

COBALT AND TANTALUM TRACERS MEASURED BY ACTIVATION ANALYSIS IN SEDIMENT TRANSPORT STUDIES

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Abstract

COBALT AND TANTALUM TRACERS MEASURED BY ACTIVATION ANALYSIS IN SEDIMENT TRANSPORT STUDIES.

The paper proposes certain principles of research to be used in investigating the origin and transport of fine-grained sediments in rivers and sea arms in connection with siltation problems of harbours and navigation channels.

An element, which either does not occur in the sediment or only occurs in minute quantities, is fixed to the mud from the river or sea arm. After the material is marked it is returned to the water course where it mixes with the solids moving naturally. At specified points throughout the water course sediment samples are taken to determine the marking element by activation analysis. This gives an insight into the flow path of the suspended matter.

The selection and successful application of tracers that can be measured by activation analysis depends on the sensitivity of detection, the natural occurrence of the relevant elements in the sediments under investigation and the fixation capacity of the tracer to the various grain size fractions. Further, the influence of the added element on the sedimentation behaviour of the mud in suspension and on the desorption properties must be considered.

The irradiation of Co and Ta with thermal neutrons gives rise to a very sensitive evaluation of the original elements present. The fixation process of Co is restricted to sediments with special characteristics; Ta, however, can adhere tightly to any sediment. Tantalum also has the advantage that its natural content in sediments is very low. Large quantities (several per cent by weight) can adhere to the sediment without changing the sedimentation properties to an appreciable extent. Hardly any losses occur during leaching experiments simulating natural conditions.

A detailed treatment is given of the chemical aspects of the method, including the behaviour of the elements used in the light of the general environmental processes of sediment constituents in deltaic systems. Finally, the scope and limits of the method are discussed.

1. INTRODUCTION

Transportation of sediments is a complex process in which the turbulent motion of the water and the properties of the sediments both play a part. A detailed analysis of the phenomenon is very difficult so the development of a method for studying the process as a whole seems important. For this the application of tracers is often considered.

Marking particles in coarse sediments is relatively easy. The particles can be marked with a superficial coating of a detectable substance whose

distinguishing property is fluorescence, magnetism or radioactivity, etc. Here, the thin coating hardly influences the properties of the sediment.

Such procedures are not possible for very fine sediments mainly consisting of clay minerals with particle sizes less than 10 to 20 microns, because surface properties play an important role in the suspension of the material. But this type of sediment is the main cause of silting in harbours and navigation channels in estuaries and at certain muddy coasts. Studies made on silting in the approaches of the port of Bangkok and on the coast of Guiana stimulated the search for a suitable tracer for fine sediments.

The application of radioactive tracers in populated areas and in remote countries meets with severe problems because of the large quantities involved. Therefore, a method had to be developed for non-radioactive tracers. The technique should exclude an on-the-spot detection of the tracer and would require a sensitive and inexpensive method for analysing the samples. For this reason activation analysis seems attractive.

2. SELECTION OF ELEMENTS BASED ON ACTIVATION ANALYSIS AND COSTS

Activation analysis is based on the possibility to induce a nuclear reaction in the atoms of the element to be determined. As a result, radioactive isotopes are formed which can be recognized by their radiation. Moreover, the measured radioactivity in the sample is directly related to the concentration of the element. Though various nuclear reactions can be used, those induced by neutrons from a nuclear reactor (n, γ -reactions) are most suitable.

For a rapid technique the element should be detectable against the background activities formed from the natural components of the tagged material. Otherwise, more intricate and time-consuming chemical separations are necessary. A purely physical determination of the specific isotope is possible by gamma-ray spectrometry (Ge-Li detector) or by coincidence-counting techniques. The choice of a suitable tracer depends on the strength of the specific signal from the induced radioisotope and on

TABLE I. DETECTION LIMITS AND CONTENTS OF SEVERAL ELEMENTS IN RHINE SEDIMENT

Element	Coincidence method Detection limit (ppm)	Gamma-ray spectrometry (Ge-Li) method Detection limit in sediment (ppm)	Natural content (ppm)	Price/kg (\$US)
Ta	-	< 1	1	125
Sb	0,2	< 0,2	2	5
Co	1	1	20	30
In	-	4	< 4	4 000
Ir	-	0,05	0,05	4 000
Tb	< 3	3	(2)	15 000
Eu	-	0,2	1	30 000

TABLE II. CONTENTS OF ELEMENTS IN SEDIMENTS FROM DIFFERENT RIVERS (Extrapolated to 100% of the fraction < 16 microns)

Element	Rhine	Ems	Chao Phya	Amazon
	(contents of elements expressed in ppm)			
Fe $\times 10^3$	54	112	40	44
Mn	2600	3300	1800	1060
Zn	3400	700	30	130
Cr	760	180	100	-
Pb	850	100	30	-
Cu	470	150	50	28
As	310	60	53	-
La	80	30	90	-
Co	24	22	12	13
Sc	12	12	19	-
Sm	7	9	8	-
Ta	1	-	-	-

the presence of signals in the same region of the gamma-spectrum originating from the relevant sample. On this basis, an analysis has been made of the elements which would give the highest sensitivity in determining Rhine sediment. The elements together with the limit of detection and the price per kg are given in Table I. The detection limit is mostly defined by the natural concentration of the tracer element in the sample.

From Table I it appears that Ta, Sb and Co are the most suitable tracers for Rhine sludge. Under certain circumstances Ir may also be useful, e. g. for solving local problems involving only small amounts of tracer. However, the usefulness of an element as a tracer is determined by the amount which can be incorporated tightly into the sediment without altering its physical-chemical behaviour, as this is directly related to the maximum detectable dilution.

3. OCCURRENCE AND GENERAL BEHAVIOUR OF METALS IN SUSPENDED MATTER IN DELTAIC SYSTEMS

In studies of metal concentrations in sediments transported with river water, one has to take into account that they depend on the size distribution of the material. Because of the higher occurrence of the metals in the finest grain-size fractions, linear relationships are always found between the contents of the elements and the fraction of particles < 16 microns (expressed as a percentage of the CaCO₃-free mineral constituents). These linear relationships make it possible to characterize the content of a specific metal of a whole group of co-genetic sediments by a single value. According to De Groot [1] this value represents the content obtained by extrapolation to 100% of the fraction < 16 microns.

Values obtained in this way may differ widely from one river to another. Table II gives the contents of a number of metals in suspended matter from four rivers. Generally, rivers in temperate climates (Rhine, Ems) have higher metal contents in their sediments than those in tropical areas (Chao Phya in Thailand, Amazon). The Rhine contains very high amounts of Zn, Cr, Pb, Cu and As as a result of industrial contamination.

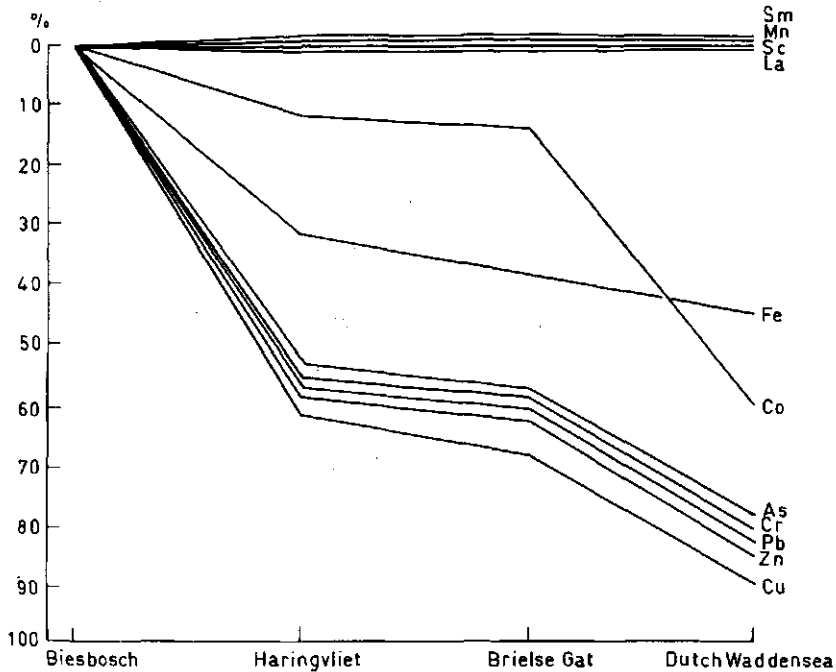


FIG. 1. Mobilization of trace elements from sediments in the Rhine delta, expressed as a percentage of the original content.

The values given in Table II apply to the river flow under normal flow conditions. As soon as the river reaches its freshwater tidal area, at least under temperate climatic conditions, a mobilization process of the metal sets in giving rise to soluble organo-metallic complexes. Figure 1 illustrates these mobilization processes for the Rhine delta. The Rhine transports its fine-grained sediments by way of the freshwater tidal area Biesbosch and the brackish Haringvliet to the sea and further along the coast to the Dutch Wadden Sea. Most of the metals in the suspended material undergo this mobilization process to varying degrees during their passage to the lower courses of the delta. The most striking changes are observed in the Fe content, which almost reaches its lowest value in the Haringvliet. The contents of Pb, As, Zn, Cr and Cu also undergo marked decreases, but longer distances are needed to reach their lowest values. Cobalt does not undergo more intensive mobilization before it reaches the marine area along the Wadden coast. The contents of Mn, La, Sc and Sm remain constant.

Extensive experimental work has provided evidence that the mobilization of the metals takes place as organo-metallic complexes. From the fact that the degree of mobilization of the various trace elements largely varies according to the series of Irving and Williams [2], it may be concluded that the stability of those complexes is the dominating factor in the intensity of the mobilization process. The formation of the complexes is strongly influenced by the decomposition of organic matter in the sediment particles. The intensive decomposition of this matter in deltas under temperate climatic conditions can, therefore, be held responsible for the rapid mobilization of metals from sediments of rivers like the Rhine and Ems.

On the other hand, only a minor decrease in organic matter content was observed during transport of sediments to the lower courses of tropical deltas. This is in agreement with the much smaller mobilization observed in the Chao Phya delta. The degree of mobilization will soon be examined in the Amazon delta.

The geochemical suitability of a marking metal depends on the natural amounts of this element in the relevant water course and on how firmly the metal is bound to the suspended matter. Of the metals mentioned in Table II, Fe, Mn, Zn, Cr, Pb, Cu, As and La are too abundant in the sediments and Fe, Cr, Zn, Cu, Pb and As easily mobilize during transport of the material. The amount of Co in river sediments is not too high, not even in the highly polluted Rhine. Further, Co does not undergo a more intensive mobilization before reaching the marine area along the Wadden coast. Therefore, Co could be considered as a marking element under conditions of not too extreme dilution of the marked suspension with the natural material. Even better possibilities from a geochemical point of view are offered by Ta, which appears in sediments only in very minute quantities. In addition, Ta compounds are generally very insoluble, so mobilization of this element could hardly be expected.

No chemical experience with Sb has been obtained, so our attention has been focussed on Co and Ta.

4. MARKING OF SEDIMENTS WITH Co AND Ta

A practicable procedure for the fixation of the relevant element to the sediment must be developed. The sedimentation behaviour of the marked sediment should not differ too much from that of the original material and the bonding should be strong enough to resist desorption processes under natural conditions.

4.1. Cobalt

Fixation of Co to sediment constituents is possible in four different ways: as intercalated Co-ions between the layers of clay lattices, as exchangeable ions in the electric double layer of clay minerals, as chelated Co fixed to the natural organic matter in the sediments and as $\text{Co}(\text{OH})_3$ precipitated on the sediment particles.

The fixation of Co as interlayer ions leads to only very small quantities being bound per unit of weight sediment and, as a result of the relatively small size of the Co-ion and its low polarizability, such ions are, according to Hüser [3], not very tightly held. The amount of Co-ions in electric

double layers depends on the cation exchange capacity of the relevant sediments and is generally 1-2 wt %. Although Co bound in this way is held relatively tightly, it is not the type and amount of Co-fixation which we are aiming at. Therefore, depending on the chemical characteristics of the relevant sediment, only Co chelated by the organic matter and coagulated Co hydroxide on the sediment particles will be considered.

4.1.1. Fixation processes

Although chelated Co-ions and coagulated Co hydroxide are the most desirable types of bonds in our objective, fixation in these forms is confined to a limited number of sediments.

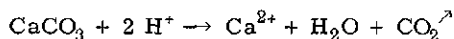
Cobalt chelated by organic matter

The chelating capacity of the organic matter in sediments from water courses primarily depends on the location. Under European conditions this property is most pronounced in sediments originating from the fresh-water part of a river, e. g. the fresh-water tidal area of the river Rhine. This type of sediment is generally characterized by a high C/N ratio (20-25); in the marine direction decomposition of organic matter takes place, as mentioned before, giving rise to lower C/N ratios (12-13) and less chelating power. The pH of the sediment should not be higher than 7.5, otherwise the Co is precipitated as hydroxide.

Fixation of Co in this way can be carried out by treating the relevant sediment in suspension with a solution of $\text{Co}(\text{NO}_3)_2$ (ratio of solid : solution = 1 : 10) under boiling conditions. Thus, Co contents can be achieved exceeding 2% by weight. The chelate bond of the Co is demonstrated by a fall in pH (released H^+ -ions) during the reaction, although part of the H^+ -ions is neutralized by the native CaCO_3 of the sediment.

Coagulated Co on sediment particles

If sediments with a pH > 7.7 and sufficient CaCO_3 are treated under boiling conditions with a solution of $\text{Co}(\text{NO}_3)_2$ (ratio of solid : solution = 1 : 10), $\text{Co}(\text{OH})_2$ is coagulated on the sediment particles. This precipitate is transformed into $\text{Co}(\text{OH})_3$ by oxidation. The coagulation process progresses sufficiently only if the H^+ -ions produced during the reaction are neutralized by native CaCO_3 :



The coagulation method allows high quantities of Co to be bound to the sediment.

4.1.2. Localization of Co in the sediment

Coagulation of Co hydroxide on the sediment particles is the most suitable way of binding Co for our purpose. It may be expected that the amount of Co precipitated is somehow related to the amount of surface exposed. This is confirmed by Fig. 2.

The real amounts of Co in the subfractions of, for example, 100 g of sediment are obtained by multiplying the specific Co content by the amount of each subfraction as illustrated in Fig. 3. The largest amounts thus appear to be present in the subfraction 2-8 microns.

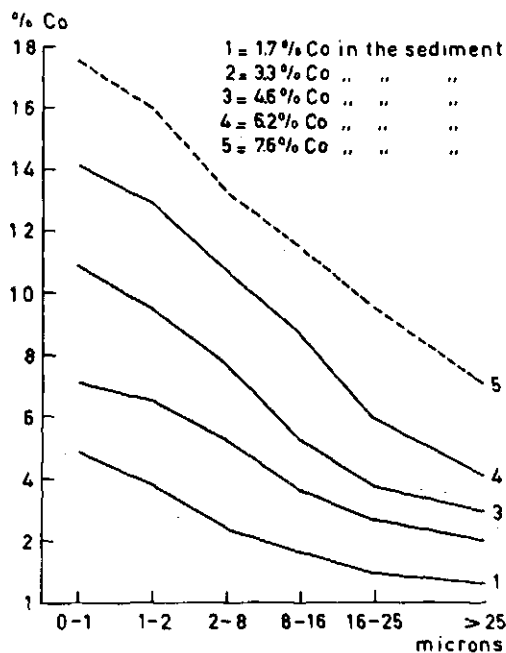


FIG. 2. Co-contents in the different granular size subfractions (per unit of weight subfraction) at different Co levels in a marine sediment.

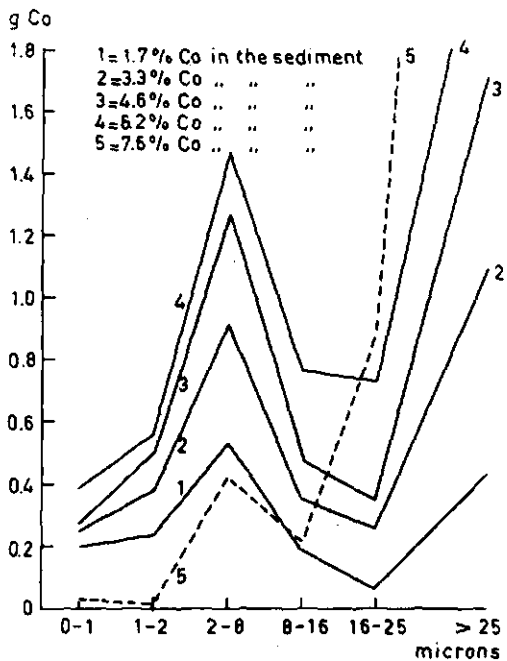


FIG. 3. Distribution of Co over the granular size subfractions per 100 g of the combined weights of the subfractions at different Co levels in a marine sediment.

From the distribution of Co over the subfractions and the amounts of subfractions present it may be concluded that there is a close relation between these two quantities, which points to a coagulation of the Co hydroxide on the particles and not to a separate precipitation. This supposition could be tested by comparing the chemical reactivity of Co hydroxide precipitated in the presence of a sediment suspension with that of Co coagulated only by addition of a 0.1N NaOH solution. In percolation experiments both precipitates were exposed to the solubilizing action of NH_4 acetate as well as the more drastic NH_4 acetate in combination with hydrazine sulphate. From the far greater solubility of the Co hydroxide that had been precipitated in the absence of sediment suspension it may be concluded that the Co adhered to the surfaces of the sediment particles.

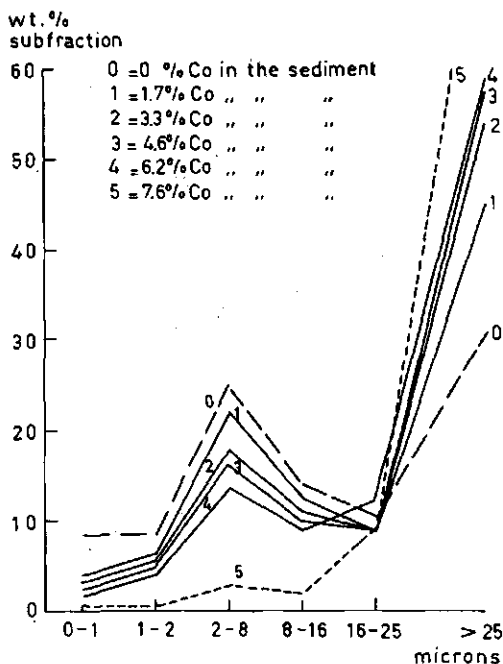


FIG. 4. Distribution of a marine sediment over the different granular size subfractions at different Co levels.

4. 1. 3. Properties of sediments marked with Co

The influence of increasing amounts of Co on the sedimentation properties of the above-mentioned marine sediment is demonstrated in Fig. 4. Sedimentation is measured by the pipette method. The density of a suspension of the material changes with time at a given depth. The size distribution changes towards coarser subfractions when larger amounts of Co are applied. General experience shows that the Co content of the sediment should not exceed 5% by weight to avoid drastic changes in the sedimentation behaviour. On the other hand, when the marked sediment is mixed with unmarked material it shows more or less similar sedimentation behaviour to the natural material.

As already stated, natural Co in sediments is not mobilized very much in estuaries. The stability of Co artificially attached to several types of sediment was studied in an extensive program of desorption experiments. The sediments with different Co levels were put into percolation tubes and treated in separate experiments with large quantities of distilled-, river- and sea-water and with 1N solutions of CaCl_2 and NH_4 acetate. Generally, not all water extractions attack the Co bonds. In the case of marine sediment with Co hydroxide on the particles, the Co is only slightly leached after long treatment with CaCl_2 . The rather drastic NH_4 acetate, which can form weak complexes with Co, leaches the element to a slight extent and probably represents the effects which take place in nature over a long time. From the results of these experiments it may be concluded that the binding of Co hydroxide to the sediment is strong enough for our purposes.

4.2. Tantalum

In contrast to Co, Ta adheres to any type of sediment. The main point of this investigation was to dissolve any Ta compound before the fixation process. The most suitable method seemed to be to dissolve TaCl_5 (a relatively inexpensive Ta compound) in dilute HF containing an amount of F expressed in gram equivalents which is half the amount of Cl. The rest of the procedure was the same as for Co.

4.2.1. Fixation process

The sediment was boiled with the solution of TaCl_5 in HF (ratio of solid : solution = 1 : 10). Only a slight increase in pH, caused by the addition of the sediment to the solution, was required to hydrolyze the dissolved Ta. This reaction appeared to be independent of the type of sediment; even material completely lacking CaCO_3 proved to be suitable.

4.2.2. Localization of Ta in the sediment

Figure 5 shows the distribution of Ta (per unit weight of subfraction) over the subfractions for different Ta levels in a marine sediment. The Ta contents were measured with the aid of ^{182}Ta . Tantalum also shows a preference for the finest subfractions of the sediment. As with Co, the largest quantity of Ta is found in the sediment subfraction of 2-8 microns (see Fig. 6).

Here too, the close relation between Ta present in the different subfractions and the amounts in these subfractions indicates a real attachment of the elements to the sediment. But because of the difficulty to obtain Ta, no experiments were done to compare the solubility of hydrolyzed Ta with and without the sediment.

If sediment particles are assumed to be spherical and to have exclusively external surfaces, a constant ratio could be expected between the fixed Ta and the total surface per unit of subfraction. This assumption has been tested by estimating specific surfaces by means of the BET¹ method, using ^{85}Kr as a measuring gas. Besides the conclusion that the particles have a much larger surface than that which corresponds to a spherical

¹ Brunauer, Emmett and Teller adsorption method.

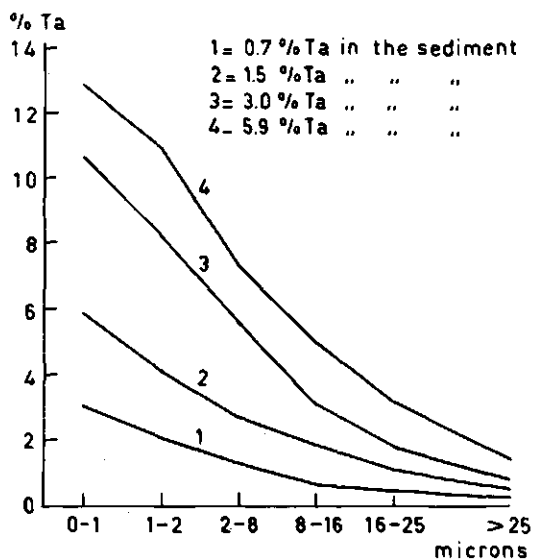


FIG. 5. Tantalum contents in the different granular size subfractions (per unit of weight subfraction) at different Ta levels in a marine sediment.

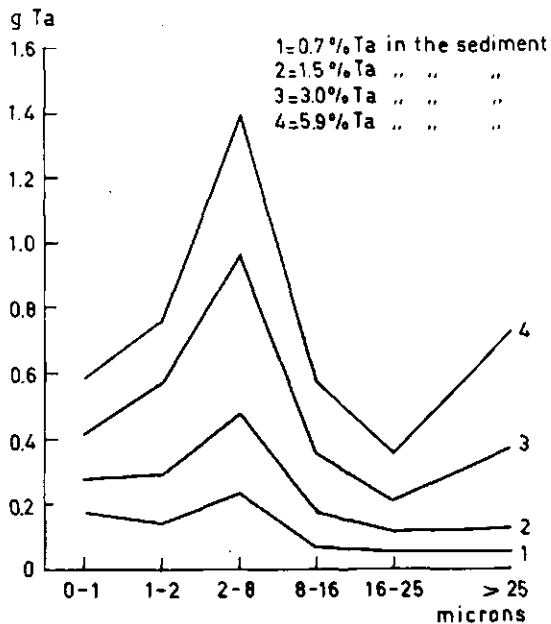


FIG. 6. Distribution of Ta over the granular size subfractions per 100 g of the combined weights of the subfractions at different Co levels in a marine sediment.

form, it was found that the ratio between the quantity of Ta and the specific surface decreased with increasing size of the subfractions. This leads to the assumption that Ta coagulates as separate grains, which are preferentially taken up by the finest subfractions. The assumption of separate grains of Ta (attached to the sediment) is supported by the observation that the specific surface of the subfractions is greatly enlarged by the fixation of the element.

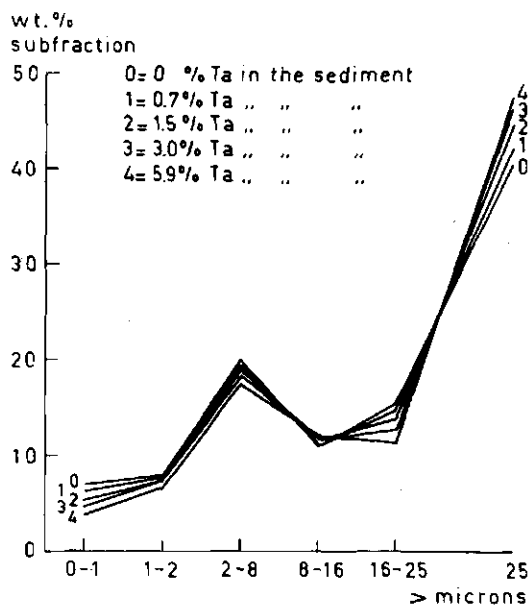


FIG. 7. Distribution of a marine sediment over the different granular size subfractions at different Ta levels.

4.2.3. Properties of sediments marked with Ta

In contrast to Co, increasing quantities of Ta ranging from 0 to 5.9% by weight hardly affect the sedimentation behaviour of the marine sediment, as shown in Fig. 7. However, this does not mean that the application of Ta is unlimited for all types of sediment. The acid concentration in the Ta solution and the acid released as a result of hydrolysis of the element dissolve the CaCO_3 in the sediment. A total loss of CaCO_3 may change the sedimentation of the material to an appreciable extent. Apart from marine sediment, which has a high CaCO_3 content, the limit of 5% by weight of Ta should not be exceeded.

Desorption experiments with Ta were carried out with sea water, 3.5M NH_4Cl + 1M NH_4F , 3M HCl , 0.5M oxalic acid and 0.5M oxalic acid + 3M HCl . Except with oxalic acid, whose reactivity with Ta is well known, only negligible quantities of Ta were dissolved. The strong resistance of this element to desorption makes it very suitable for marking fine-grained sediments.

5. SCOPE AND LIMITS OF THE METHOD

The possibilities of the method are discussed in relation to the procedure to be followed in a tracer experiment. Such an experiment should be preceded by a survey leading to at least one simple model of the overall process under study, including the order of magnitude of the important parameters.

An amount (mass m , selected in accordance with the problem studied) of the sediment to be studied is taken from the selected location. It may also originate from elsewhere, but its properties (granulometric characteristics) should be comparable to the properties of the local sediment. This amount of sediment is marked with a quantity αm of the tracer, α being the concentration of the tracer in the sediment. For Co and Ta the maximum concentration is about 5% by weight.

The marked sediment is introduced into the system at a known location and in such a way that its behaviour represents that of the natural material. This may also restrict the magnitude of m . The marked material is now incorporated in the processes of transportation by which it is dispersed over a certain area while it is mixed with a mass (M) of sediment in that area. This mass is characteristic of the scale of the system; it is proportional to the rate of dispersion of the sediment and increases with time.

The ultimate concentration (β) of the tracer in the mass M will vary in space and time, the average being $\bar{\beta} = \alpha m/M$. β should be higher than β_0 = detection limit.

Samples should be taken from the bottom and from the suspension in a spatial pattern at certain intervals of time. The dimensions of the pattern should be increased with time. A good location-fixing system is imperative. About 100 samples are generally sufficient to provide a spatial picture of the distribution of β . With a series of about 10 successive samplings the total number of samples will be of the order of 1000. This number is more or less independent of the size of the cloud, but depends on the required accuracy of the investigation.

The samples are analysed by irradiation in a nuclear reactor and by subsequent measurement of the activity significant for the element under consideration. The related costs will be of the order of \$15 per sample.

The result of the experiment is a spatial pattern of β , which gradually changes with time. From this, the answers to the problem have to be derived. If the experiment is only based on a vague picture of the overall process, the results may be of limited value. However, it may provide more insight into the process and may be a starting point for a more adequate experiment. It may lead to a better estimate of M and to an improved pattern of sampling.

An estimate of the price of the experiment may be made on the basis of figures for M , β and p where p is the price of the marking element per kg. For an experiment in which the processes of mixing lead to $\beta = \beta_0$, the price of the tagging element will be $\alpha mp = M \beta_0 p$. If $M = 10^8$ kg, $\beta_0 = 1$ ppm (Ta) and $p = \$125$ per kg, the price will be \$12 500 (\$60 000 for the same experiment with Co, when $\beta_0 = 20$ ppm). If the analysis costs are assumed to be \$15 000, the total price (without handling and sampling costs) would be of the order of \$27 500.

This makes the method applicable for intermediate and small-sized experiments in restricted areas, e. g. for measuring sedimentation in

harbours and dispersion of spoil ground in a river or estuary. Other applications may be possible in laboratory experiments with sediments and in soil science.

A C K N O W L E D G E M E N T

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R E F E R E N C E S

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D I S C U S S I O N

A. CAILLOT: Without in any way wishing to criticize your paper, I feel I should point out that clay particles are not inert. The particles interact with one another in the same way as they do with their aqueous environment. Hence any labelling technique has to make allowance for the physico-chemical properties of the material that affects the hydrodynamic behaviour of the particles.

It is surprising that amounts of tracer as large as 50 g/kg of sediment do not alter the characteristics of the material to a greater extent. In studies carried out in France using less severe chemical techniques - the results of which were reported at the 1966 meeting - amounts of tracer a hundred times smaller brought about changes in certain sedimentary characteristics, especially the particle settling rate. But it is true that the changes are less marked when the salinity exceeds 3‰.

A. J. de GROOT: In Fig. 7 of my paper I have shown the Ta-labelled sediments compared with a sediment that does not contain Ta but is further treated in the same way (i. e. by boiling) as the labelled material. I agree with you that the natural material does not have exactly the same sedimentation characteristics. The boiling process has a kind of peptizing effect and the extent of this depends on the type of organic material in the sediment; it will be greater under river conditions and less pronounced under marine conditions. The latter include the area of interest to us, namely the harbour of Rotterdam. But even in this case there is a slight deviation.

However, in applying this method under our conditions, we have no other choice than to use the high concentrations of labelling element that were mentioned.

Furthermore, we hope that the labelled material, in consequence of a buffering effect of the natural material, will behave more or less like the latter. Experimental evidence indicating this has already been obtained.

I think our method is an important step forward as compared with the use of fine-grain glass material into which labelling elements have been

incorporated (United Kingdom), and our method is closer to those you suggest.

D. B. SMITH: I note that in both of the last two papers, although costs have been partially analysed, no one has acknowledged the benefit of the radioactive tracer method which produces in-situ results immediately a measurement is made. A method of this kind enables the operator to follow dynamic movements, to know where the tracer is going and to adapt the survey accordingly.

The activation analysis method is only satisfactory for the study of slow movements. I wonder whether there is any chance that samples could be analysed rapidly, say, within 24 hours of being obtained, so that in the following sampling period one could use these results to determine where additional samples should be taken.

A. J. de GROOT: In densely populated areas, such as the inner harbour of Rotterdam, we are not allowed to use field methods involving radioactivity.

It would be difficult to get results by activation analysis within 24 hours of sampling; it takes at least a few days.

T. FLORKOWSKI: In connection with Dr. Smith's comment I may mention that a portable neutron generator is now being developed for fast neutron activation analysis of tracers in the field. We hope it will solve some of the problems of field application and measurement of tracers. I also believe that ^{252}Cf neutron sources will be available within a few years.

G. COURTOIS: Dr. de Groot, it seems to me that in the movement of sediments, especially in estuaries, it would be impossible to distinguish all the activable tracers because of the NaCl concentration. The ^{24}Na would completely mask the other activable tracers.