ACTIVATION ANALYSIS APPLIED TO SEDIMENTS FROM VARIOUS RIVER DELTAS

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I. Introduction

In deltaic systems a transport of sand and fine-grained material occurs from the rivers *via* the fresh-water tidal area to the nearby coast. Especially sediments with diameters less than 50 μm can move with the water over large distances.

Much information has already been obtained about the transport of mud and its chemical behavior for a number of deltas in western Europe and in some tropical regions using manganese as an accompanying element [1-3].

Afterwards the change in concentration of the trace elements Fe, Cu and Co during the movement of the sediments from the rivers to the adjacent coastal areas was also investigated [4]. The trace elements were determined in acid extracts by conventional chemical methods. Such methods are cumbersome and do not necessarily lead to true values. It was therefore interesting to carry out some checks by nondestructive activation analysis. Moreover, this technique has provided extra information about the trace elements Cr, As, La, Sc and Sm. The results of this work are presented.

II. Experimental

Due to a preferred occurrence of the trace elements in the finest grain-size fractions, linear relationships are always found between the contents of trace elements and the fraction of particles <16 μm (expressed as a

percentage of the $CaCO_3$–free mineral constituents) in samples from the same location. In Figure 1 these relationships are shown for a number of elements in sediments of the river Ems. These linear relationships make it possible to characterize the content of a specific trace element of a whole group of cogenetic sediments by a single value. This value represents the content obtained by extrapolation to 100% of the fraction $<16\ \mu m$.

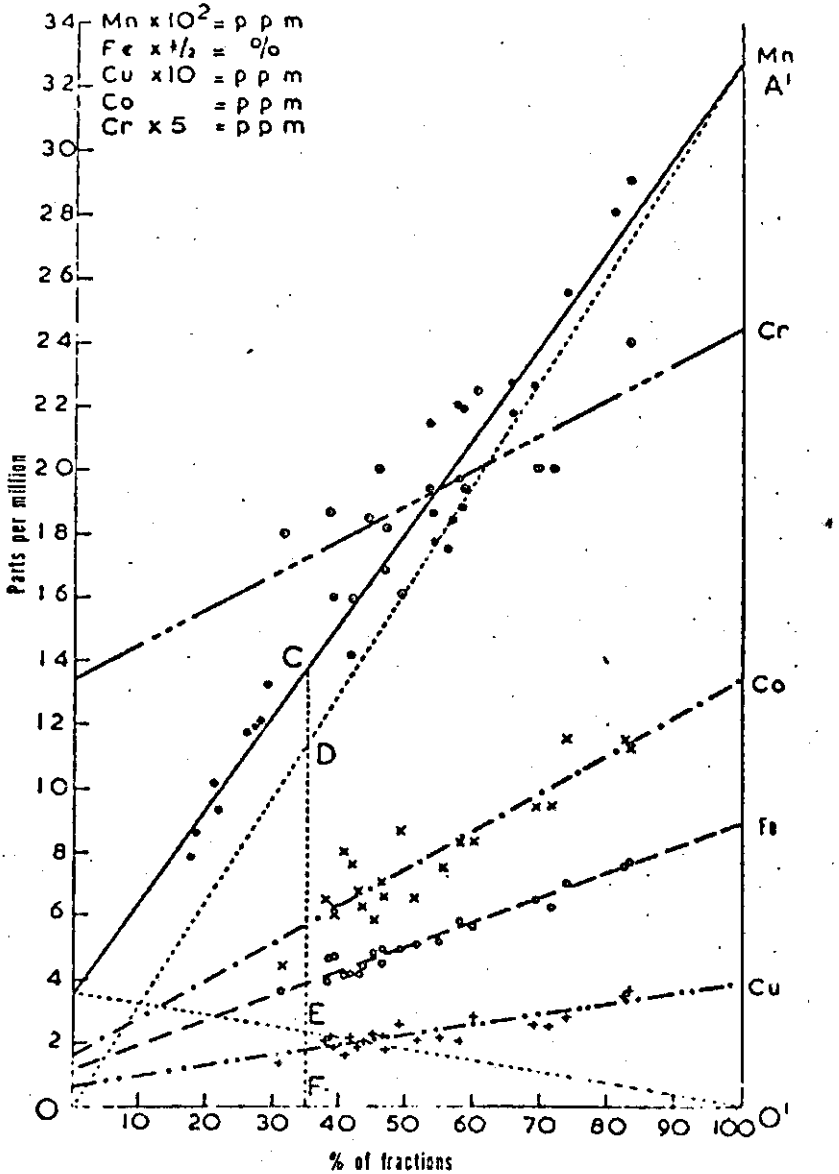

Figure 1. Linear relationships between trace element contents and percentage of fraction $<16\ \mu m$ (Ems sediments).

The activation analysis has been carried out at the Reactor Institute at Delft. Samples of the order of 400 mg were irradiated during short (1 hour for Mn, Sm, La, Zn, As) and somewhat longer (4 hours for Sc, Cr, Co) periods in the H.O.R. (neutron flux 3×10^{12} n·cm^{-2}·sec^{-1}). After cooling (4 hours for Mn; 2 days for Sm, La, Zn, As; 2 weeks for Sc, Cr, Co) the gamma spectra were measured using a 16 cm^3 Ortec Ge(Li) detector connected with an Intertechnique 4000 channel pulse-height analyzer.

III. Results

For a number of deltas, samples were taken from various regions ranging from the inner part of the delta with freshwater conditions to the outer marine environment (compare Figures 2, 4, 6). Results of the

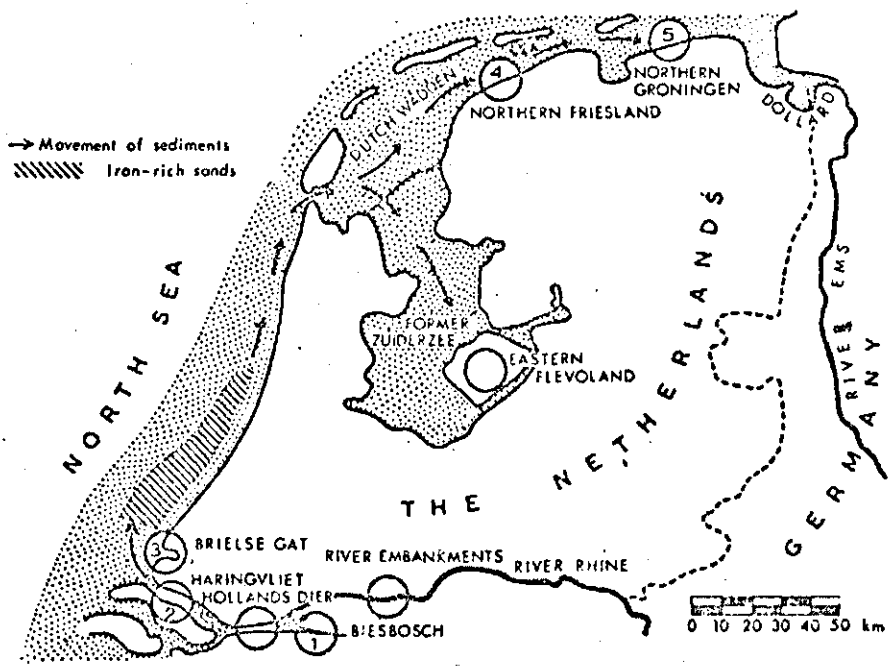

Figure 2. Rhine delta (Netherlands), movement of sediments.

analyses are presented in Tables 1, 2, 3 and Figures 3, 5, 7. When comparing the data obtained from both chemical and activation analyses, a good agreement is found for manganese and also for the single value of zinc. However, for cobalt the data from chemical analyses are 25 to 50% too low, probably as a result of insufficient dissolution in the acid extraction procedure. Still, the conclusions regarding the behavior of this element during the transport of the sediments are not affected.

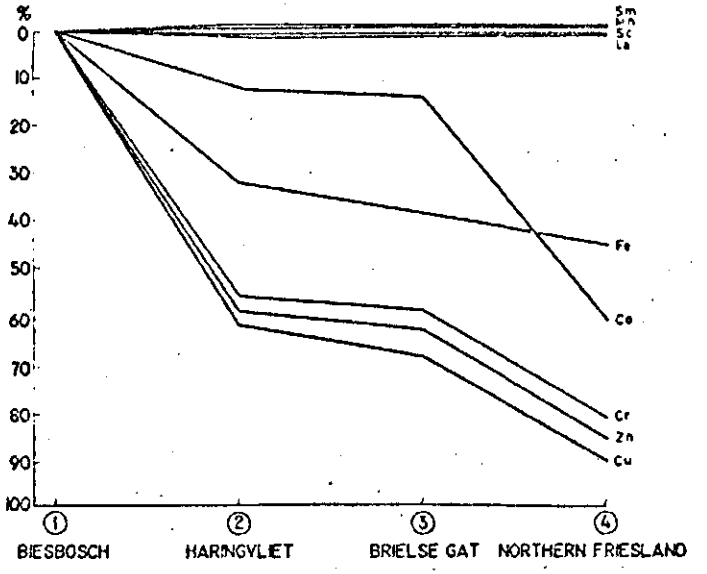

Figure 3. Mobilization of trace elements in the Rhine delta, expressed as a percentage of the original content.

A. Rhine Delta (Netherlands)

Sediments of the river Rhine are distinguished by the high Zn, Cr, Cu and As contents.

As shown in Figure 3, there are differences in the rate of mobilization of the various trace elements. From the river down to and including the sea as far as Friesland, the Mn, La, Sc and Sm contents remain constant. The Groningen sediments show a lower manganese content as a result of preceding deposition along the Friesian coast during which reduction occurs.

Table 1. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

Rhine delta (Netherlands)

	Location		Fe × 10³	Mn		Zn		Cr	Cu	As	La	Co		Sc	Sm
			CA[a]	CA	AA[b]	CA	AA	AA	CA	AA	AA	CA	AA	AA	AA
Rhine to sea ↓	Biesbosch	(1)	54	2600	2600	3400	3900	760	470	310	80	24	43	12	7
	Haringvliet	(2)	37	2600	2700	1500	ND[c]	300	180	ND	80	18	35	12	7
	Brielse Gat	(3)	33	2600	3000	1300	ND	310	150	ND	70	18	33	11	8
	Northern Friesland	(4)	32	2600	2500	400	ND	140	50	ND	80	10	16	12	7
	Northern Groningen	(5)	35	1800	ND	300	ND	140	40	ND	(80)	8	16	13	(8)

[a] CA = chemical analysis.
[b] AA = activation analysis.
[c] ND = not detected.

The other elements undergo losses to varying extent during passage of the sediments to the lower courses of the delta. The most striking element in this respect is Fe, which reaches nearly its lowest state already in the Haringvliet. The Zn, Cr and Cu contents also undergo intensive decreases, which, however, need a longer distance to reach lowest values. Finally, Co does not undergo a more intensive mobilization before the marine area along the Wadden coast.

B. Ems Delta (Germany)

Sediments of the river Ems show substantially higher Fe and Mn contents when compared to those of the Rhine. To the contrary, the striking abundances of Zn, Cr, Cu and As found in the Rhine sediments are not observed here.

The sequence of mobilization of the trace elements is the same as found for the river Rhine, although the mobilization processes generally take place within a shorter geographical distance.

C. Chao Phya Delta (Thailand)

Here, one sample was prepared from various locations in the fresh water tidal area and one other from only one location in a fully marine area (Channel).

There is a remarkably low content of a number of elements in this tropical delta. Only the La and Sm contents are comparable with those of the western European deltas. On the other hand, Sc contents are much higher.

As appears from Figure 7 there is a much smaller mobility of trace elements in this tropical delta as compared to the mobility in deltas under temperate climatic conditions.

Table 2. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

		Ems delta (Germany)										
		$Fe \times 10^3$	Mn		Zn	Cr	Cu	La	Co		Sc	Sm
Location		CA[a]	CA	AA[b]	CA	AA	CA	AA	CA	AA	AA	AA
← Ems to sea												
Diele	(1)	112	3300	3300	700	160	150	80	22	40	12	9
Leerort	(2)	53	3300	3300	400	100	50	60	17	24	14	9
Ditzum	(3)	44	3300	ND[c]	300	120	40	80	13	21	14	10
German Dollard	(4)	36	3100	ND	200	100	30	60	9	13	11	9
Dutch Dollard	(5)	37	2100	ND	200	120	40	70	11	16	13	9

[a] CA = chemical analysis.
[b] AA = activation analysis.
[c] ND = not detected.

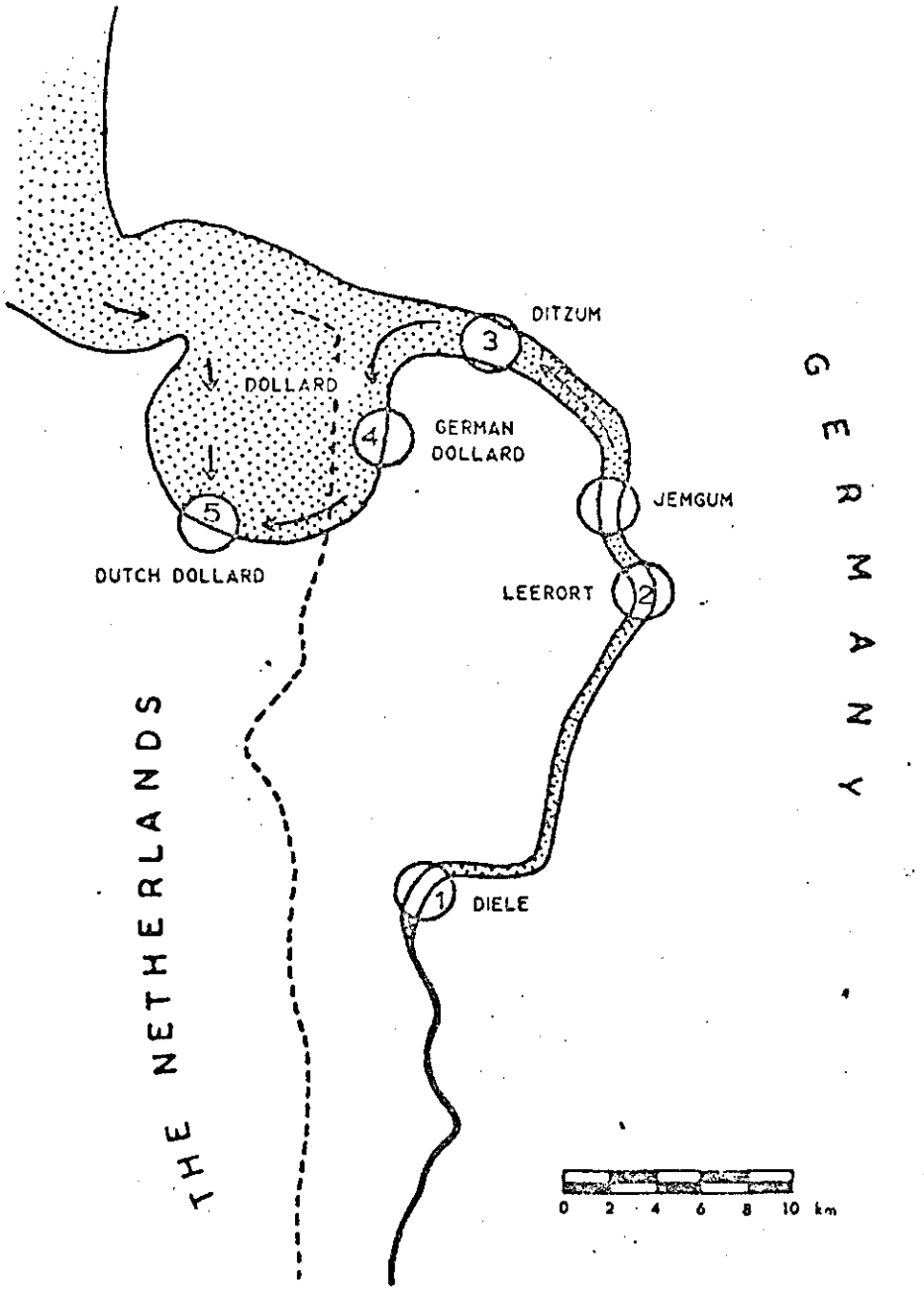

Figure 4. Ems delta (Germany), movement of sediments.

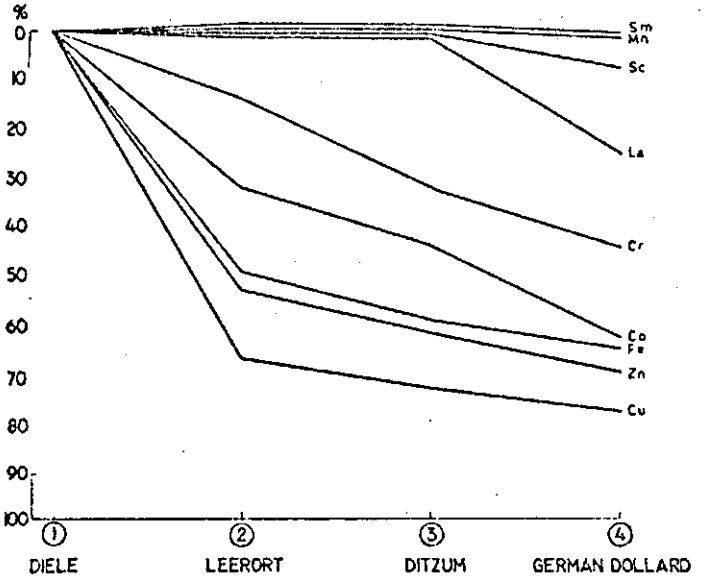

Figure 5. Mobilization of trace elements in the Ems delta, expressed as a percentage of the original content.

IV. Discussion

Extensive experimental work carried out in the Institute for Soil Fertility has produced evidence that the mobilization of trace elements takes place as organometallic complexes. From the fact that the degree of mobilization of the various trace elements largely corresponds with the series of Irving and Williams [5] it may be concluded that the stability of those complexes is the dominating factor in the intensity of the mobilization process. In the formation of the complexes the decomposition of organic matter present in the sediment particles plays an important role. The intensive decomposition of this matter in deltas under temperate climatic conditions can therefore be held responsible for the rapid mobilization of trace elements from sediments of 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 the Chao Phya delta. This is in agreement with the much smaller mobilization observed here.

Apart from this, the absolute concentrations of the various trace elements can be of strong interest for the agricultural aspects of Holocene soils, derived from mud sediments. The ultimate trace element contents of arable soils will depend on the original contents in the river solids and on the mobilization of the elements during the various stages of soil genesis.

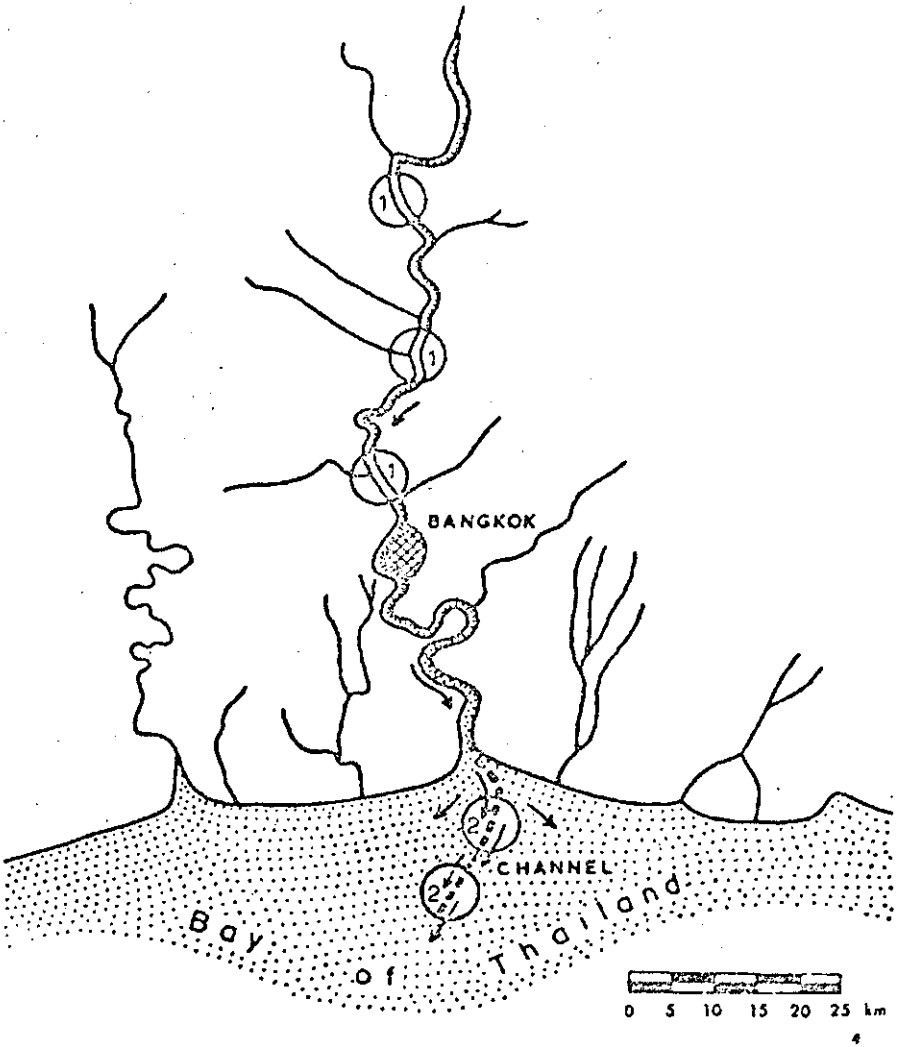

Figure 6. Chao Phya delta (Thailand), movement of sediments.

These processes may, under certain conditions, lead to concentrations of trace elements which are marginal for plant growth and animal health. For instance in the lower parts of the Rhine and Ems deltas, too-low copper concentrations are sometimes found.

Furthermore, manganese deficiency is found frequently to occur in the younger embankments of the Biesbosch area in spite of high manganese levels. This is caused by high zinc/manganese ratios and consequent suppression of manganese uptake.

As is shown, the level of trace elements is rather low in tropical areas while no mobilization takes place within the deltaic area. The

Table 3. Contents of trace elements, expressed in ppm, in sediments (extrapolated to 100% of the fraction <16 μm).

Chao Phya delta (Thailand)

Location	Fe × 10^3 CA[a]	Mn CA	Cr AA[b]	Cu CA	La AA	Co CA	Co AA	Sc AA	Sm AA
↓ to sea									
River (1)	40	1800	100	50	90	12	21	19	8
Channel (2)	40	1300	100	40	80	13	21	19	8

[a] CA = chemical analysis.
[b] AA = activation analysis.

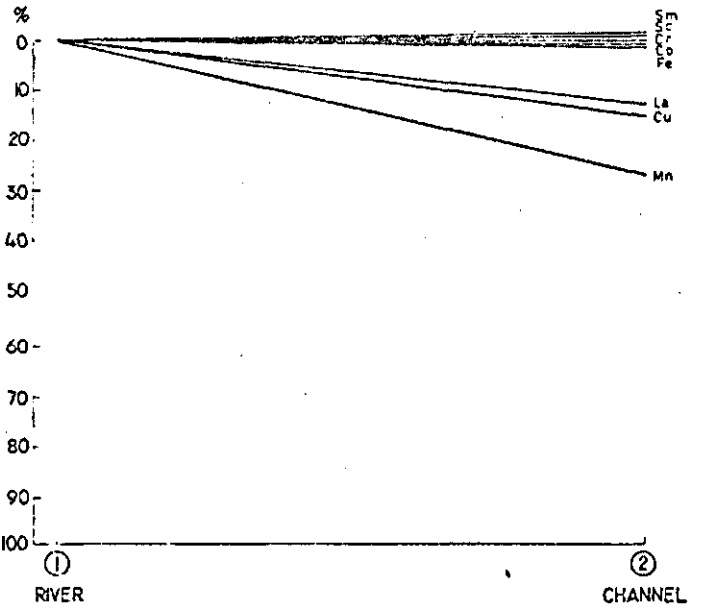

Figure 7. Mobilization of trace elements in the Chao Phya delta, expressed as a percentage of the original content.

consequences of this extreme behavior of trace elements for the cultivation of rice in these types of deltas (Amazon and Chao Phya) is now intensively studied. The pertinent information for such studies is very easily obtained by the nondestructive activation analysis of large numbers of samples on a routine basis. In this respect computer techniques are important and are being started at the Reactor Institute in Delft.

Moreover, activation analysis provides extra information about elements on which the study is not primarily focussed. As an example, the origin and consequence of high chromium and arsenic contents found in the Rhine sediment need further investigation. Also the differences observed in the content of manganese and scandium may be of geological interest. In this respect it is interesting to note that a preliminary qualitative inspection of our spectra has also revealed the presence of barium, indium, titanium, vanadium, europium, rubidium, cesium, hafnium, gold, ytterbium, thorium, cerium, aluminum, calcium, and lutetium in measurable quantities.

Finally, the information obtained can be used for selecting activated and immobile tracers for civil engineering and agricultural studies such as those concerning sludge deposition in harbors and soil transport during tillage.

V. References

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