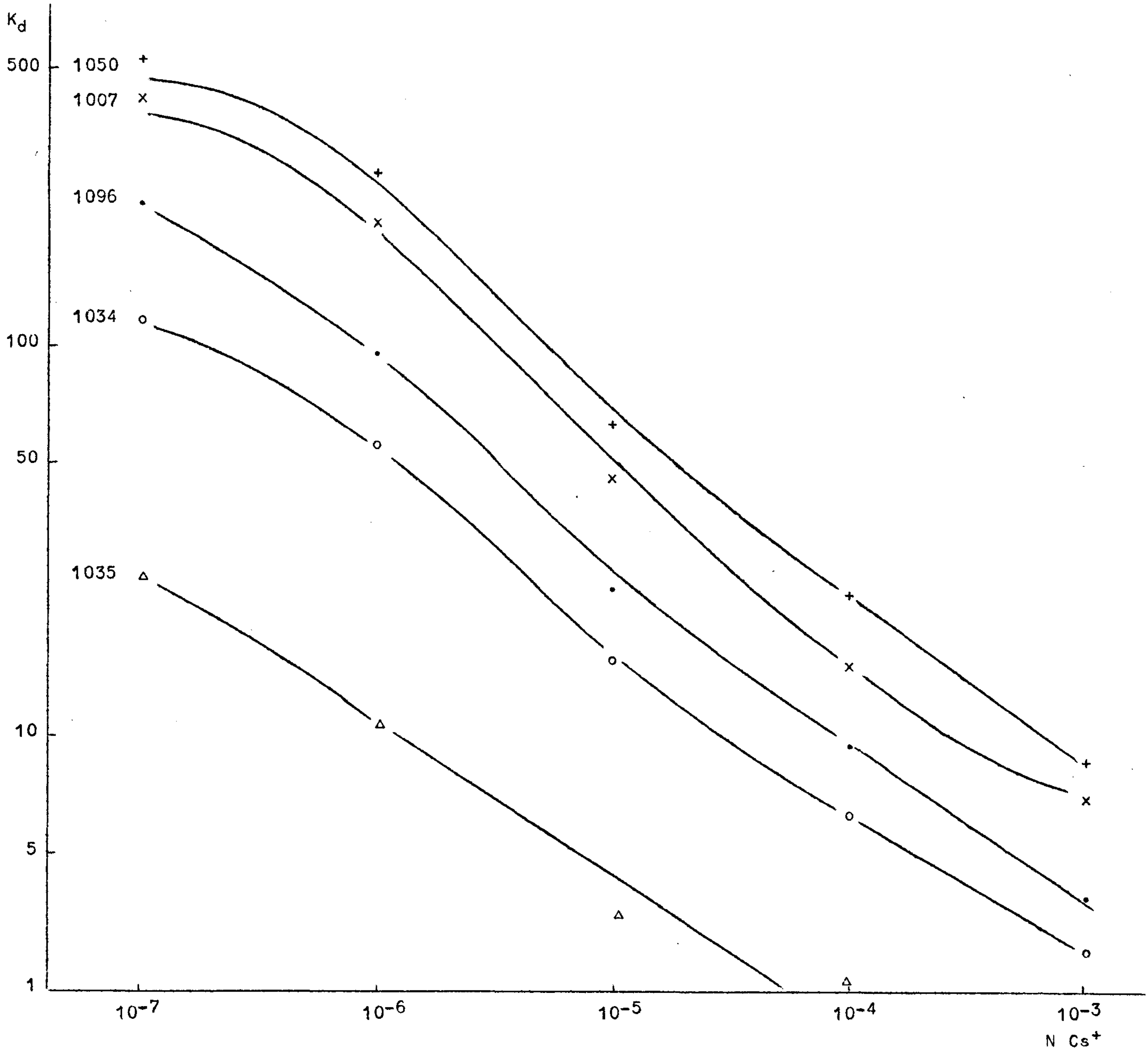

fig. 18.
$Cs^{137}$ sorption versus Cs concentration.

a state of suspension and subsequently precipitates. Also, the thin layer method will be more appropriate in conditions where a simple contact exists between the water and the sediments without having these latter return to a state of suspension.

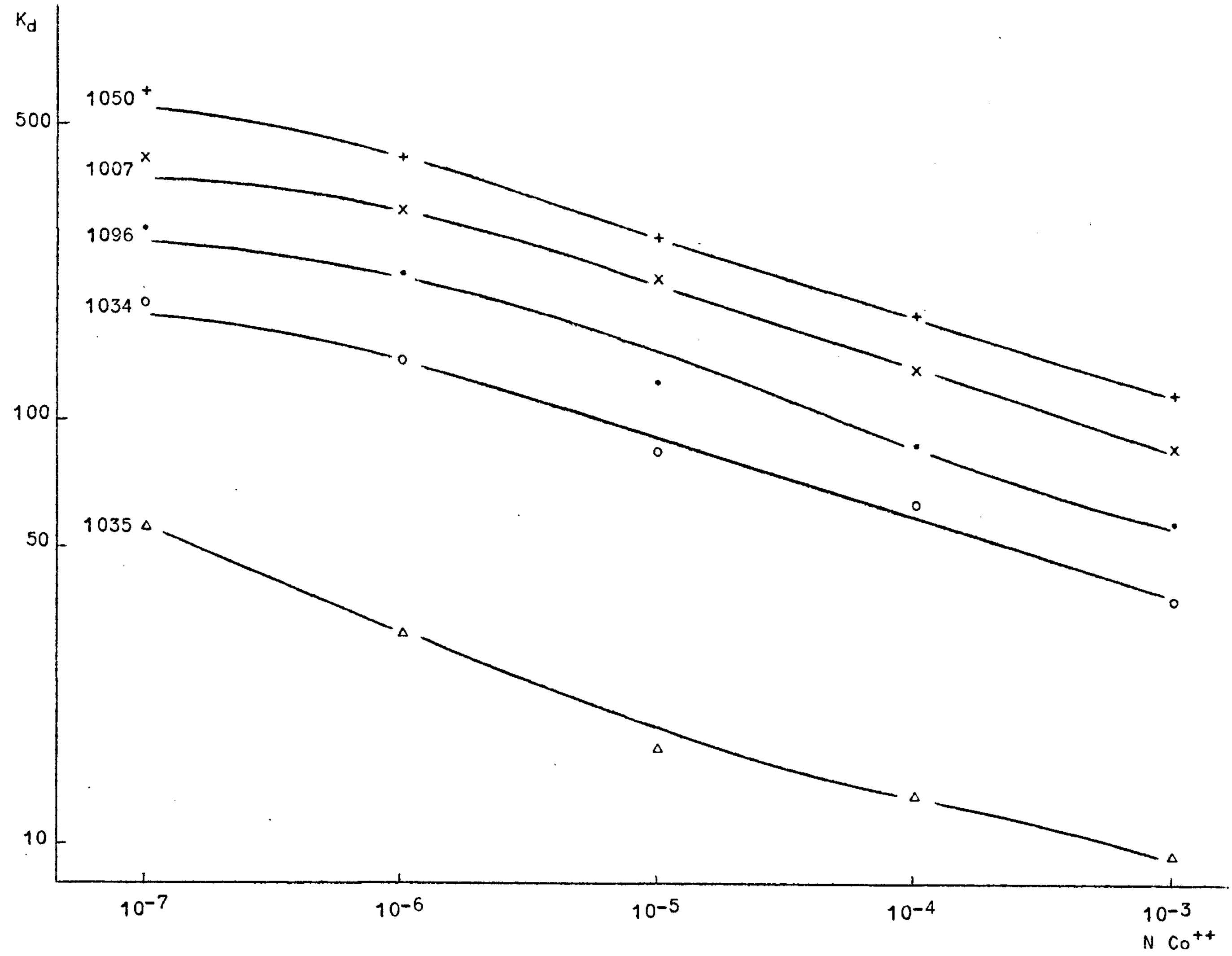

fig. 19.
$Co^{60}$ sorption versus Co concentration.

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