

## POTENTIALLY BIOAVAILABLE PHOSPHORUS IN SEDIMENTS OF THE WESER ESTUARY

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### ABSTRACT

Forms of phosphorus in sediments, suspended matter and dredged material of the Weser Estuary were studied. Highest concentrations are shown by the nonapatite inorganic phosphate fraction, which is considered to be the most reactive and preferred "available" P component. Apatite phosphate is negligible and organic phosphorus plays only a secondary role. The latter P form is closely associated with the organic carbon contents of the samples.

### INTRODUCTION

The bioavailability of phosphorus is - in addition to the physico-chemical conditions in the water - closely related to its chemical form in solid matter.

Kurmies<sup>1</sup> described the various phosphate associations and crystallized forms in soils. The main components are calcium phosphates (e.g. apatite), aluminum phosphates (e.g. variscite, evansite, wavellite and amorphous precipitates), iron phosphates (strengite, vivianite and amorphous precipitates), and organically-bound phosphorus.

The most labile solid phosphate components are the Fe- and Al-phosphates. These occur preferably either in a chemically sorbed state or on the surface of particles or are held in a matrix made up of phosphate-bonding components such as gibbsite, goethite or amorphous aluminosilicates.<sup>2</sup>

The phosphate bound on aqueous Fe (and probably Mn) oxides constitute a potential that - under anaerobic conditions - would be

expected to result in high remobility rates<sup>3</sup>.

Calcium-associated phosphate goes into solution only to a small extent. Under natural conditions the dissolution rate of apatite is less than 1% when in contact with water during sedimentation.<sup>4</sup>

#### EXPERIMENTAL METHODS

With regard to the classification of Williams<sup>5</sup>, the determination of the various chemical binding forms is possible with a sequential extraction procedure. The analytical procedure, modified by Williams<sup>6</sup> and used here is outlined diagrammatically in Fig. 1.

The reducible components bound mostly on Fe-oxidhydrate and therefore mobilizable are first determined with a dithionite-citrate-bicarbonate extraction (DCB- $\text{PO}_4$ ). The remaining undissolved Fe- and Al-phosphates are ascertained with 1 N NaOH (NaOH-I- $\text{PO}_4$ ).

The overall portion of inorganic phosphates (T-I- $\text{PO}_4$ ) can be obtained in a separate sample after an extraction with 1 N HCl lasting 12 h. The T-I- $\text{PO}_4$  consists of the apatite phosphate (A- $\text{PO}_4$ ) and the nonapatite inorganic phosphate portion (NAI- $\text{PO}_4$  = DCB- $\text{PO}_4$  + NaOH-I- $\text{PO}_4$ ). The total phosphate contents (T- $\text{PO}_4$ ) obtained by heating at 550°C for one hour is taken as the control sample, which is subsequently extracted with 1 N HCl and determined on a third sample.

The organic phosphorus (O-P) is obtained by determining the difference between total phosphate and total inorganic phosphate or after heating the residue of T-I- $\text{PO}_4$  (1 h at 550°C) and subsequent extraction with 2 N HCl.

#### RESULTS AND DISCUSSION

We applied the sequential extraction procedure to different solid substances from the Weser Estuary. Selected data shown in Fig. 2 indicate highest concentrations for the NAI- $\text{PO}_4$  fraction, that is for the reactive phosphate fraction.

For sediments, the grain size fraction <63  $\mu\text{m}$  has been analyzed. The different phosphate contents in sediments and dredged ma-

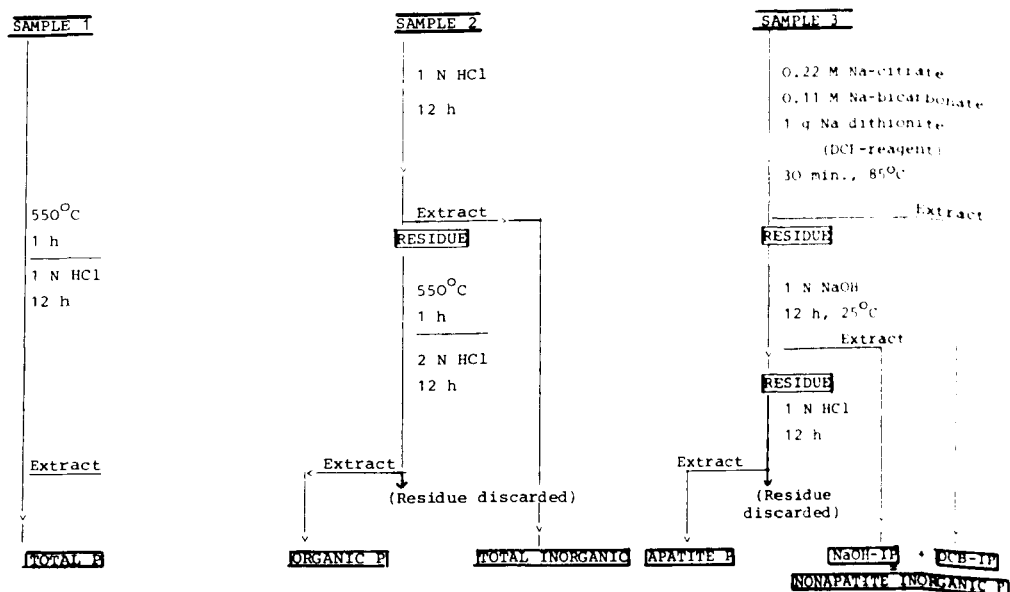


Fig.1: Outline of an analytical procedure used to determine total  $\text{PO}_4$ , total inorganic  $\text{PO}_4$ , organic P, apatite  $\text{PO}_4$  and nonapatite inorganic P.

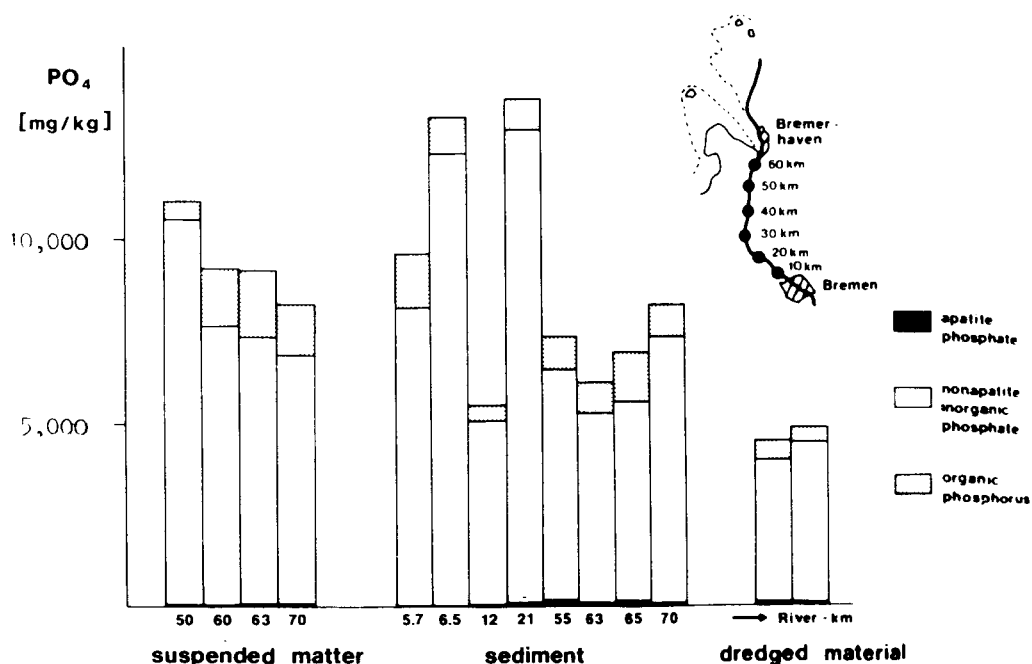


Fig. 2: The speciation of phosphorus in sediments, suspended matter and dredged material of the Weser Estuary.

terial are thought to originate chiefly through grain size effects, a fact which has also been pointed out by Salomons & Gerritse.<sup>7</sup>

The contents in suspended matter are in the same order of magnitude as in sediments.

Apatite phosphate contents are negligible and organic phosphorus plays only a secondary role. The latter is closely associated with the organic carbon contents of the samples, which lie for dredged material and sediment at 3% and for suspended matter at ca. 6%.

For comparison, Table 1 shows the values of several rivers and lakes. The P contents of the Weser River are in the same order of magnitude as those of the Elbe, Ems and Rhine Rivers. The values of the lake sediments are generally lower. The portion of "potentially available P" amounts to about 80% of total P for the heavily polluted samples. Sediment cores, for example from Lake Erie, clearly show that these P amounts can be traced chiefly to anthropogenic effects. The potentially available P of surface water is 50% of total P, but at a depth of 35 cm (= approx. 1850)<sup>4</sup> it is only 15%. The sediment cores from Lake Ibanuma show a similar development.

Sample location	Total P (mg/kg)	Potent.avail.P (mg/kg or	Organic P percentage of total P)
L. Erie <sup>4,5</sup>	188-2863	38-2329	0-286
core no. 2 core depth			
0-1 cm	1420	730	400
1-2 cm	1230	600	320
35-40cm	540	80	80
L.Ontario <sup>8</sup>	370-1730	36- 620	6-340
L.Leman <sup>14</sup>	421-2000	85- 500	84-350
L.Inbanuma (Japan)			
& Shinkawa R. 0-5 cm	1000-6090	480-5260	190-440
(4 cores) 30-40cm	340- 440	70- 170	20-110
Elbe R. <sup>12</sup>			
Geesthacht	111-8278	80-92% of Tot.P	5-38% of Tot.P
Hamburg	81-7866		
Rhine R. <sup>7</sup> (1973)	3230-6360	>75% of Tot.P	4.8% of Tot.P
Meuse R. (2971/72)	1760-6500		1% " " "
Ems R. (1971)	3820-8910		17.7% " " "
Scheldt R. (1974)	1700-5550		11.8% " " "
Ems Estuary (1971)	1770-8910	70% of Tot.P	7.4 - 17.7% of Tot.P
Weser R. Sediment	1756-4462	1718-4261	133-484
Suspended matter	2697-3586	2337-3400	169-591
Dredged material	1468-1550	1223-1256	122-155

Table 1: Examples of studies on phosphorus speciation in aquatic sediments.

As the reactive and preferred "available" phosphate fraction (for its uptake by plants and its part in short-term chemical reactions), chiefly the  $\text{NAI-PO}_4$  component is in consideration; the same is true for a part of the organically bound phosphorus. A test proposed by Williams et al.<sup>8</sup> on phosphorus uptake by the algae *Scenedesmus quadricauda* indicates that the available phosphorus is not a constant proportion of total particulate phosphorus but is directly related to the nonapatite inorganic phosphate. (Linear regression analysis indicated that cell uptake averaged about 75% of the  $\text{NAI-PO}_4$ . Apatite phosphate did not support algal growth.).

Analogous to the question of association and availability of heavy metals<sup>9</sup> - for which the exchangeable and easily reducible fraction is preliminary available for the short-term reactions (extractable with acidified hydroxylamine hydrochloride<sup>10</sup> or similar reagents)-the  $\text{NAI-PO}_4$  fraction should be further sub-categorized for the phosphates.

Here too, the anaerobic milieu could have great influence, so that the experiments should be so set up as to simulate these conditions. Golterman<sup>11</sup> used for the determination of available phosphorus 0.05 M Ca-NTA and added 1% ascorbic acid as a reducing agent. In this way, the iron-bound phosphate can be extracted, which is normally released under anaerobic conditions.

As in metal partitioning, the pH conditions, i.e. carbonate contents, should be especially carefully observed for the transfer from solid substrate to plants.

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