

# Available phosphorus in lake sediments in The Netherlands

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## Abstract

The amount of phosphorus available to algae in the sediments of four lakes in the western part of the Netherlands has been assessed by means of chemical extraction and bioassay techniques. In addition to direct chemical sediment analyses, extractions were carried out with an NTA column method and a stepwise  $\text{NH}_4\text{Cl}$ - $\text{NaOH}$ - $\text{HCl}$  shaking method, the latter supposedly separating the weakly bound, the Fe- and Al-bound and the Ca-bound phosphates in the sediments. Bioassays, with sediment as the sole source of P, were made with *Scenedesmus quadricauda* in modified Skulberg's Z8 medium to determine the amount of phosphates available to algae.

The average total P concentration of the sediments varied from 0.8 to 3.6  $\text{mg P g}^{-1}$  dry wt and correlated well with the net external P loading of the lakes. Uptake of P by algae in the bioassays varied from 0.4 to 36% while NTA extracted 36–69% of the total P. The ratio  $\text{NH}_4\text{Cl}$  extracted/ $\text{NaOH}$  extracted/ $\text{HCl}$  extracted phosphates is different from lake to lake, although in all lakes the highest extractions (27–62% of total P) are found in the NaOH fraction. However, in the peaty sediments of these lakes, the NaOH step extracted not only the Fe- and Al-bound phosphates but, also, large amounts of humus compounds. Hence, this fraction also contains non-available organic P.

The results are related to soil type and chemical characteristics of the sediments, and compared with data from other authors. A positive correlation was found between phosphate available to algae and NTA- and NaOH-extractable P, but the correlation with total phosphorus was higher. Moreover, algal-extractable P proved to be positively correlated with total iron and clay content and negatively with the amount of organic matter.

It is concluded that the sediments in the investigated lakes show great variability and that the chemical extraction techniques cannot replace the bioassays to assess the amount of phosphorus available to algae.

## Introduction

Due to the growing population and the increasing nutrient load of the river Rhine, eutrophication in the Netherlands has progressed so far in the last decades that most of the inland lakes should now be considered hypertrophic (Leentvaar 1980).

In 1970 the gross P-load of the surface waters in the Netherlands was estimated at an average of 6  $\text{g P m}^{-2} \text{y}^{-1}$  (Golterman 1976, 1977), of which 4  $\text{g P}$

$\text{m}^{-2} \text{y}^{-1}$  remained in the sediments. In the area of the Rijnland Water Authority, situated on the delta of the Rhine (Fig. 1), the values are even higher: A gross P-load of 14–15  $\text{g P m}^{-2} \text{y}^{-1}$  is estimated, of which between 3 and 7  $\text{g P m}^{-2} \text{y}^{-1}$  deposits in the area, depending on climatic and hydrological conditions (Schmidt-van Dorp 1978; Klapwijk 1981). Large differences in P-loading exist between the lakes within the area. About 10% of the P-load originates from the Rhine, while 70% comes from

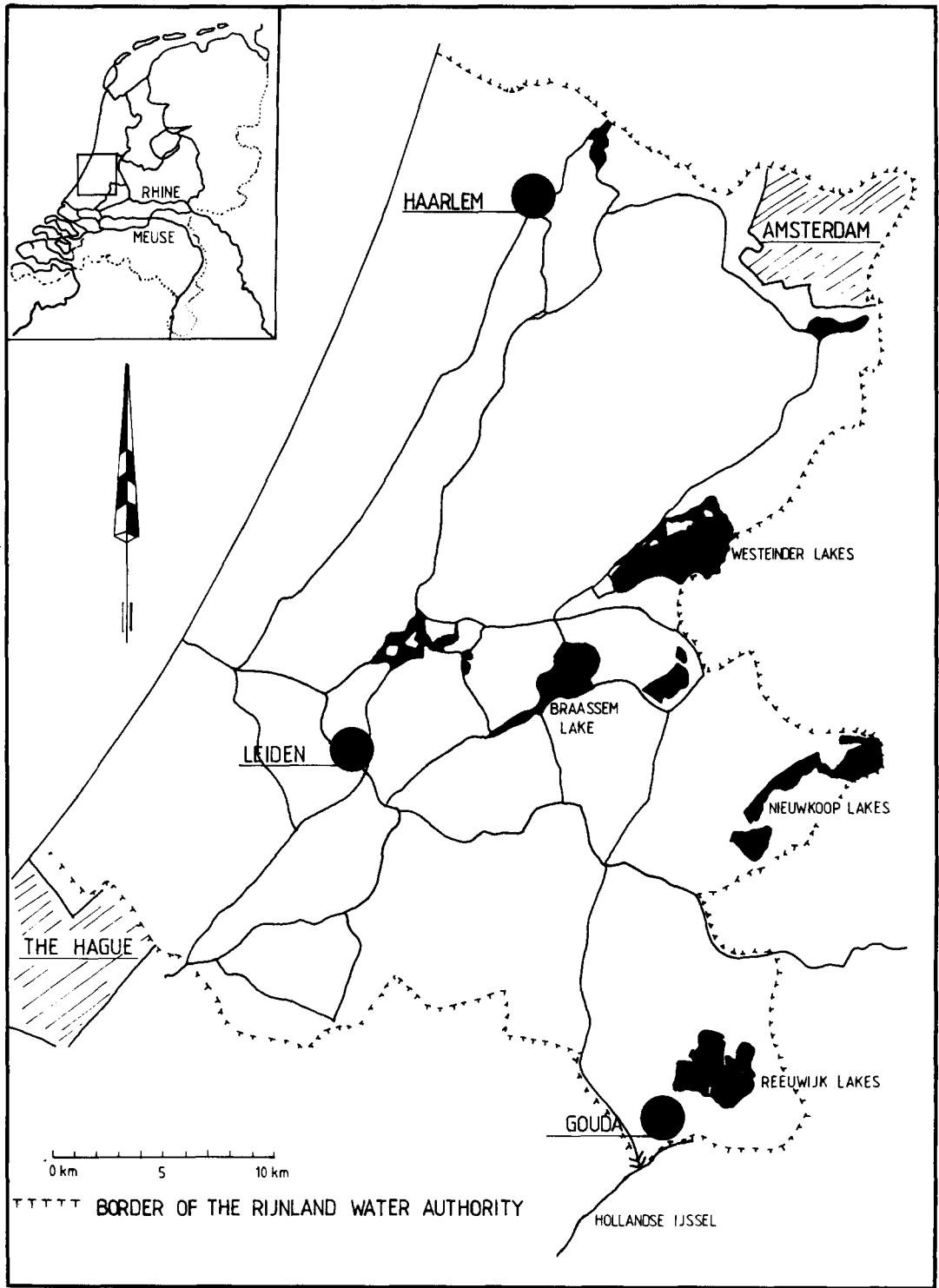


Fig. 1. The area of the Rijmland Water Authority, its location in the Netherlands (inset), and the location of the sampled lakes.

purified and unpurified wastewater.

As a lake restoration experiment, P-removal was implemented in 1979 at three sewage treatment plants, in the south-east of the Rijnland area. The effects on the lakes are being followed by limnological studies, which include plankton analysis and bioassays.

It is expected that the effects of the reduced P-load will be delayed by the release of phosphates from the sediments (see also Golterman 1977). Golterman *et al.* (1969) proved that algae can use sediment phosphate for their growth. Therefore it seemed necessary to investigate how much phosphate is accumulated in the sediments and how much of it is potentially available for algal growth.

In this paper, the first results of an investigation in four lakes, using bioassay and chemical extraction techniques, are presented. This research program will be continued and extended to the remaining lakes in Rijnland.

#### Sampling area, materials and methods

The Rijnland Water Authority encompasses a densely populated area (about  $10^6$  inhabitants in 1 000 km<sup>2</sup>) situated between the cities of Amsterdam, Haarlem, The Hague and Gouda (Fig. 1).

In the 'boezem' of Rijnland, an interconnected system of canals and lakes and ditches, the water level is kept constant at 0.6 m below mean sea level. Water can be pumped in near Gouda, from the Hollandse IJssel, a branch of the Rhine, while excess water can be pumped out to the sea. The boezem supplies a great number of inlying polders with water. Some lakes, such as the Braassem Lake and the Westeinder Lakes, form part of this boezem system. Others, such as the Nieuwkoop and Reeuwijk

Lakes situated in polders at about 2 m below main sea level, are separated from the boezem but are also dependent on it for their water supply.

Lake characteristics, including morphometry, hydrology and phosphate loading, are given in Table 1. The top layer of the sediments from a number of sampling stations in the lakes was collected with a Lenz bottom grab (Schwoerbel 1972). After separation into an upper (0–5 cm) and a lower (5–15 cm) layer, the samples were transported to the laboratory in glass jars and stored at 4 °C. Dry weight was estimated by drying duplicate samples at 103 °C. The remaining analyses and the bioassays and chemical extractions were carried out after partial dewatering of the samples by squeezing (30–40 min; up to 600 kPa), or by slight drying (30–40 °C; 48 h).

Loss on ignition (LOI) was determined after heating to 600 °C. Particle size (<2 µm, <16 µm, <50 µm) was determined using the pipette method. Percentage CaCO<sub>3</sub> was measured volumetrically after shaking with hydrochloric acid. Anion exchange capacity (AEC) was assessed by treating the sediment with ammonium phosphate and subsequent percolation with ammonium chloride, and measuring the P content in the eluents. Chemical oxygen demand (COD) was measured by titration with ferrous ammonium sulphate, after oxidizing with potassium dichromate. Kjeldahl-nitrogen (Kj-N) was measured after digestion with sulphuric acid + Wieninger selenium mixture and total phosphorus (t-P) was measured after digestion with sulphuric acid + persulphate. Subsequently, determinations of NH<sub>4</sub><sup>+</sup> and ortho-P were made on a Technicon AA II autoanalyser. Total iron (Fe), total calcium (Ca) and total aluminium (Al) were determined by atomic absorption spectroscopy on a Perkin-Elmer S400 spectrophotometer. Particle

Table 1. General characteristics of morphometry, hydrology and phosphate loading of Braassem Lake, Westeinder Lakes, Reeuwijk Lakes and Nieuwkoop Lakes.

Lake	Surface (× 10 <sup>6</sup> m <sup>2</sup> )	Mean depth (m)	General sediment composition	Situation of lake	Residence time (y)	Gross P-load (g P m <sup>-2</sup> y <sup>-1</sup> )	Net P-load (g P m <sup>-2</sup> y <sup>-1</sup> )
Braassem	4.6	4.0	Clay	Boezem	0.13	20.6	3.7
Westeinder	9.3	2.7	Sand/ Peat	Boezem	4.8	0.9	0.3
Reeuwijk	8.2	1.9	Peat	Polder	8.2	1.0	0.5
Nieuwkoop	10.9	1.5	Peat	Polder	7.2	0.7	0.5

Table 2. Physical and chemical analyses of the sediment at the sampling stations in the investigated lakes.

Sampling station	Dry weight (%)	<2 $\mu\text{m}$ (%)	<16 $\mu\text{m}$ (%)	<50 $\mu\text{m}$ (%)	CaCO <sub>3</sub> (%)	LOI (%)	COD (mg g <sup>-1</sup> )	K <sub>J</sub> -N (mg g <sup>-1</sup> )	Fe (mg g <sup>-1</sup> )	Al (mg g <sup>-1</sup> )	Ca (mg g <sup>-1</sup> )	t-P (mg g <sup>-1</sup> )	AEC (mol PO <sub>4</sub> /0.1 g)
<i>Braasseem Lake</i>													
271	18	70	87	91	7	16	295	8	23	5	9	4.8	10
	(0-5 cm)												
	17	61	74	90	7	10	328	8	23	4	13	2.7	20
	(5-15 cm)												
273	18	66	90	96	8	22	358	9	23	6	16	4.5	18
	(0-5 cm)												
	28	55	70	96	10	35	337	8	22	4	13	2.3	31
	(5-15 cm)												
Mean $\pm$ s.d.	20 $\pm$ 5	63 $\pm$ 6	80 $\pm$ 10	93 $\pm$ 3	8 $\pm$ 1	21 $\pm$ 11	330 $\pm$ 26	8 $\pm$ 0.5	23 $\pm$ 0.5	5 $\pm$ 1	13 $\pm$ 3	3.6 $\pm$ 1.3	20 $\pm$ 9
<i>Westender Lakes</i>													
279	26	3	7	96	59	17	255	5	4			0.4	36
	(0-5 cm)												
280	8	14	34	98	11	49	722	17	19			1.0	26
	(0-5 cm)												
	15	5	34	95	10	63	503	12	15			0.6	14
	(5-15 cm)												
281	14	7	10	88	19	37	581	12	9			0.6	29
	(0-5 cm)												
282	9	13	29	93	14	49	800	19	14			1.1	31
	(0-5 cm)												
	9	14	22	88	18	22	425	9	12			0.5	25
	(5-15 cm)												
283	9	5	26	98	15	48	790	18	16			1.3	15
	(0-5 cm)												
	10	8	16	97	15	49	835	19	17			1.3	31
	(5-15 cm)												
284	11	1	19	90	8	65	953	12	4			0.3	29
	(0-5 cm)												
Mean $\pm$ s.d.	13 $\pm$ 6	8 $\pm$ 5	22 $\pm$ 10	94 $\pm$ 4	19 $\pm$ 16	44 $\pm$ 16	652 $\pm$ 225	14 $\pm$ 5	12 $\pm$ 6			0.8 $\pm$ 0.4	26 $\pm$ 7
<i>Reeuwijk Lakes</i>													
119.14	13	6	11	98	14	50	666	19	14			0.7	15
	(0-5 cm)												
	11	6	15	98	23	46	763	18	14			0.5	31
	(5-15 cm)												
134.08	11	21	32	96	7	37	589	15	20			1.0	30
	(0-5 cm)												
	12	11	26	94	1	50	748	6	14			0.9	5
	(5-15 cm)												
218.03	7	11	20	87	2	54	1181	29	16			1.3	15
	(0-5 cm)												
	15	13	19	89	2	54	841	21	10			0.6	11
	(5-15 cm)												
Mean $\pm$ s.d.	12 $\pm$ 3	11 $\pm$ 6	21 $\pm$ 8	94 $\pm$ 5	8 $\pm$ 9	49 $\pm$ 6	798 $\pm$ 207	18 $\pm$ 8	15 $\pm$ 3			0.8 $\pm$ 0.3	18 $\pm$ 10
<i>Nieuwkoop Lakes</i>													
94.09	6	4	18	96	0.3	62	1298	30	12			0.9	13
	(0-5 cm)												
	7	6	16	95	3	63	1171	28	11			0.8	7
	(5-15 cm)												
94.11	8	6	18	97	16	50	878	24	8			1.2	32
	(0-5 cm)												
	9	4	14	97	16	52	872	23	8			0.8	38
	(5-15 cm)												
94.12	6	3	12	89	1	58	1056	25	13			0.8	8
	(0-5 cm)												
	7	7	16	97	2	53	1089	26	15			1.0	9
	(5-15 cm)												
94.19	7	4	19	98	4	58	1000	23	9			1.0	10
	(0-5 cm)												
	8	2	7	89	8	60	1003	21	8			0.7	11
	(5-15 cm)												
94.20	7	3	17	93	24	60	867	24	8			1.1	27
	(0-5 cm)												
	8	2	15	86	13	52	829	23	8			0.8	23
	(5-15 cm)												
Mean $\pm$ s.d.	7 $\pm$ 1	4 $\pm$ 2	15 $\pm$ 4	94 $\pm$ 4	9 $\pm$ 8	57 $\pm$ 5	1016 $\pm$ 142	25 $\pm$ 3	10 $\pm$ 3			0.9 $\pm$ 0.1	18 $\pm$ 11

size, %  $\text{CaCO}_3$  and AEC were measured according to Al and Holland (1977), and all other analyses were made according to the standard methods of the Nederlands Normalisatie Instituut.

Bioassays with sediment as sole phosphate source were carried out in duplicate using *Scenedesmus quadricauda* (Turp.) de Brébisson as test-organism, and a modified Skulberg's Z8 50% medium (see Bolier *et al.* 1981) with an equimolar amount of KCl instead of  $\text{K}_2\text{HPO}_4$ . A 1-week-old culture of starved *Scenedesmus quadricauda*, on 10% Z8 with 5% P, was used to avoid cells which could have taken up luxury-P. The cultures were incubated on a shaking table (100 rpm) in 150 ml Jena erlenmeyers with 100 ml medium. About 200 mg of partly dried sediment and  $6.10^6$  cells were used as inoculum under the following conditions:  $20 \pm 1^\circ\text{C}$ ; light:  $70 \mu\text{E m}^{-2} \text{s}^{-1}$ ; day/night regime: 12/12 h. Growth of the algae was followed by counting the cells in approximately  $1 \text{ mm}^3$ , in a Bürker-Turk counting chamber. After reaching the maximal yield,  $1 \text{ mg P l}^{-1}$  as  $\text{K}_2\text{HPO}_4\text{-P}$  was added to one of the duplicate cultures in order to test whether the maximum growth was limited by phosphate. Available phosphate was calculated by comparing the maximum yield with a (linear) standard, established from the maximum yields in bioassays with *S. quadricauda* cultured in the same medium and under the same conditions, but with known amounts of  $\text{K}_2\text{HPO}_4$  (0-30-50-100-250-500-1000  $\mu\text{g P l}^{-1}$ ) instead of sediment.

Extraction with nitrilotriacetic acid (NTA) was performed essentially according to Golterman (1977): 1-1.5 g partly dried sediment was suspended in 50 ml 0.01 M neutralized NTA solution in a column (2.5 cm diameter). After settling of the sediment, 450 ml NTA solution was added and percolated at a rate of  $100 \text{ ml h}^{-1}$ . Total P was determined in the extract.

Selective fractionation of phosphates was performed according to Hieltjes & Lijklema (1980), using the following stepwise extraction scheme: Loosely bound +  $\text{CaCO}_3$  adsorbed phosphates, iron + aluminium bound phosphates, calcium bound phosphates were selectively extracted respectively by  $\text{NH}_4\text{Cl}$ , NaOH and HCl. Extraction was carried out on a shaking table (120 rpm) at a temperature of  $20 \pm 1^\circ\text{C}$ . After each extraction step the solution was filtered through a  $0.45 \mu\text{m}$  P-free membrane filter, the NaOH step being preceded by centrifugation. As the NaOH extracts

were strongly coloured by humus compounds, ortho-P could not be determined by the available methods. Therefore, in these cases, calculation of the extracted P was based on total P analyses, departing from the method described by Hieltjes & Lijklema (1980). The amount of P in the HCl extract was sometimes measured as total P (Braassem Lake and Reeuwijk Lakes) because ortho-P could not be measured, for unknown reasons.

## Results

In Table 2 the physical and chemical analyses of the sediment at 16 sampling stations and at two depths in the investigated lakes are summarized. From this table it can be seen that the clay content ( $\% < 2 \mu\text{m}$ ) in Braassem Lake is much higher than in the other lakes. The highest values for  $\text{CaCO}_3$  were observed in the Westeinder Lakes. LOI, COD and Kj-N are relatively low in Braassem Lake, but high in the other lakes, especially in the Nieuwkoop Lakes. The clay content decreases and the amount of organic matter increases in the following order: Braassem Lake, Westeinder Lakes, Reeuwijk La-

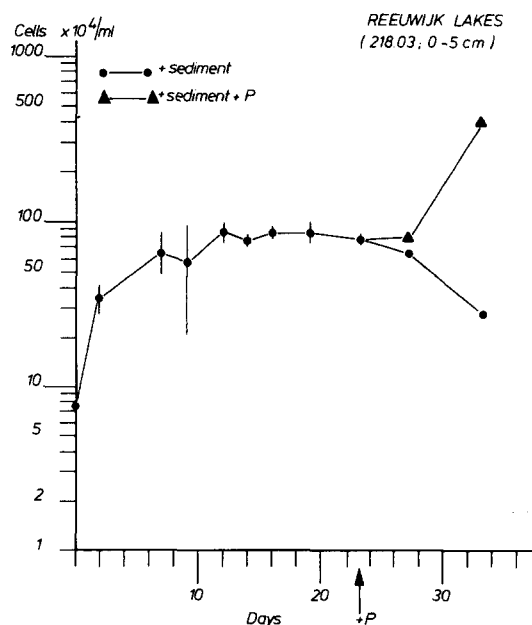


Fig. 2. Growth of *Scenedesmus quadricauda* (means  $\pm$  s.d.) in a bioassay with sediment from Reeuwijk Lakes as only source of phosphate. On the 23th day  $1 \text{ mg P l}^{-1}$  is added to one of the duplicate cultures (arrow).

Table 3. Algal-available and chemical-extractable phosphates determined by different methods. All values expressed as percentage of total sediment phosphorus. Values for bioassay calculated by comparing with standard; values for  $\text{NH}_4\text{Cl}$  extraction based on ortho-P, NTA and NaOH extractions based on total-P, HCl extraction of Braassem and Reeuwijk sediments based on total-P, of Westeinder en Nieuwkoop sediments on ortho-P determinations. See text.

Sampling station		Bioassay	NTA extraction	Selective extraction with		
				$\text{NH}_4\text{Cl}$	NaOH	HCl
<b>Braassem Lake</b>						
271	(0- 5 cm)	31	42	21	83	16
	(5-15 cm)	24	41	8	58	10
273	(0- 5 cm)	41	46	12	50	17
	(5-15 cm)	46	68	7	58	18
Mean $\pm$ s.d.		36 $\pm$ 10	49 $\pm$ 13	12 $\pm$ 6	62 $\pm$ 14	15 $\pm$ 4
<b>Westeinder Lakes</b>						
279	(0- 5 cm)	0	51	40	50	10
280	(0- 5 cm)	5.5	71	40	67	9
	(5-15 cm)	9.8	103	43	69	-
281	(0- 5 cm)	0	58	30	45	23
282	(0- 5 cm)	4.7	60	32	51	4
	(5-15 cm)	0	76	35	60	8
283	(0- 5 cm)	6.2	71	34	36	7
	(5-15 cm)	3.4	50	36	45	4
284	(0- 5 cm)	0	80	58	47	-
Mean $\pm$ s.d.		3.3 $\pm$ 3.6	69 $\pm$ 17	39 $\pm$ 8	52 $\pm$ 11	9 $\pm$ 6
<b>Reeuwijk Lakes</b>						
119.14	(0- 5 cm)	16	23	13	37	47
	(5-15 cm)	6	49	17	18	63
134.08	(0- 5 cm)	10	36	9	55	36
	(5-15 cm)	9	33	5	17	42
218.03	(0- 5 cm)	13	12	4	22	20
	(5-15 cm)	2	40	7	10	25
Mean $\pm$ s.d.		9 $\pm$ 5	36 $\pm$ 13	9 $\pm$ 5	27 $\pm$ 5	39 $\pm$ 16
<b>Nieuwkoop Lakes</b>						
94.09	(0- 5 cm)	0	54	14	48	4
	(5-15 cm)	0	42	33	61	6
94.11	(0- 5 cm)	0	29	22	41	5
	(5-15 cm)	3.4	47	21	34	5
94.12	(0- 5 cm)	0	27	19	60	10
	(5-15 cm)	0	36	28	48	9
94.19	(0- 5 cm)	0	28	14	53	9
	(5-15 cm)	0.3	33	26	57	10
94.20	(0- 5 cm)	0	26	17	47	6
	(5-15 cm)	0	41	28	40	11
Mean $\pm$ s.d.		0.4 $\pm$ 1.1	36 $\pm$ 9	22 $\pm$ 6	46 $\pm$ 9	8 $\pm$ 3

kes and Nieuwkoop Lakes. The total P content is 4-5 times higher, and the total Fe is about 2 times higher in Braassem Lake than in the other three lakes. Most parameters show no clear difference between the top 0-5 cm layer and the lower 5-15 cm layer; total-P and Kj-N, however, show slightly higher values in the top layer.

In Fig. 2 a growth curve of *Scenedesmus quadricauda* is shown for a bioassay with Reeuwijk sediment as sole source of P. The increase after addition

of phosphate on the 23rd day clearly shows that growth was limited by phosphate.

In Table 3 the results of the bioassays and the chemical fractionation of P forms are summarized. The highest percentage of P available to algae was found in bioassays with Braassem sediment (about 36%), and Reeuwijk sediment (about 9%). The fractions of available phosphate in bioassays with Westeinder and Nieuwkoop sediment appeared to be extremely low (3.3 and 0.4%, respectively). The

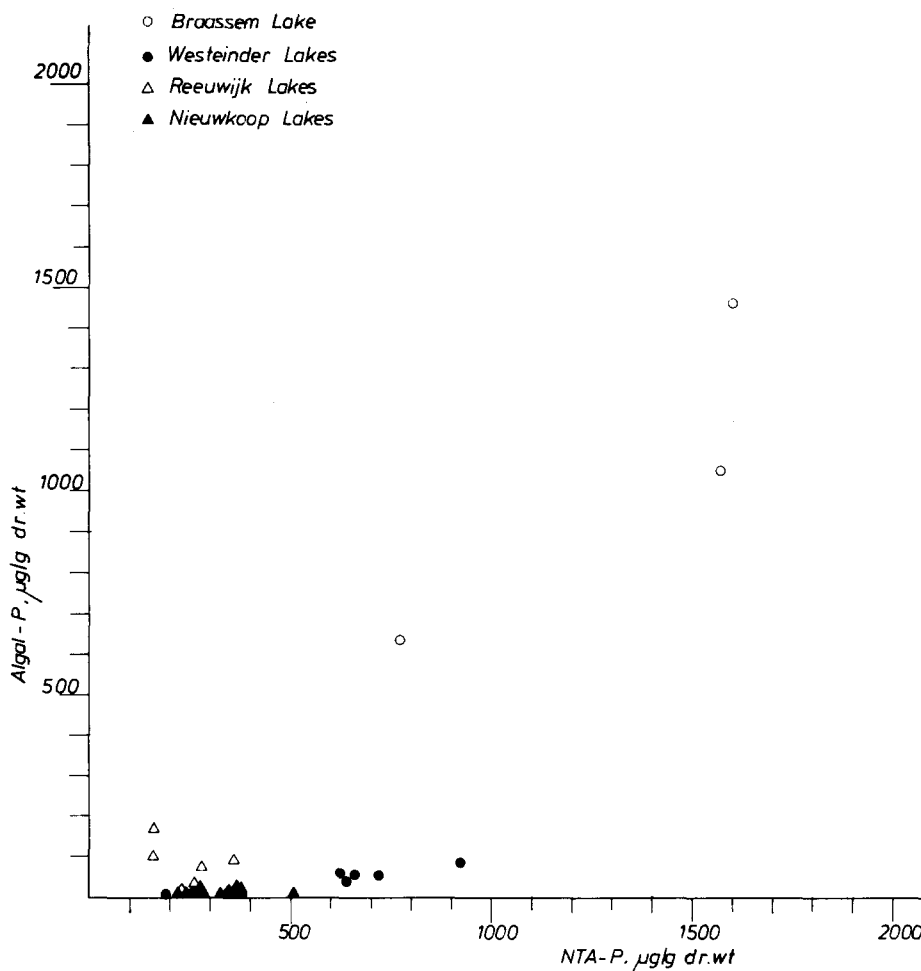


Fig. 3. The relationship between algal-extractable phosphate (algal-P) and NTA-extractable phosphate (NTA-P) in sediment samples of four lakes.

amount of phosphate extracted by NTA is much higher in all lakes, ranging from 36% (Reeuwijk and Nieuwkoop) to 69% (Westeinder) of the total P-content. In the selective extractions, the NaOH step extracted the highest percentage from all sediments. However, the ratio between the  $\text{NH}_4\text{Cl}$ , NaOH and HCl fractions varied with each lake. Neither the NTA extractable phosphate, nor the NaOH fraction (or the  $\text{NH}_4\text{Cl} + \text{NaOH}$  fraction) is quantitatively comparable to the amount of algal-extractable phosphate. In all lakes the chemical treatments extracted much more phosphate than did the algae.

No clear difference was seen in phosphate availability, between the top layer and the underlying sediment, assessed by different methods.

In Fig. 3 the amount of P extracted by NTA is plotted against the amount taken up by the algae in bioassays. For Braassem sediments the relationship between algal-extractable and NTA-extractable P is fairly good, but the Braassem samples deviate radically from the other lakes. Because of the lack of normality in the data-set, due to the values of the Braassem sediment, the computation of product-moment correlations (Grobler & Davies 1979) is not possible with our sediment data. Therefore, we computed Spearman's non-parametric rank-correlation coefficients (Sokal & Rohlf 1969) between the different extraction methods and between algal-extractable phosphate and some sediment properties; these are summarized in Table 4.

This table shows that both the NTA-extractable

Table 4. Spearman's rank correlation coefficients ( $r_s$ ) between algal extractable phosphates (algal-P) and different chemical extractable phosphates and some sediment properties.

Chemical-extractable P by:						
	NTA	NH <sub>4</sub> Cl	NaOH	NH <sub>4</sub> Cl+NaOH	HCl	
Algal-P/-	0.45**	0.13	0.38*	0.36	0.14	
Sediment properties:						
	total-P	Fe	<2 $\mu$ m	CaCO <sub>3</sub>	COD	LOI
Algal-P/	0.58***	0.82****	0.69****	0.09	-0.47**	-0.43**

\*P < 0.05; \*\*P < 0.02; \*\*\*P < 0.01; \*\*\*\*P < 0.001.

In all cases n = 29, except for algal-P/HCl extr.-P, in which n = 17.

and the NaOH-extractable phosphates are positively correlated ( $\alpha = 0.05$ ) with algal-extractable phosphates. However, neither the NH<sub>4</sub>Cl- and HCl-extractable phosphates nor the sum of NH<sub>4</sub>Cl + NaOH-extractable phosphates show any significant correlation with algal-extractable P. The amount of algal-extractable P is very positively correlated with total phosphorus, total Fe and clay content, but CaCO<sub>3</sub> is not correlated with algal-extractable P. A negative correlation is found between algal-extractable P and the parameters COD and LOI, indicating organic matter.

## Discussion

The average total P content in the four lakes corresponds fairly well with their net P-load (Table 1). From a comparison of the P content of our lakes with data from other authors, e.g. Williams *et al.* (1971, 1980), Grobler & Davies (1979) and Hieltjes (1980), it appears that the P content of Braassem sediment is rather high and that the P content in Westeinder, Nieuwkoop and Reeuwijk sediments is relatively low.

In this study the amount of algal-extractable P was calculated by comparing the maximal yield of a sediment bioassay with a calibration standard (established by the maximal yields in bioassays from known amounts of ortho-P, and cultured simultaneously under the same conditions). We consider this to be a better procedure than calculating the P available to algae from experimentally determined fixed coefficients, between algal biomass and P content (Golterman 1977; Golterman *et al.* 1969; and Grobler & Davies 1979), because different

experimental conditions may influence the P content per cell.

Our results on the percentage of available phosphate, established by means of bioassays, are low. The results from Westeinder and Nieuwkoop Lakes are especially low when compared to the data of Golterman (1969, 1977, 1980), Grobler & Davies (1979) and Williams *et al.* (1980). The difference between methods for calculating the phosphate availability to algae may be a reason for this, as previously mentioned.

In the bioassays with sediment the pH sometimes rose to 11, especially in fast growing cultures. This might promote the extraction of Fe- and Al-phosphates (Hieltjes 1980) and therefore increase the amount of P available to algae relative to the natural situation. In the investigated lakes pH values up to 9 are sometimes measured, due to the occurrence of algal blooms.

The % P extracted by NTA in our sediments is generally much higher than the % NTA-extractable P recorded by Golterman (1977), Grobler & Davies (1979, 1981) and Williams *et al.* (1980). Moreover our data from four lakes suggest, just like the results from Boström and Pettersson (1981), that the % extractable P varies from lake to lake, according to the type of sediment (see Table 3).

Our findings are not in agreement with Golterman (1977), who found that the amount of phosphate extracted with NTA, from sediments of several Dutch lakes, was similar in quantity to that extracted by algae such as *Scenedesmus* sp. Only in the case of Braassem sediments did NTA extract P amounts to the same order of magnitude as that in the bioassays. NTA extracted 4–90 times more P than algae, in the sediments of our other lakes. Our



results disagree even more strongly with those of Grobler & Davies (1979, 1981), using *Selenastrum capricornutum*, who found that algal available phosphate in sediments in South African reservoirs was generally 4–5 times higher than the NTA-extractable P. From Fig. 3, it can be seen that the relationship between algal-extractable and NTA-extractable P seems to depend on the type of sediment. For example, the ratio algal-P/NTA-P is much lower in the Westeinder Lakes than in Braassem Lake.

The NaOH fraction of the Hieltjes and Lijklema fractionation procedure probably contained organic P, due to the extraction of brown humus compounds and the necessity to measure total P instead of ortho-P (previously stated). According to Golterman (1973) and Williams *et al.* (1980), organic P is not available to algae. The fractionation scheme of Hieltjes & Lijklema (1980) therefore required an adaptation for use in peaty sediments. Siebers *et al.* (1981), using Mössbauer spectroscopy, also proved the lack of selectivity of an NaOH extraction for iron-phosphates in a sludge sample.

In none of the four lakes is either the NaOH fraction or the  $\text{NH}_4\text{Cl} + \text{NaOH}$  fraction in the same order of magnitude as the amount of phosphate extracted in bioassays, as Hieltjes (1980) found with sediment from 'De Grote Rug' reservoir. In our experiments NaOH extracted 2–10 times more phosphorus than algae from most sediments. This ratio was least in the Braassem sediments, and corresponded well with their relative low peat content.

Although calculated correlations between algal-extractable P and NTA-P, and NaOH-P, are significant, the correlation coefficients are not very high and in both cases much lower than the correlation between algal-P and total P (Table 4). The advantages of applying an NTA extraction (or a selective extraction according to Hieltjes & Lijklema 1980) to these sediment samples are not clear, because of the uncertain predictions of phosphorus available to algae. Even a normal total P determination showed better correlation with algal-extractable P.

Our findings with respect to the nature of algal-extractable phosphates are in fairly good agreement with the literature. Hieltjes (1980) stated that most of the algal extractable P is associated with iron or is adsorbed onto clay, and this is supported by the data from Table 4. The statement of Golterman (1973) that organic phosphates are not easily

used by algae, also fits in very well with our findings. On the other hand, little algal available P seemed to be adsorbed onto carbonates, in this study.

Insufficient data were available to warrant any further statistical analysis. A continuation of this research over the remaining lakes in Rijnland, with more sampling stations, is necessary to make better statistical analyses.

## Conclusions

1. The P content of the sediments in the four investigated lakes in Rijnland varied from about 1 mg P  $\text{g}^{-1}$  dry wt in Westeinder, Nieuwkoop and Reeuwijk Lakes, to about 4 mg P  $\text{g}^{-1}$  dry wt in Braassem Lake. It correlates very well with the net P-load of the lakes.
2. The amount of algal extractable P in bioassays varied from 0.4% (Nieuwkoop Lakes) to 36% (Braassem Lake) of the total P content.
3. Chemical extraction methods with NTA and stepwise fractionation with  $\text{HN}_4\text{Cl-NaOH-HCl}$  extracted more phosphorus, and probably other forms, than algae. Therefore, these methods cannot be used to predict the amount of P available to algal growth in our lakes.
4. The percentage extractable P (both algal and chemical) varied from lake to lake, probably depending on the type of sediment.
5. Although a positive correlation has been established between algal extractable P vs. NTA-P and NaOH-P, the correlation between algal-P and total P is better. The NTA and NaOH extraction methods did not show a specific selectivity for algal-available phosphorus.
6. The chemical extraction method modified by Hieltjes & Lijklema (1980) cannot be applied for use with peaty sediments without revision.
7. Algal-extractable P was positively correlated with total P, total Fe and clay content, and negatively with the amount of organic matter.

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