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TRACE METAL CONCENTRATIONS IN ESTUARINE SEDIMENTS: MOBILIZATION, MIXING OR PRECIPITATION

by

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CONTENTS

I. INTRODUCTION

A decrease in the seaward direction has been observed in the trace metal concentrations in the estuarine sediments of the rivers Rhine and Ems. The interpretation of this decrease has been the subject of much controversy. De Groot (1966, 1973), Martin, Jednack & Pravdic (1971) and de Groot & Allersma (1973) have proposed models by which trace metals become released from fluvial suspended matter upon entering the estuary. This mobilization should be caused by the formation of complexes between the metal ion sorbed to the sediments and organic ligands released by the intensive decomposition of organic matter. Müller & Förstner (1975) have proposed that the mixing of uncontaminated marine with contaminated fluvial sediments may equally well explain this phenomenon. Recently Duinker & Nolting (1976, 1977) have presented evidence for the occurrence of mixing and of precipitation processes in the Rhine estuary. Their conclusions are based on measurements of dissolved and particulate trace metals.

The conflicting interpretations and opinions may be analysed by the use of stable isotope methods enabling the distinction between marine

and fluvial sediments in an estuary. The fact is that if the mixing ratio of marine to fluvial sediments and the relevant trace metal concentrations are known, it is possible to calculate the trace metal concentrations in the estuarine deposits. If the trace metals behave conservatively, the calculated and observed concentrations should be equal. Calculated values exceeding the observed would point to mobilization processes. Lower calculated values, on the other hand would indicate the occurrence of precipitation or adsorption processes.

The methods for distinguishing between marine and fluvial sediments in the estuaries of the Rhine and the Ems have recently been published (SALOMONS, 1975; SALOMONS, HOFMAN, BOELENS & MOOK, 1975). We have applied these to the trace metal problem in the Rhine and Ems estuaries (Fig. 1). The samples are taken from the set as used by DE GROOT (1966, 1973). Some additional samples from the Rhine estuary (Hollands Diep) have been re-analysed for trace metals.

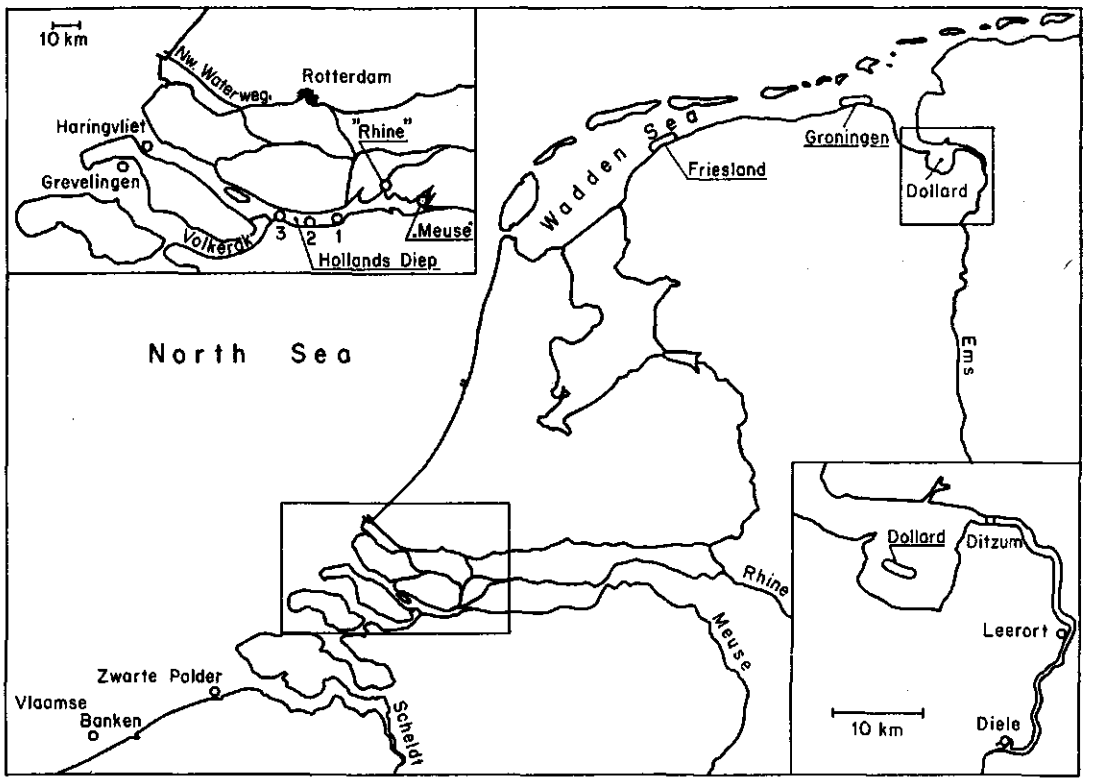

Fig. 1. The area studied, showing the sample locations.

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II. RESEARCH METHODS

Stable isotope geochemistry, used to determine the origin of the estuarine carbonates and clay minerals is based on small differences in the chemical behaviour of isotopes of an element (^{18}O and ^{16}O; ^{13}C and ^{12}C), causing variations in their natural abundances. This phenomenon has been shown to be very useful in sediment transport studies (SALOMONS, 1975; SALOMONS, HOFMAN, BOELENS & MOOK, 1975; SCHULTZ & CALDER, 1976). The isotope concentrations are reported as the relative deviations (δ) of the isotopic ratio ($R = {}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$) from an international standard (st). The standard for the oxygen isotopic composition of the clay minerals is SMOW (Standard Mean Ocean Water). The standard for the carbon isotopic composition of the carbonates is PDB (Belemnites from the Peedee formation of South Carolina, USA serve as the standard).

$$\delta(^{13}C \text{ or } ^{18}O) = (R - R_{st}) \times R_{st}^{-1} \times 10^3 \ (‰)$$

Marine carbonates have a $\delta^{13}C$ value of about 0‰ on this scale, the fluvial values vary depending on the rivers and can be as low as —5‰ (Table I). Assigning δ values to the marine (δ_m) and fluvial (δ_f) component the mixing ratio of these in estuarine sediments (X) is simply calculated from the measured δ:

$$X = (\delta - \delta_f) \times (\delta_m - \delta_f)^{-1}$$

If the trace metal concentrations in the marine and fluvial sediment (C_m and C_f respectively) are known, the concentration in the estuarine sediment (C), assuming a simple mixing of sediments, is:

$$C = XC_m + (1 - X)C_f$$

The above similarly applies to the ^{18}O abundance in the clay minerals. The $\delta^{18}O$ value to be appointed to marine clays is about +20‰ while the fluvial values vary down to about +16‰ (Table I).

The spread in the carbon isotopic composition of the sedimentary carbonates from the same locality is about 0.3‰ and that in the oxygen isotopic composition of the clay minerals about 0.4‰. Due to this spread the calculated percentages of marine or fluvial sediments in the estuarine deposits have an absolute accuracy of about 10%.

To further substantiate the results on the mixing of marine and fluvial sediments in estuaries, use can be made of another natural tracer which is associated with the clay minerals; *viz.* magnesium. It occurs in three different forms. A small part is exchangeable, another part is incorporated in the carbonates, whereas the main part is associated

with the silicates (clay minerals). The clay magnesium content reported in this paper is obtained by subtracting the first two forms from the total magnesium content.

The grain size composition of the sediments in the sample areas may vary considerably. Because the trace metals are associated with the finely grained particles, a wide range in trace metal concentration is observed, showing a positive correlation with the amount of finely grained particles, as expressed by the percentage of particles less than 16 μm in diameter (Fig. 2c). The mineralogical (Fig. 2b) as well as the major element composition (Fig. 2a) also correlate with this parameter. In order to compare the sedimentary composition, the concentrations at 50% < 16 μm will be used. These values are obtained by analyzing from each separate locality a large number of samples and constructing the curves shown in Fig. 2.

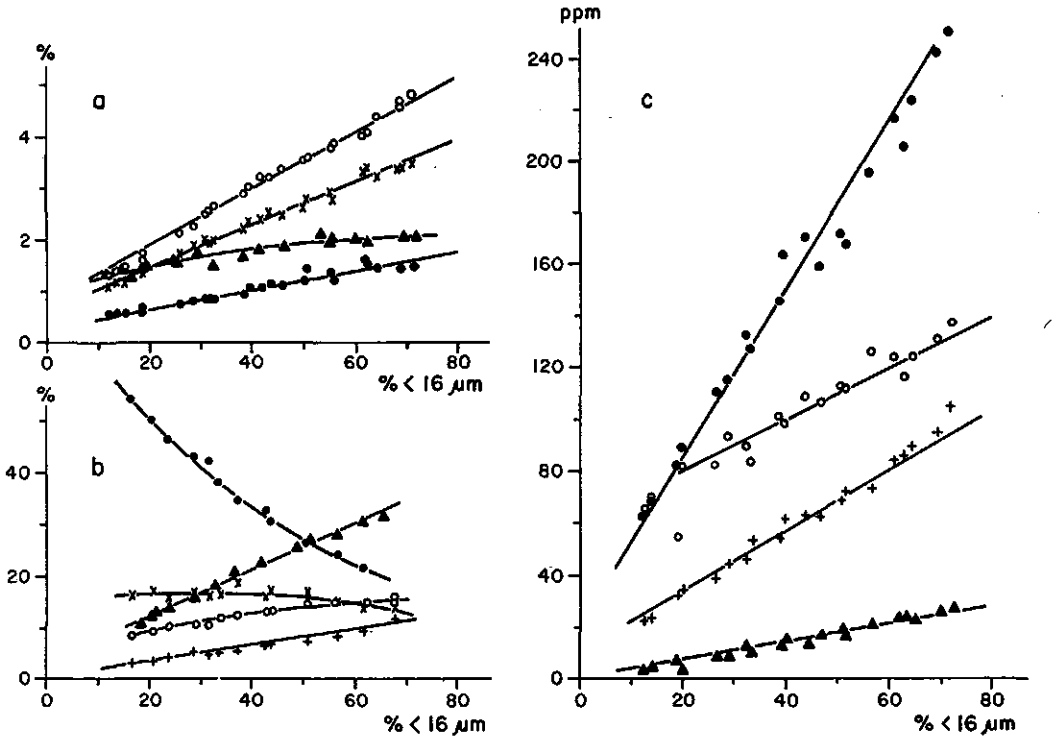

Fig. 2. Composition of the sediments studied in relation to the amount of finely grained particles in the sediments (% < 16 μm). a. The major elements (in %): Al (○), Fe (×), P (× 0.1) (●) and K (▲). b. The minerals (in %): quartz (●), feldspars (×), carbonates (○), organic matter (+) and clay (▲). c. The trace metals (in ppm): Zn (●), Cr (○), Pb (+) and Cu (▲).

III. EXPERIMENTAL TECHNIQUES

The trace metal concentrations in the sediments have been determined by atomic-absorption spectrometry after digesting the sample in a

mixture of hot HNO_3, H_2SO_4 and $HClO_4$ (Zn, Cu, Cr and Ni) or in concentrated HNO_3 (Pb and Cd).

For isotopic analysis the sediment samples were treated with 95% H_3PO_4. The resulting CO_2 was measured mass spectrometrically with a Varian M86 according to standard procedures (MOOK & GROOTES, 1973).

IV. RESULTS

1. THE EMS ESTUARY

The river Ems forms a small estuary located in Germany close to the Dutch border (Fig. 1). The average flow of the river Ems is estimated at 83 $m^3 \cdot sec^{-1}$, the mud discharge is about 65,000 $ton \cdot year^{-1}$ (HINRICH, 1974). The limit of salt penetration is between Leerort and Ditzum. The sediments were sampled at Diele, Leerort and Ditzum in 1971.

The analytical results of these and other nearby coastal sediments (Wadden Sea area) are given in Tables I and II and shown in Fig. 3. The mineralogy of the sediments as well as the composition of the minerals clearly show gradients in seaward direction. The carbonate content, for instance, increases from about 2.5 to 10%, whereas the strontium content of the carbonates decreases from 5600 to 1100 ppm. The composition of the sediments at Ditzum closely resembles those of the nearby coastal area.

The strontium content of the carbonates is a very sensitive tracer for the carbonate fraction, leading to a marine origin of roughly 90% of the carbonates deposited at Leerort. The dolomite content as well as the isotopic composition of the carbonates fit in with such a strong marine influence. The $\delta^{18}O$ values of the clay minerals vary over a small range from about 19.8 to 19.3‰. The values point to a mainly marine origin of the clay minerals. The magnesium content of the silicates in the sediment samples at Diele is about 0.4%, at Leerort 0.6% and in nearby coastal sediments also 0.6%, all data referring to the concentrations at 50% $<$ 16 μm. Although this tracer is not very sensitive, it suggests that the clay minerals at Leerort are of marine origin mainly.

In the Ems estuary the landward transport of marine sediments seems to exceed the salt water penetration. At Leerort, which is located in the freshwater tidal area, about 90% of the sediments are marine derived. POSTMA (1967) attributes this phenomenon, which was even more pronounced in 1976, to a diffusion of suspended matter from the turbidity maximum against the residual flow of fresh water. Large

gradients in metal concentrations in the seaward direction are found for those metals for which large differences in concentrations are observed between marine and fluvial sediments. If these differences are small (chromium and nickel), the gradients in the seaward direction are also small (Fig. 3). This observation is in qualitative agreement with a predominant mixing process.

The calculated and measured trace metal concentrations are very much similar showing that the mixing of marine and fluvial sediments is the main cause for the observed decrease. However, the calculated values tend to be slightly lower. The slight differences can be explained by the possible occurrence of precipitation-adsorption processes.

2. THE RHINE-MEUSE ESTUARY

The sediments of the Rhine-Meuse estuary were sampled in 1957 and 1958, before the closure of the Haringvliet and the Grevelingen by dams. The situation at that time is shown in Fig. 1. The main mud discharge from the rivers Meuse (0.7×10^6 ton·year^{-1}) and Rhine

TABLE I

Total carbonate, dolomite content, strontium content and isotopic composition of the carbonates, and the isotopic composition of the clay fraction smaller than 2 μm in various sediments of the Ems estuary, the Rhine-Meuse estuary and adjacent marine areas. Salinity ranges at the sampling localities are indicated in the first column.

Locality	*Salinity*	*Carbonates*				*Clays*
	(‰)	*Total* (%)	*Dolomite* (%)	*Sr* ($\mu g.g^{-1}$)	$\delta^{13}C$	$\delta^{18}O$
Ems						
Diele	0.2	2.5	0.4	5600	−5.0	+19.8
Leerort	0.2	7.9	1.2	1350	−0.6	+19.2
Ditzum	3	10.0	1.4	1100	−0.5	+19.3
Dollard	5–20	10.4	1.4	1000	−0.5	+19.5
Groningen	27–31	11.7	1.3	1100	−0.1	+19.2
Friesland	25–32	16.9	1.3	1100	−0.5	+19.8
Rhine-Meuse						
Rhine	0.2	16.0	2.1	850	−3.6	+16.6
Meuse	0.2	5.8	0.9	850	−3.3	+15.8
Hollands Diep 1	0.2–4				−2.0	+16.6
Hollands Diep 2	0.2–8	12.0	0.9	950	−1.3	+17.2
Hollands Diep 3	0.2–12				−1.2	+19.1
Haringvliet	2–25	19.3	1.5	1150	−0.6	+19.1
Grevelingen	25–30	20.2	1.0	1300	−0.5	+19.2
Zwarte Polder	28–30	20.4	0.4	1300	+0.0	
Vlaamse Banken	31–34	25.7	0.7	1300	+0.3	+20.0

(1.6×10^6 ton·year^{-1}) was through the Haringvliet, whereas about 10% was discharged through the Volkerak (TERWINDT, 1967). The limit of salt penetration was located in the Hollands Diep (PEELEN, 1967).

The marine suspended matter is transported along the Belgian and Dutch coast in a northerly direction. Samples of this material were collected at the Vlaamse Banken and at the Zwarte Polder. The composition is given in Table I. The large differences between the mineralogy, as well as the composition of the individual minerals in the marine and fluvial sediments are obvious. The $\delta^{13}C$ values of the carbonates differ by 4‰, $\delta^{18}O$ of the clay minerals by 4‰ and the strontium contents of the carbonates by 450 ppm. The total carbonate as well as dolomite contents also show large differences.

The estuarine sediments of Hollands Diep and Haringvliet show intermediate values. In the Haringvliet the composition approaches that of the nearby marine sediments (Grevelingen). From the intermediate values in the Hollands Diep we may conclude that the estuarine sediments consist of mixtures of marine and fluvial origin. The mean $\delta^{18}O$ value of the clay minerals in the Hollands Diep is +17.6‰, thus differing from those of the Rhine (+16.6‰) as well as the Meuse (+15.8‰). Apparently, no specific $\delta^{18}O$ values can be assigned to

TABLE II

Trace metal concentrations in various sediments of the Ems estuary, the Rhine-Meuse estuary and adjacent marine areas; n is number of samples analysed.

Locality	*Trace metals (μg.g^{-1})*						
	Cu	*Zn*	*Ni*	*Pb*	*Cr*	*Cd*	*n*
Ems							
Diele	77	586	42	82	107	3	14
Leerort	23	220	33	59	97	0.8	18
Ditzum	11	153	27	45	84	0.5	14
Dollard	24	150	27	47	85	0.7	18
Groningen	25	175	21	65	100	0.6	18
Friesland	29	235	22	80	100	0.8	18
Rhine-Meuse							
Rhine	294	2420	54	533	642	14	20
Meuse	160	1516	44	382	216	28	14
Hollands Diep 1	192	2012	58	385	391	17	10
Hollands Diep 2	185	1875	59	354	383	17	7
Hollands Diep 3	138	1488	56	329	288	12	10
Haringvliet	99	870	31	213	224	5	20
Grevelingen	48	393	25	124	142	1.7	19
Zwarte Polder	29	212	22	74	100	0.6	15
Vlaamse Banken	26	190	19	75	92	0.6	22

fluvial clays as a whole. Assuming that the clay minerals in the Hollands Diep are solely derived from the river Meuse—the samples have been taken on its southern bank—it appears that about 45% of this

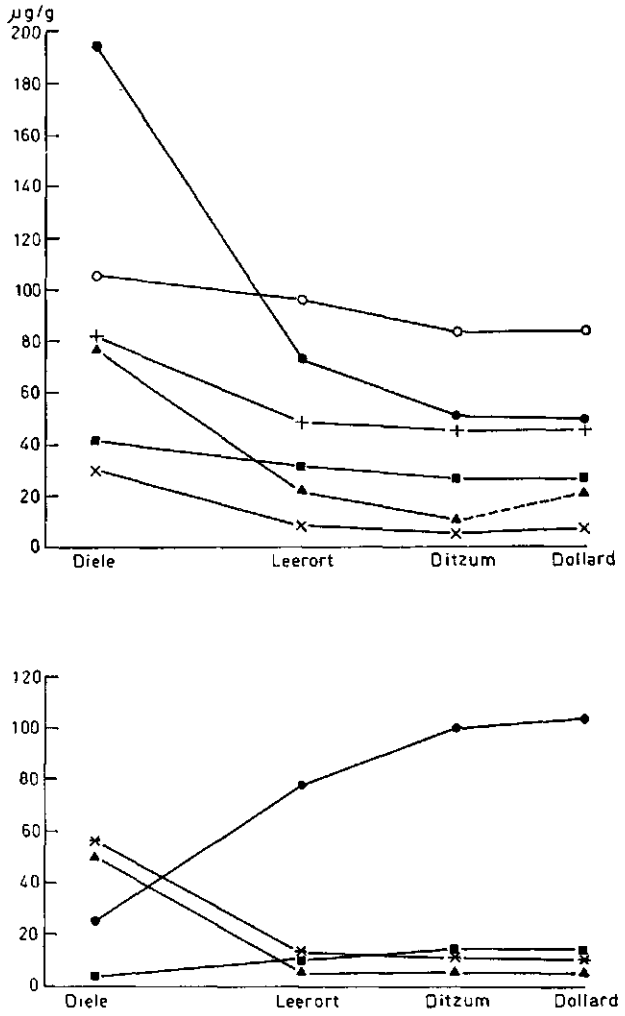

Fig. 3. Concentrations in sediments of the Ems estuary: a. The trace metals (in $\mu g.g^{-1}$): Zn (●), Cu (▲), Ni (■), Cr (○), Cd (× 0.1) (×), Pb (+). b. The natural tracers (in ‰): carbonate (●), dolomite (■), strontium (× 10^{-4}) (*) and $\delta^{13}C$ (× −1) (▲).

sedimentary component is marine derived. On the other hand, the assumption that a mixing of Rhine and Meuse components takes place according to the ratio of their mud discharges (2 : 1) leads to a contribution of 35% of marine clay. The mean $\delta^{13}C$ values of the carbonates in the Hollands Diep is −1.2‰. Since the $\delta^{13}C$ of the Rhine and Meuse carbonates are identical, the amount of marine carbonates can be calculated unambiguously, resulting in about 45% to be of marine origin.

Because it is not exactly known whether the sediments from the rivers Rhine and Meuse are already homogeneously mixed in the

Hollands Diep, the best estimate to be made is that 35 to 45% of the sediment is of marine origin.

Since we may assume that in the Haringvliet the Rhine and Meuse mud are homogeneously mixed it is possible to calculate the composition of a hypothetical fluvial sediment. According to $\delta^{13}C$ and $\delta^{18}O$ of the carbonates and the clay minerals about 75% of the sediments found in this area appear to be marine derived. Both the strontium as well as the dolomite content agree with such strong marine influence. Our final conclusion, therefore, is that in the Rhine-Meuse estuary a landward transport of marine sediments occurs. Because almost all trace metal concentrations in the Rhine and Meuse sediments differ (Table II) and the degree of mixing in the Hollands Diep is not exactly known, it is difficult to calculate the trace metal concentrations to be expected. The equal fluvial nickel concentrations, however, allow to calculate the nickel contents of the Hollands Diep sediment. Assuming a marine contribution of 40% a nickel concentration of about 38 $\mu g \cdot g^{-1}$ is expected. However, the measured concentrations (58 $\mu g \cdot g^{-1}$) are much higher. In fact they even exceed the fluvial concentrations. Apparently, mixing as well as precipitation-adsorption processes take place. The physico-chemical nature of these processes and the important parameters are presently being studied. Under the assumption that in the Haringvliet the fluvial components are well mixed, the trace metal concentrations can be calculated (Table III). The results show that in the Rhine-Meuse estuary the mixing of marine and fluvial sediments is mainly responsible for the decrease in trace metal concentrations in the seaward direction. The differences between the measured and calculated values (all positive) are probably the result of the occurrence of precipitation-adsorption processes.

TABLE III

The calculated and observed trace metal concentrations at Leerort (Ems estuary) and in the Haringvliet (Rhine-Meuse estuary).

Metal	*Concentration* ($\mu g.g^{-1}$)			
	Leerort		*Haringvliet*	
	Calculated	*Measured*	*Calculated*	*Measured*
cadmium	0.7	0.8	5.0	5.0
chromium	86	97	195	224
copper	17.1	22.6	82	99
nickel	28.0	33.3	25.8	30.8
lead	49.0	58.6	177	213
zinc	196	220	675	870

3. CONCLUSIONS

Based on differences in the isotopic composition of fluvial and marine sediments, the sediments in the estuaries of the rivers Rhine and Ems are concluded to consist of a mixture of the two components. The upstream transport of marine sediments may exceed the limit of salt penetration. Because trace metal concentrations in the marine sediments are low compared to those in the fluvial sediments, the mixing results into a decrease in metal concentrations downstream.

The good agreement between the metal concentrations calculated (from the measured mixing ratios of marine and fluvial sediments) and those observed in the estuarine deposits shows that the mixing process mainly controls the trace metal concentrations. No evidence was found for mobilization.

Generally the observed values, however, are slightly higher. This difference can be ascribed to precipitation-adsorption processes (DUINKER & NOLTING, 1977). It should be noted that the conclusions given above only apply to the sediments deposited in the estuaries of the Rhine and Ems.

V. SUMMARY

A decrease is observed in the trace metal concentrations of bottom sediments in the seaward direction in the estuaries of the rivers Rhine and Ems.

Naural tracers, primarily stable isotopes, used for distinguishing between marine and fluvial sediments show that this decrease is caused by the mixing of marine (low metal concentrations) and fluvial (high metal concentrations) sediments. Evidence is found for a limited occurrence of precipitation-adsorption processes.

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