

SOME OBSERVATIONS ON THE OCCURRENCE OF PHOSPHORUS IN RECENT SEDIMENTS FROM WESTERN EUROPE

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ABSTRACT

Near shore and fluvial sediments from the Netherlands and surrounding areas are composed of org-P, Fe-Al phosphorus and Ca-phosphorus. In marine sediments the org-P constitutes about 25% of the total phosphorus in the sediments. In Lake Yssel higher concentrations of organic phosphorus are found, whereas in fluvial sediments concentrations tend to be lower. The phosphorus in the highly contaminated river Rhine is mainly present as Fe-Al phosphorus. In sediments from the Dollard area (Wadden Sea), a diagenetic recycling of phosphorus takes place which results in high concentrations of phosphorus in the oxidised surface layer of the sediment. The phosphorus in this layer becomes reprecipitated as Fe-Al phosphate.

The oxidised surface layer may act as a chemical barrier against the upward flow of some metals and nutrients from the interstitial water to the surface waters.

INTRODUCTION

Phosphorus is an important element in the aquatic environment which has been subject to large increases due to man's activities. Particulate phosphorus (the word phosphorus is used as a general term to indicate the presence of various P-compounds, both organic and inorganic, in sediments) concentrations in the river Rhine increased nearly 8-fold between 1920 and 1973 (Salomons and Sissingh, 1976). The concentrations of phosphorus in rivers from Northern Germany are of the same order of magnitude (Brümmer and Lichtfuss, 1978).

In the aquatic environment phosphorus is a reactive element and, after sedimentation in particulate forms, it is released to the interstitial waters. Concentrations in pore waters from near-shore sediments from the Netherlands vary between 0.1 and 12 mg/l P (Salomons, unpublished results). Deposited sediments in the near-shore environment and lakes may act as a reser-

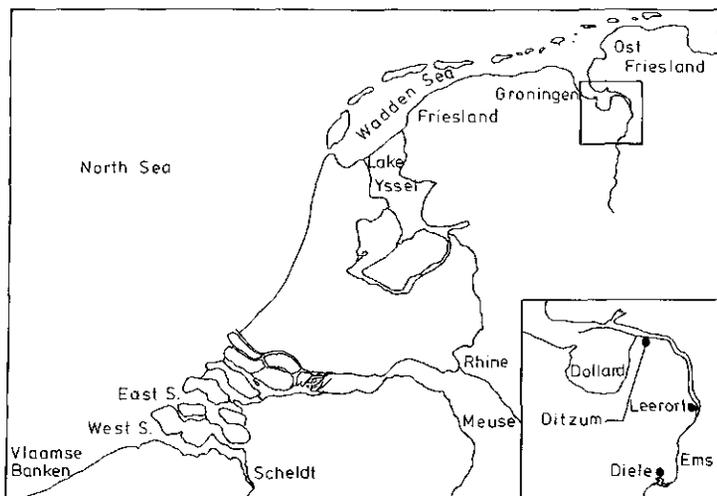


Fig. 1. The investigated area, showing the sampled localities.

voir of phosphorus for algal growth, even after the discharge of phosphorus in river systems is reduced (Golterman, 1977).

To understand the various processes affecting phosphorus in the aquatic environment its speciation, both in solution and in particulate form, should be identified. Several methods exist for determining the speciation of particulate phosphorus in soils and sediments (Chang and Jackson, 1957; Sommers et al., 1972; Williams et al., 1970, Kurmies, 1972; Hieltjes and Lyklema, 1978).

The amount of organic phosphorus in sediments is important for an understanding of the carbon cycle in the aquatic environment as well as for the release of phosphorus from the sediments to the pore waters. Therefore, we undertook some work on the determination of organic phosphorus in sediments by comparing a number of methods described in the literature. For the determination of Ca-phosphorus and Fe-Al phosphorus, we relied on the method developed by Kurmies (1972) which was also used by Lichtfuss and Brümmer (1978) for their study of sediments from Western Germany.

A first overall picture of the speciation of particulate phosphorus in marine and fluvial sediments has emerged from our investigations. The following data will be discussed:

- distribution of phosphorus in relation to grain-size fractions
- occurrence of organically bound phosphorus
- diagenetic processes affecting phosphorus after deposition
- changes in the speciation of phosphorus in sediments from the river Rhine with time.

This article is the 6th in a series dealing with the composition of recent sediments from Western Europe. Former articles dealt with carbonates

(Salomons, 1975), the clay fraction (Salomons et al., 1975), the organic matter (Salomons and Mook, 1981) and trace metals (Salomons and Mook, 1977; Salomons and De Groot, 1978).

EXPERIMENTAL METHODS

When investigating organic phosphorus compounds in soils, mud and other materials, it is useful to have an extraction method whereby all organic P compounds can be extracted and kept in solution with as little degradation as possible. A method capable of doing this has been mentioned in earlier papers (Gerritse and Zugec, 1977; Gerritse and Eksteen, 1978; Gerritse, 1978) and consists of an extraction with a solution of trichloroacetic acid (TCA), followed by an extraction with an alkaline solution of disodium ethylene diamine tetra-acetic acid (EDTA). Both TCA and EDTA also inactivate enzymes and micro-organisms. The procedure, however, is rather time-consuming. Two other methods have been compared with the TCA/EDTA method in order to find a more rapid method with the same reliability. The two methods are:

- a solution of HF (40%), HCl (36%) and TiCl_4 in a volume ratio of 10:200:9 (Tinsley and Ozgavasci, 1975; Gerritse and Zugec, 1977)
- 2.5 M HCl (Wenzel, 1956).

With the TCA/EDTA method, total organic phosphorus is found from the sum of the differences between total and inorganic phosphorus in both extracts. With the other two methods, total organic phosphorus is found from the differences between total P (after destruction) and total inorganic P in the extract. In all methods, the procedure is to extract 1 to 5 g of dried sample (depending on P-content) with 50 ml of extractant for 5 to 10 min on a boiling water bath, while refluxing. After filtration and washing with 25 ml of extractant followed by water, inorganic P is determined in the filtrate. Inorganic P (= ortho-P) was determined colorimetrically using ascorbic acid as a reducing agent (Murphy and Riley, 1962). It was found that, when Ti was present in the extractant, the time necessary to obtain a stable colour of phosphomolybdate with the Murphy and Riley method increased from about 20 min at a final concentration of Ti of 0.01 mol/l to 4 h at a final Ti concentration of 0.05 mol/l.

The three methods have been compared for a variety of materials ranging from sediments to pig, calf and chicken slurries (Fig. 2 and 3). The total phosphorus concentrations range from 0.1% (marine sediments) to 25% chicken slurry). Good agreement was found between the amount of organic-P found with the TCA/EDTA, the Tinsley method, as well as the "Wenzel" method. We conclude that all three procedures used are comparable. For ease of analysis, we selected the simple "Wenzel" method to determine the amount of organic phosphorus in sediments.

For the determination of Ca-phosphorus and Fe—Al-phosphorus we relied on the method developed by Kurmies (1972).

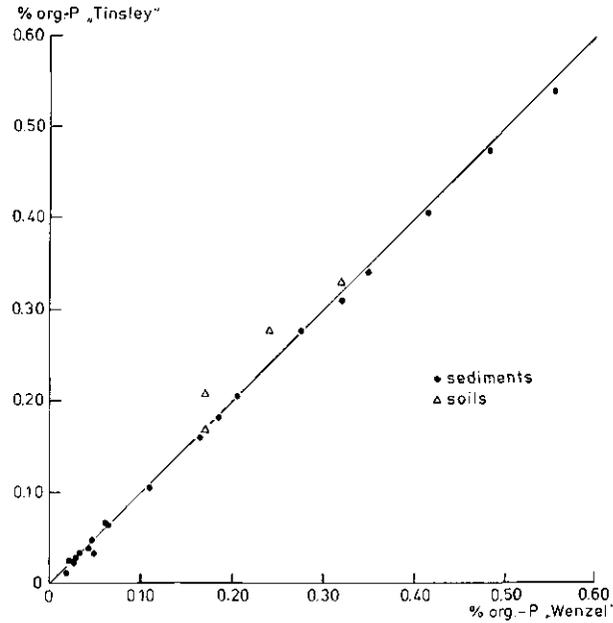


Fig. 2. The correlation between the "Wenzel" and the "Tinsley" methods for determining organically bound phosphorus.

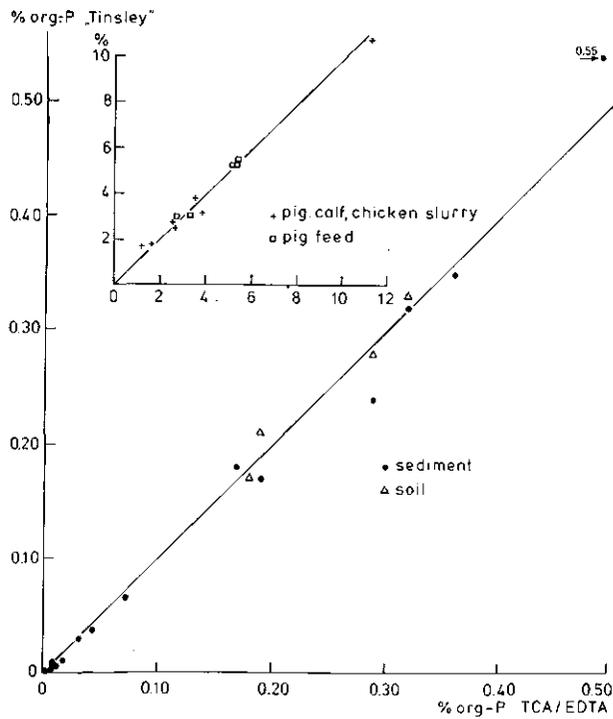


Fig. 3. The correlation between the "Tinsley" and the "TCA/EDTA" methods for determining organically bound phosphorus.

RESULTS AND DISCUSSIONS

Total phosphorus in sediments

A wide range of phosphorus concentrations is often observed in sediment samples from one locality. High concentrations are found in clay-rich samples, whereas the concentrations are low in sandy samples. The concentrations, however, show a positive correlation with the amount of finely grained particles, as expressed by the percentage of particles with diameters less than $16\ \mu\text{m}$ in the samples analysed. The results for a number of contrasting localities, the rivers Ems, Scheldt, Meuse and the Wadden Sea area, are given in Fig. 4. Similar conclusions have been found for phosphorus in sediments from the Northern part of Germany (Brümmer and Lichtfuss). The mineralogical, major and minor element compositions also show this correlation (Salomons and Mook, 1977). To substantiate further the fact that phosphorus is associated with finely grained particles, grain-size fractions of sediment samples from the Ems and Wadden Sea were isolated. Total phosphorus concentrations were determined in the fractions $0-2\ \mu\text{m}$, $2-16\ \mu\text{m}$, $16-53\ \mu\text{m}$ and $53-105\ \mu\text{m}$. The results, expressed as percentages of the total phosphorus concentrations, are presented in Fig. 5. The clay-sized fraction ($0-2\ \mu\text{m}$) contains more than 70% of the total phosphorus present. To compare the composition of sediments from different sedimentation areas, it is not possible to use individual samples directly because of possible differences in grain-size composition. In order to compare the composition between sedimentation areas or to determine changes in compo-

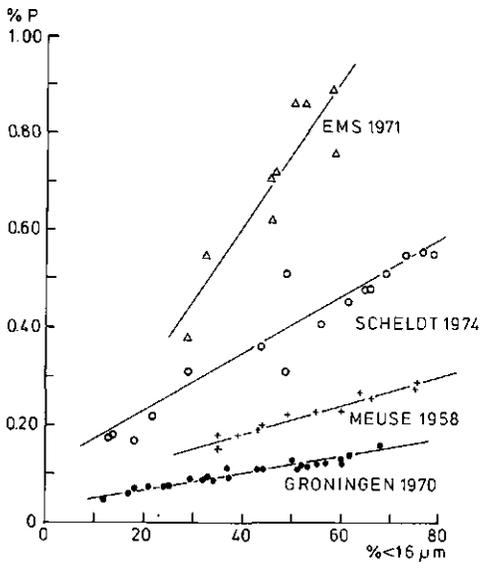


Fig. 4. The correlation between total phosphorus concentrations in sediments and the percentage of particles with diameters less than $16\ \mu\text{m}$.

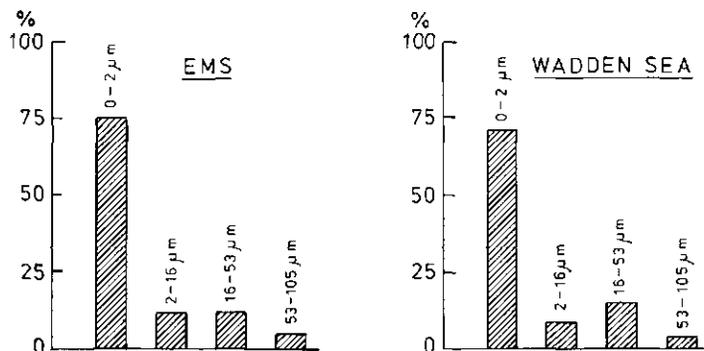


Fig. 5. The occurrence of phosphorus in grain-size fractions, expressed in % of the total phosphorus concentration.

sition with time, corrections have to be made for the grain-size distribution (De Groot et al., 1976).

Up to now, no single method has been adopted for presenting phosphorus concentrations in sediment samples. To compare the phosphorus concentrations from different sedimentation areas and to determine the development of phosphorus concentrations with time, the concentrations at 50% < 16 μm will be used in this study. These values are obtained by analysing from each separate locality a large number of samples and constructing curves as shown in Fig. 4. The value of 50% < 16 μm corresponds to the mean grain-size composition of estuarine sediments from the Rotterdam harbour, a major sedimentation area in the Netherlands. Furthermore, this value is close to the mean grain-size composition of suspended matter from the river Rhine (Van Eck, personal communication).

Baseline data for phosphorus

Baseline data for phosphorus in deposited sediments were established by analysing sediments samples from the river Rhine sampled in 1922, from the Dollard area (Wadden Sea), sampled in 1921 and from the Zuiderzee sampled in 1933. These sediment samples have been kept in the archives of the Institute for Soil Fertility. Data on their heavy metal concentrations have recently been published (Salomons and De Groot, 1978). The results of the analyses are presented in Fig. 6.

The differences in concentrations, if the differences in grain-size distribution of the individual samples are taken into account, are not very large. The concentration at 50% < 16 μm for all samples is 0.076%, for the marine sediment samples (Dollard) it is 0.080 and for the samples from Lake Yssel the value is 0.069% P. These values correspond rather well with the concentrations for the average shale (Turekian and Wedepohl, 1961) 0.07%. The value of 0.076% will be used as a baseline for the Netherlands. Compared with this baseline value, the concentrations in the river Rhine in 1973

TABLE 1
THE PHOSPHORUS AND ORGANIC PHOSPHORUS CONCENTRATIONS IN THE
SEDIMENTS ANALYSED (Fig. 1)

N refers to the number of samples analysed. P_{\min} refers to lowest phosphorus concentration found P_{\max} to the highest concentration.

P_c is the calculated phosphorus concentration at 50% < 16 μm calculated from the regression line $y = bx + a$. y is the total phosphorus concentration and x is the % < 16 μm . r^2 is the correlation coefficient

P_{org} is the amount of organic phosphorus given as a percentage of the total phosphorus concentration.

	N	P_{\min} %	P_{\max} %	P_c %	P_{org}	r^2	a	b
<i>Fluvial sediments</i>								
Rhine 1922	15	0.060	0.095	0.078	20	0.277	0.060	0
Rhine 1958	8	0.165	0.354	0.265	6.4	0.906	0.141	0.002
Rhine 1965	14	0.214	0.483	0.329	1	0.831	0.144	0.004
Rhine 1970	16	0.252	0.527	0.470	7.8	0.932	0.159	0.006
Rhine 1973	10	0.323	0.636	0.578	4.8	0.987	0.142	0.009
Meuse 1958	12	0.150	0.287	0.210	22.4	0.948	0.068	0.003
Meuse 1971/1972	30	0.176	0.650	0.403	1	0.934	0.025	0.008
Ems 1964/1965	19	0.207	0.557	0.401	11.0	0.709	0.050	0.007
Ems 1971	9	0.382	0.891	0.749	17.7	0.811	0.016	0.015
Scheldt 1974	18	0.170	0.555	0.407	11.8	0.906	0.119	0.006
<i>Marine sediments</i>								
Westerschelde 1974 (W)	15	0.041	0.135	0.101	20.7	0.855	0.040	0.001
Oosterschelde 1975 (E)	15	0.048	0.129	0.093	27.3	0.870	0.035	0.001
Friesland 1970	25	0.073	0.174	0.114	19.3	0.892	0.031	0.002
Groningen 1970	25	0.047	0.158	0.120	19.3	0.932	0.035	0.002
Leybocht 1975	8	0.093	0.158	0.114	22.9	0.950	0.020	0.002
Ost-Friesland 1969	12	0.074	0.145	0.132	20.4	0.762	0.039	0.002
<i>Estuarine sediments</i>								
<i>Ems-estuary (1971)</i>								
Diele	9	0.382	0.891	0.749	7.4	0.811	0.016	0.015
Leerort	12	0.126	0.272	0.217	15.4	0.896	0.060	0.003
Ditzum	11	0.177	0.207	0.141	17.7	0.514	0.054	0.002

The range of values found for org-P is similar to data reported for the Narragansett Bay sediments (Poon, 1977). After deposition, some recycling of phosphorus in the sediment may take place as a consequence of biological activity. However, no data are available for the areas concerned. In principle, it is possible to study the biological recycling of phosphorus with radioactive tracers (Gerritse et al., 1977, 1978). In sediments, however, the overwhelming influence of adsorption of both inorganic and organic phosphorus will complicate the analysis to such an extent that results of tracer studies cannot simply be translated into a complete phosphorus cycle.

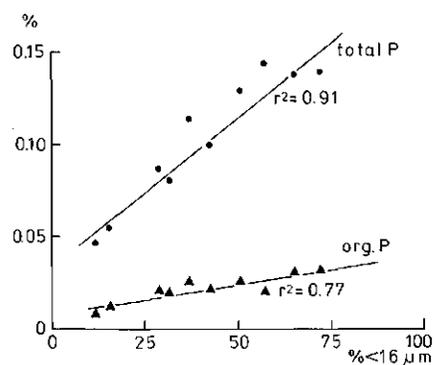


Fig. 7. The correlation between total phosphorus and organic phosphorus concentrations and the amount of particles less than $16\ \mu\text{m}$ in diameter in the sediment samples analysed. The correlation between total and organic phosphorus is 0.71.

In the Ems-estuary, the org-P concentrations increase in the seaward direction whereas the total-P concentrations decrease. These variations in the estuary are caused by the mixing of marine (low total-P, high org-P) with fluvial sediments (high total-P, low org-P) in the estuary (Salomons and Mook, 1977).

High concentrations of organically bound P are found in sediments from lake Yssel, which is fed by a distributary of the river Rhine. In the sediments of this lake about 60% of the phosphorus in the sediments is present as org-P.

Diagenetic processes affecting phosphorus in sediments

During our investigations some puzzling phenomena were observed in the Dollard area. Phosphorus concentrations in the oxidised part of the sediment were very high compared with those in the reduced underlying layers. High concentrations were also observed for manganese and iron (Table 2).

Phosphorus and manganese concentrations have increased more than twice in the surface layers compared with the sediment at greater depth. Inspection of data available for other areas (Groningen and Oosterschelde) showed that in these areas the phosphorus concentration tends to be higher in the surface

TABLE 2
THE CONCENTRATIONS OF PHOSPHORUS, IRON AND MANGANESE IN SURFACE (UPPER 2 mm) AND IN REDUCED LAYERS IN THE DOLLARD AREA
The data represent the calculated concentrations at $50\% < 16\ \mu\text{m}$.

	Phosphorus ($\mu\text{g/g}$)	Iron ($\mu\text{g/g}$)	Manganese ($\mu\text{g/g}$)
Surface layer (oxidised)	1720 ± 140	25900 ± 600	1230 ± 220
Reduced layer (2–10 cm)	660 ± 90	21120 ± 470	580 ± 45

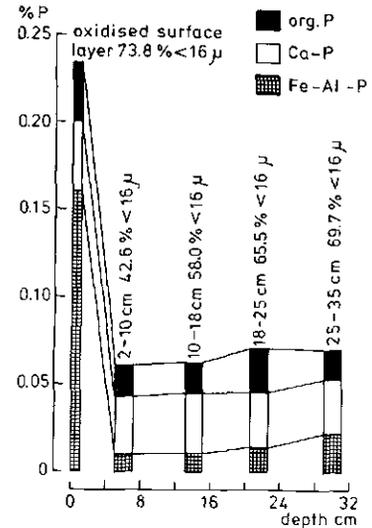
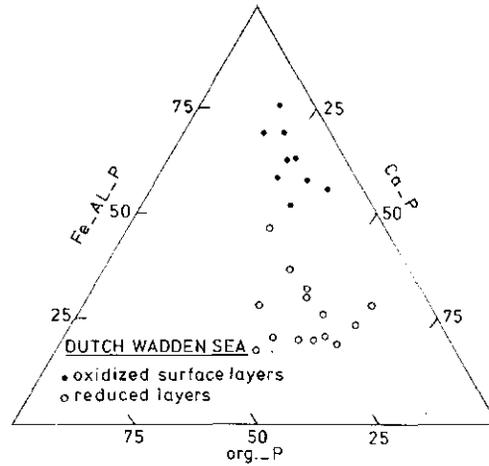


Fig. 8A. The speciation of phosphorus in sediments from the Dollard area (Wadden Sea).

Fig. 8B. The speciation of phosphorus along a profile in the Dollard (Wadden Sea).

TABLE 3

THE MEAN CONCENTRATIONS OF P, Fe AND Mn IN PORE WATERS FROM THE DOLLARD AREA

The values between brackets are the minimum and maximum concentrations found.

P (mg/l)	Mn (mg/l)	Fe (mg/l)	pH
1.6 (0.1-3.8)	1.9 (1.4-3.0)	0.3 (0.05-1.7)	7.8 (7.5-8.2)

layers. However, the differences for phosphorus are statistically within the standard deviation; for manganese the concentrations in Groningen are statistically different between the surface and reduced layers. In the Oosterschelde, a vast sedimentation area was sampled, no differences could be detected.

Therefore we selected the Dollard area for a more detailed study into this phenomenon. Both the surface layers and the reduced layers were investigated for the speciation of phosphorus (Fig. 8A), additionally two profiles were taken. Samples were taken with a plastic tube which was pushed into the sediment. The sediment columns, inside the plastic tube, were transported to the laboratory, and the pore waters extracted under nitrogen using a modified press after Presley et al. (1965). The first 30 ml of pore waters were not used for analysis, due to contamination by oxygen which remains in the filters even after purging the sediment press with nitrogen before filling.

The results of the pore water analysis are presented in Table 3.

Figure 8A shows that the speciation of phosphorus is different between the surface and the reduced layers; Fe—Al phosphates dominate in the surface layers.

In Fig. 8B, the speciation of phosphorus along a profile is shown. About 60% of the phosphates in the surface layer consist of Fe—Al phosphates, organic phosphorus is 13% and Ca—P is 28%. In the reduced layer Fe—Al phosphorus makes up only 22% of total P, the dominant form is Ca—P (48%) and org-P is 30%. The absolute concentration of Ca—P is constant with depth, org-P is slightly higher in the surface layer, whereas Fe—Al phosphorus is predominant in the surface layer. Bioturbation in the area studied is not important, as shown by the differences in concentrations of phosphorus and iron between the surface layers and deeper layers of the sediment. The enrichment of phosphorus, iron and manganese in the surface layers can be explained with the aid of the diagenetic recycling model proposed by Hallberg (1972, 1974, 1978). Dissolved phosphorus together with other enriched components in the pore water migrate upward in the sediment column as a consequence of concentration gradients between the pore water and surface water. The upward movement is enhanced by consolidation resulting in an upward movement of pore water. When the upward migrating metals and phosphorus encounter the oxygen-rich surface layer, they are reprecipitated. The precipitation of iron together with phosphorus is a very rapid process and has been shown by experiments on sampling of pore waters (Bray et al., 1973; Troup et al., 1974). As a result Mn, Fe and P become enriched in the surface layer. The results of the speciation show that the reprecipitation takes place as Fe—Al phosphate. After renewed deposition, the former surface layer becomes reduced and mobilization of Fe, Mn and P takes place. The released trace metals start migrating upward again and become reprecipitated in the new surface layer. This process results in an upward migrating enriched surface layer. This investigation also illustrates that manganese is not a good tracer for sediment transport studies because it does not fulfill the condition of conservative behaviour after deposition (Salomons et al., 1978). The oxidised surface layer, therefore, acts as a chemical barrier against the upward flow of metals (iron and manganese) and phosphorus in the Dollard area. Under extreme conditions the oxidised surface layer may form a hard pan and act additionally as a physical barrier. However, these pans have not been observed in the area studied.

Changes in the speciation of particulate phosphorus in the river Rhine with time

The river Rhine is subject to a high phosphorus load, particulate phosphorus concentrations increased from 0.08% to 0.63% in 1973. The question arises how the "extra" input of phosphorus is incorporated in the sediments. By analysing sediment samples taken in 1922, 1958, 1965 and 1973, it has been possible to determine the changes in speciation. The results are presented in Fig. 9.

Compared with an increase in total-P of about 8, the org-P concentrations

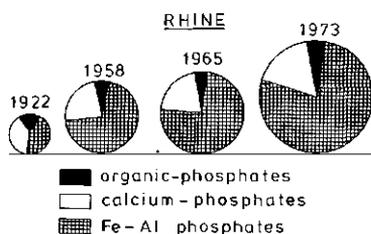


Fig. 9. The changes in the speciation of phosphorus in sediments from the river Rhine with time.

have only doubled. The Ca-P concentrations increased, though their relative contribution decreased. The concentration of Fe-Al-P increased both absolutely as well as relatively. The major part of the extra input of P into the river system is present as iron-aluminum phosphates. Similar observations have been reported for the river Elbe by Brümmer and Lichtfuss (1978).

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