

Phoslock® Treatment Het Groene Eiland

Interim Report November 08



Dr. Said Yasseri, Institut Dr. Nowak
Ir. Patrick Van Goethem, Phoslock Europe GmbH
November 2008

Content

1. Introduction.....	3
2. The application	4
2.1. Other measures	4
2.2. Phoslock®	4
2.2.1. General information on Phoslock®	4
2.2.2. The application of Phoslock®	4
3. Results and Discussion	5
3.1. Water column.....	5
3.1.1. Introduction.....	5
3.1.2. Visual appearance	5
3.1.3. Evolution of phosphorus and chlorophyll concentration.....	6
3.1.4. Secchi depth and nutrient ratio.....	7
3.2. Sediment	8
3.2.1. Introduction.....	8
3.2.2. Sediment analysis.....	8
3.2.3. Sediment fractionation.....	9
4. Conclusions.....	10
Appendix 1: Results summary for water samples	11
Appendix 2: Analysis of sediment samples	12
Appendix 2a: Result summary for sediment samples	12
Appendix 2b: Sediment P fractionation:	12

1. Introduction



Figure 1: Top view picture of Het Groene Eiland before modifications. (taken from Google Earth).

“Het Groene Eiland” is part of the larger bay, “De Gouden Ham”, which itself was formerly part of the River Maas. In February 2008, “Het Groene Eiland” became a separate lake when a series of dams between it and “De Gouden Ham” were built. An application of Phoslock[®] was undertaken on “Het Groene Eiland” in April 2008 following the completion of the dams in order to reduce phosphorus levels in the lake and reduce the incidence of blue green algal blooms which had become common in both water bodies in previous years.

The surface area of “Het Groene Eiland” is 5.3 ha, with an estimated average depth of 2.5 m. The (estimated) volume of water in the lake is 130 000 m³. Closing the water body with dams has resulted in a very long residence time.

According to reports about water quality in “The Gouden Ham” in 2006 and 2007 (“Zwemwaterprofiel blauwalgen, De Gouden Ham” by Grontmij & DHV and “Onderzoek Blauwalgen De Gouden Ham, Rapportage 2007” by Drema), “De Gouden Ham” experienced algal blooms dominated by the blue green algae *Microcystis*. Analysis of sediment pore water also shows the presence of *Microcystis*. Blooms of this type of algae give rise to high levels of the toxic compound microcystin of which levels higher than 20 µg/L result in public swimming bans. These occurred several times over the past two years. Relative high biomass concentrations are also evident from the analysis of chlorophyll-a concentrations up to 62 µg/L.

Nutrient concentrations were also monitored over the summers of 2006 and 2007. Values for phosphate for the summer of 2006 (from “Zwemwaterprofiel blauwalgen, De Gouden Ham” by Grontmij & DHV) were around 0.04 mg/L PO₄-P and 0.10 mg/L total P (which in both cases was the limit of detection for the technique used). Towards the end of summer 2006, the values increased slightly to 0.08 mg/L PO₄-P and 0.15 mg/L total P.

Results for summer 2007 (from “Onderzoek Blauwalgen De Gouden Ham, Rapportage 2007” by Drema) show significantly higher values, with values of up to 2.5 ppm PO₄ (which would correspond to 2.5 mg PO₄/L or 0.83 mg PO₄-P/L). It is however unclear how reliable these results are as other samples tested in October 2007 show conflicting results with phosphate values of below 0.05 mg PO₄-P/L and total phosphorus values between 0.10 and 0.92 mg P/L. Where relevant, however, these results are included in the graphs shown in Chapter 3.

The “Het Groene Eiland” sediment was reported to consist mainly of sand and to a lesser extent sludge/clay. Sediment pore water was also analyzed for total phosphorus (1000 mg P/kg dry weight) and phosphate (120 mg P/kg dry weight) on the 15 of October 2007 (“Analyserapport, Code:R20071026047”).

2. The application

2.1. Other measures



Figure 2: Construction of dams at “Het Groene Eiland”

In addition to the application of Phoslock®, a number of other measures were taken before and after the application for the improvement and/or manageability of the water quality.

As indicated previously, a series of dams were constructed in order to make “Het Groene Eiland” a lake and limit the influence of water from “De Gouden Ham”.

Fish and bird stocks were also managed in order to limit grazing of water plants and the input of nutrients from bird droppings.

Macro fauna in the littoral zone were also managed through the planting of reeds to absorb and subsequently harvest phosphorus. A number of high trees were also removed in order to prevent the shading of the littoral zone and input of nutrients from leaves.

2.2. Phoslock®

2.2.1. General information on Phoslock®

Phoslock® is a natural product, produced from modified bentonite clay and developed by the Land and Water Division of Australia’s CSIRO (Commonwealth Scientific and Industrial Research Organisation) to significantly reduce the amount of “Filterable Reactive Phosphorus” (FRP) present in the water column and in the sediment pore water of a water body. FRP corresponds to the soluble phosphate (PO₄) fraction and is an important growth limiting factor for blue green and other algae. By binding FRP, total phosphorus levels in the water column are likely to be reduced as well.

2.2.2. The application of Phoslock®



Figure 3: applying a Phoslock® slurry from a pontoon at “Het Groene Eiland”

On the 16th and 17th of April 2008 11 tonnes of Phoslock® were applied using a pontoon based application system to remove 110 kg Phosphorus from the available nutrient pool of both the water column and the releasable fraction of the sediment for the entire lake. Phoslock® was mixed with in situ water pumped from the lake in a venturi mixing system installed on the pontoon and then sprayed evenly over the surface of the lake, except for the shallow areas near the bathing areas.

3. Results and Discussion

3.1. Water column

3.1.1. Introduction

Lakes are dynamic systems with seasonal variations in for example nutrient and algal concentrations due to sunlight and temperature. Applying Phoslock® influences this system by making less phosphorus available to the biomass. However seasonal variations should still be taken into account when evaluating results. Pre-treatment sampling of the lake was undertaken by the Institut Dr Nowak (IDN) on two occasion and by a number of other organizations on multiple occasions. Post-treatment sampling was undertaken by IDN. Results from the pre-treatment monitoring undertaken by both IDN and the other institutions are presented in the graphs below, however care is required when comparing results as different analytical methods and different detection limits may have been used.

A full overview of the results obtained by IDN is presented in Appendix 1. The results are presented in graphs in the next section with a discussion of the results following.

3.1.2. Visual appearance

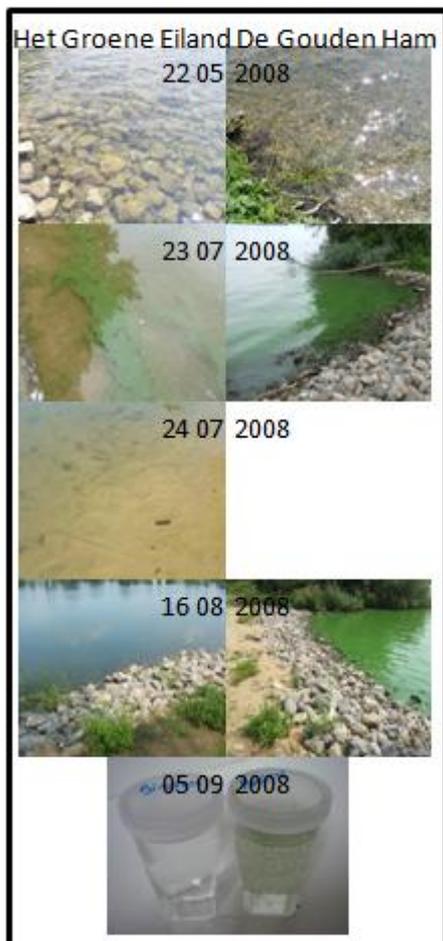


Figure 4: Photoseries of Het Groene Eiland (left) and De Gouden Ham (right)

Although somewhat subjective, the visual appearance of the water provides an indication of water quality. As only water from “Het Groene Eiland” was sampled and analysed, comparing its visual appearance with that of “De Gouden Ham” will give an idea on the difference in water quality between these two water bodies which were formerly in direct contact with each other.

Shortly after the application of Phoslock®, no visual difference could be noticed. On the 23rd of July, an algal bloom became apparent in both water bodies, although less pronounced in “Het Groene Eiland”. However already on the 24th of July, algae in “Het Groene Eiland” were no longer visually present. This relative clear state remained for the rest of the summer and continued into the autumn. In “De Gouden Ham”, on the other hand, algae remained visible after the 23rd of July.

3.1.3. Evolution of phosphorus and chlorophyll concentration

Phoslock[®] was applied in mid April. The main goal of the treatment was to limit or prevent release of phosphorus from the sediment into the water column and remove phosphate in the water column by binding the phosphate to the Phoslock[®] particles. After the application, total phosphorus concentrations in the water decreased slowly with ortho-phosphate remaining very low or below the detection limit (0.01mg P/L).

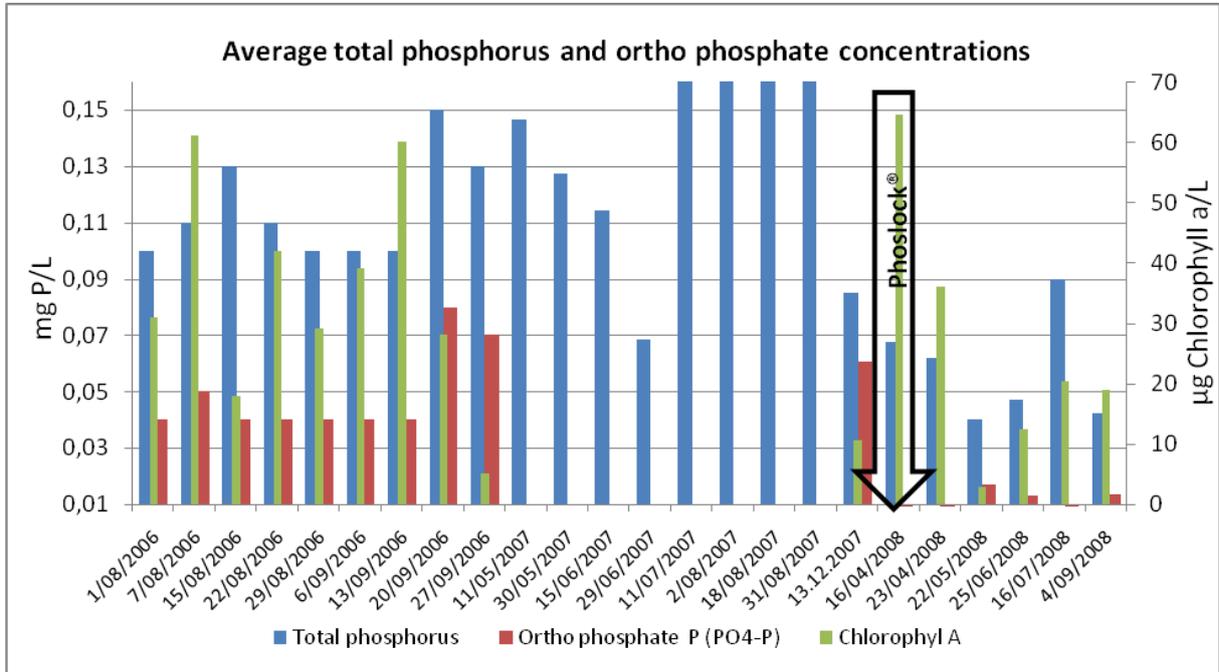


Figure 5: Phosphorus concentrations at “Het Groene Eiland”/”Gouden Ham”. (Remarks: results from 2006 are from Zwemwaterprofiel by Grontmij & DHV, total P and PO₄ had detection limits of 0.1 and 0.04 mg P/L respectively; results from summer 2007 are from Drema, results from July and August 2007 were higher than 0.4 mg P/L, phosphate and chlorophyll concentrations were not reported; results after autumn 2007 are from Institut Dr Nowak and specific for “Het Groene Eiland”, limit of detection was 0.01 mg P/L.)

One week after the application, there had only been a very small decrease in phosphorus concentrations as there was only a limited amount of phosphate in the water at the time of the application.



Figure 6: Burned logs near Het Groene Eiland at the 22nd of May.

On the 22nd of May, a natural algal crash seemed to occur in which algae died and stored phosphorus was released and subsequently converted to phosphate. This is shown by the very low chlorophyll-a concentration and the reappearance of ortho-phosphate (see Figure 5). The lower total phosphorus would be the result of phosphate binding with Phoslock[®] near the sediment as there would still have been available binding sites on the Phoslock[®].

It is also possible however that the slight increase in phosphate was also caused by ash runoff from the burning of the trees that had been removed when the dams were constructed. The influence of the ash is also indicated by the higher potassium content (see figure

7) that was recorded in the samples taken from May onwards. Ash and burned logs were removed shortly after May 22nd.

In the next sampling the concentration of ortho-phosphate decreased slightly by further take up by Phoslock® and to some extent by algae (as chlorophyll-a and total phosphorus levels increased slightly). Overall chlorophyll-a levels remained low.

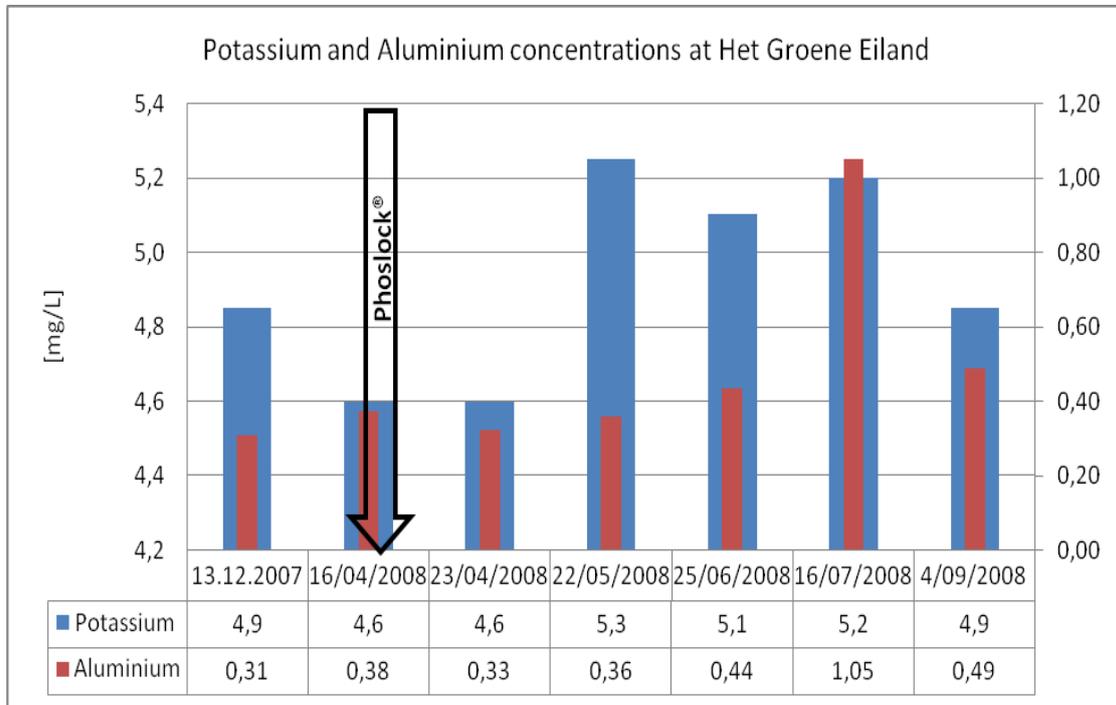


Figure 7: Potassium (K) and Aluminium (Al) concentrations at Het Groene Eiland (Results Institut Dr Nowak).

The high total phosphate concentration on the 16th of July was measured after storm events and didn't coincide with high chlorophyll-a levels. The high concentration of aluminium in these samples (see figure 7) indicates turbulence in the water body where sediment material would have been resuspended. This level can be considered low in comparison with phosphorus concentrations in previous years and doesn't indicate high phosphorus release from the sediment. The samples taken on the 4th of September also contained a lower total phosphorus concentration in line with the results of April to June.

3.1.4. Secchi depth and nutrient ratio

In the previous year, the secchi depth decreased over summer, becoming lower than 1m. After the application of Phoslock®, there was on average a steady increase in secchi depth, with a very high secchi depth at the time of the algal crash (22nd of May 2008).

It is interesting to note that high nutrient ratios (N:P) generally corresponded to high secchi depths in the results (see Figure 8).

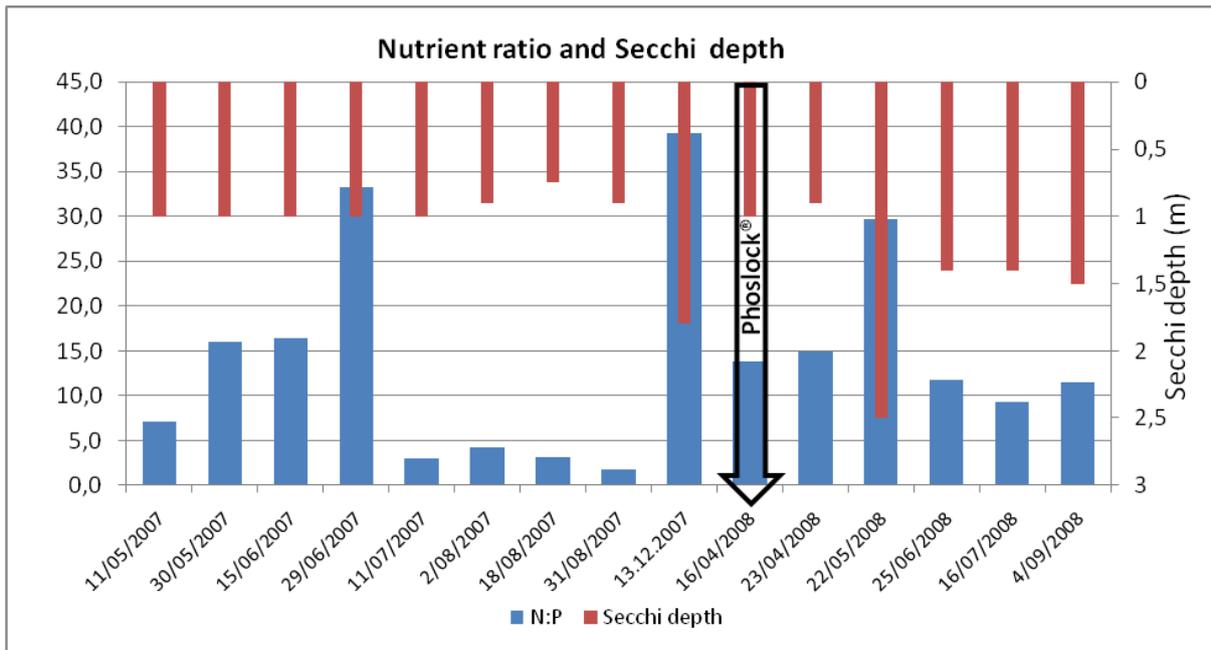


Figure 8: Nutrient ratio versus Secchi depth for Het Groene Eiland. (Remarks : secchi depth measurements before November 2007 show values cut off at 1 m. Results from summer 2007 are from Drema; results after autumn 2007 are from Institut Dr Nowak.)

3.2.Sediment

3.2.1. Introduction

Like most water bodies, the sediment in “Het Groene Eiland” is the largest reservoir of phosphorus, although not all phosphorus is releasable to the same degree. The distinction between the different fractions of phosphorus can be made by sediment fractionation.

At “Het Groene Eiland” three sediment samples were taken by the Institut Dr Nowak. The first one was taken on 13th of December 2007 to estimate the required dosage of Phoslock. The second was taken on the 16th of April 2008 (before the start of the application) as a reference point to evaluate the effect of Phoslock®. The third was taken one month after the application on the 22nd of May 2008 to evaluate the change in sediment characteristics following the application of Phoslock®. The second and third samples were fractionated using the Psenner method (modified by Hupfer).

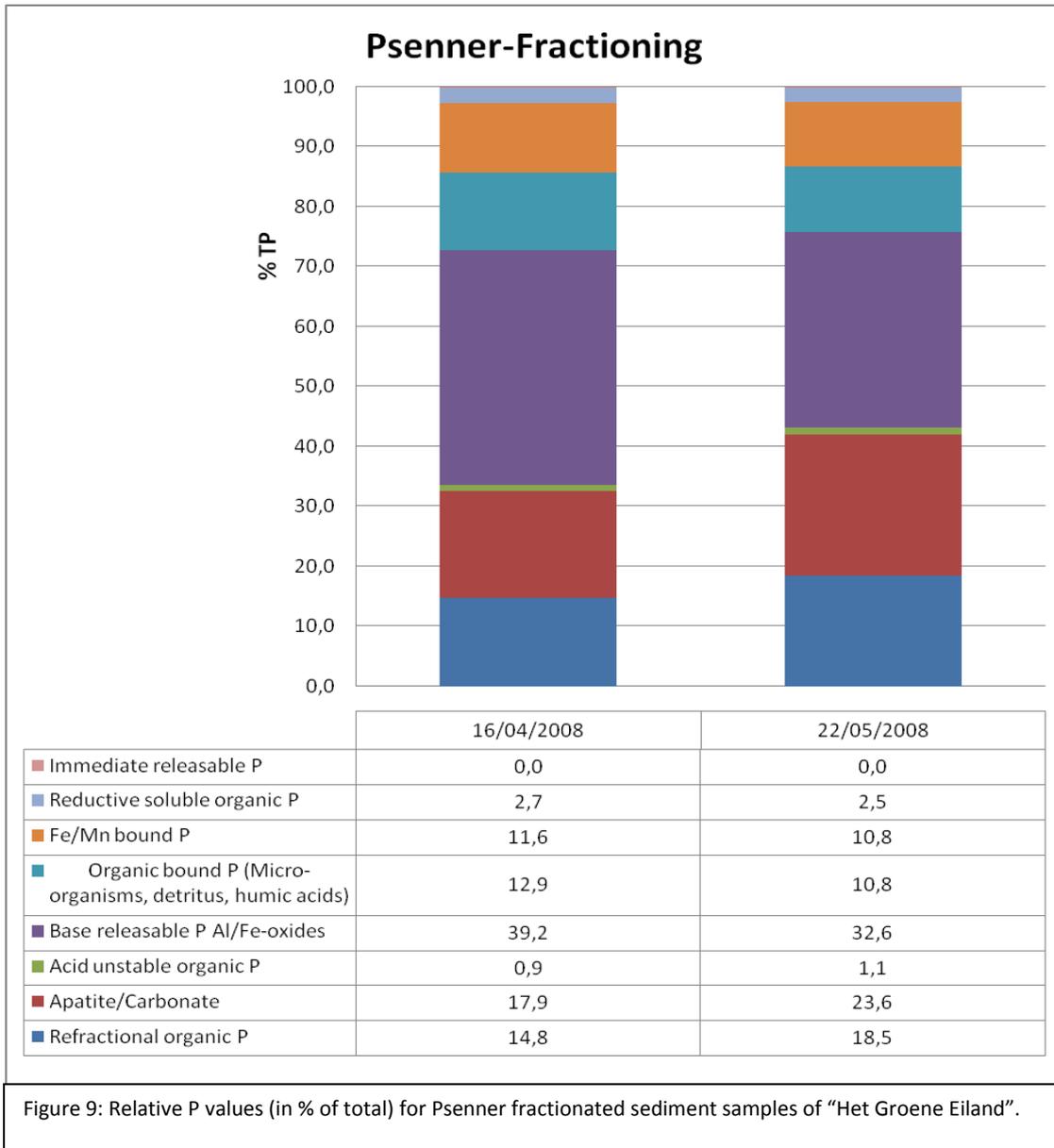
3.2.2. Sediment analysis

Comparing the results of the sediment analyses (see appendix 2a), the most apparent change can be seen in the lanthanum concentration. The lanthanum fraction increased significantly after the application of Phoslock® (going from 24 to 200 mg/kg DW) as was to be expected as Phoslock® is a lanthanum modified bentonite. Other concentrations were relatively unaffected by the application. (Remark: Chrome and Zinc concentration on the 16th of April are likely to be affected by an impurity in the sediment sample.)

Sediment pore water held significantly lower levels of total phosphorus (from 0.53 mg P/L on the 16th of April to 0.14 mg P/L on the 22nd of May) and phosphate (from 0.39 mg PO₄-P/L to 0.02 mg PO₄-P/L).

3.2.3. Sediment fractionation

The releasable P-fraction is composed of immediately releasable P, reductive soluble organic P, Fe/Mn bound P and organic bound P (micro-organisms, detritus, humic acids). The total phosphorus concentration in the sediment after the application of Phoslock® is comparable to the concentration before, but as can be seen by the sediment fractionation, the releasable fraction has decreased (both in absolute and relative values).



4. Conclusions

The application of Phoslock® to “Het Groene Eiland” has influenced the lake system by reducing the overall availability of phosphorus to biomass by binding phosphate in water, preventing phosphate release from the sediment and storing phosphorus in the sediment in an unreleasable form. As a result the overall phytoplankton biomass has decreased, which in turn has increased the visibility of the water. This effect became most pronounced when visually comparing the water of “Het Groene Eiland” with the untreated water of “De Gouden Ham”.

The increased visibility and the absence of blue green algae blooms are secondary effects of the Phoslock® treatment, but were the main goals for the customer and recreational users of the lake. Therefore with the current results the treatment of Het Groene Eiland by Phoslock® can be considered successful.

Appendix 1: Results summary for water samples

Het Groene Eiland
Middle of lake near pontoon

max waterdepth (m) 4,9 4 4 4 4,2

date		16/04/2008	23/04/2008	22/05/2008	25/06/2008	16/07/2008	4/09/2008
depth	m	1	0,9	2,5	1,4	1,4	1,5
Secchi depth							
ISO 7027-C2:2000-04							
pH							
DIN 38404-C5:1984-01							
1 m		8,75	9,13	7,9	8,9	8,35	8,22
2 m		8,72	8,9	7,9	8,88	8,31	
3 m		8,73	8,5	7,7	8,56	7,86	8,06
4 m		7,62	7,69	7,6	7,94	7,29	
elektric conductivity at 25 °C							
DIN EN 27888							
1 m	µS/cm	339	340	360	389	380	380
2 m	µS/cm	-	-	-	-	378	
3 m	µS/cm	-	368	366	392	380	375
4 m	µS/cm	356	-	-	-	387	
Redox-potential							
DIN 38404-C6							
1 m	mV	163	163	-	-	121	210
2 m	mV	-	-	-	-	116	
3 m	mV	-	160	-	-	144	177
4 m	mV	153	-	-	-	163	
Water temperature							
DIN 38404-C4:1976-12							
1 m	° C	9,8	14,1	18,4	21,6	20,4	18,1
2 m	° C	-	13,3	18,0	21,2	20,2	
3 m	° C	-	11,5	17,5	20,2	19,5	17,7
4 m	° C	10	10,8	17,3	19,3	18,5	
Dissolved oxygencontent							
EN 25814-G22:1992-10							
1 m	mg/l	13,7	13,3	7,63	8,95	9,91	8,78
2 m	mg/l	13,5	12,7	7,54	8,71	9,84	
3 m	mg/l	13,5	8,62	5,26	6,76	7,56	7,77
4 m	mg/l	4,82	0,4	4,36	0,23	0,34	
Total phosphor							
ISO 6878-D11:2004-09							
1 m	mg/l	0,056	0,064	0,037	0,041	0,070	0,048
3 m	mg/l	-	0,060	0,043	0,053	-	0,037
4 m	mg/l	0,079	-	-	-	0,11	
Ortho-phosphaat-phosphor (PO4)							
ISO 6878-D11:2004-09							
1 m	mg/l	< 0,01	< 0,01	<0,01	<0,01	<0,01	0,013
3 m	mg/l	-	< 0,01	0,017	0,022	-	0,014
4 m	mg/l	< 0,01	-	-	-	<0,01	
Ammonium-nitrogen (NH4-N)							
ISO 11732-E23:1997-09							
1 m	mg/l	0,095	0,17	0,43	<0,04	0,17	<0,04
3 m	mg/l	-	0,26	0,56	0,07	-	0,06
4 m	mg/l	0,52	-	-	-	0,35	
Nitrite-nitrogen (NO2-N)							
ISO 11732-E23:1997-09							
1 m	mg/l	<0,02	0,021	<0,02	<0,02	<0,02	<0,02
3 m	mg/l	-	<0,02	<0,02	<0,02	-	<0,02
4 m	mg/l	<0,02	-	-	-	<0,02	
Nitrate-nitrogen (NO3-N)							
ISO 10304-2-D20:1996-11							
1 m	mg/l	0,34	0,06	0,82	0,14	<0,02	<0,02
3 m	mg/l	-	0,14	0,84	0,14	-	<0,02
4 m	mg/l	0,33	-	-	-	<0,02	
Total nitrogen (TNb)							
ENV 12260-H34:1996-06							
1 m	mg/l	0,77	0,95	1,1	0,48	0,65	0,55
3 m	mg/l	-	1,2	1,3	0,51	-	0,56
4 m	mg/l	0,70	-	-	-	1	
Chlorophyll A							
DIN 38412-L16:1985-12							
1 m	µg/l	63,3	51,5	1,8	16,6	29,0	26,1
3 m	µg/l	-	20,7	4,1	8,3	-	
4 m	µg/l	65,7	-	-	-	11,8	
Phaeopigment-content							
DIN 38412-L16:1985-12							
1 m	µg/l	21,5	20,5	57,7	2,6	9,7	22,2
3 m	µg/l	-	15,5	53,7	14,2	-	
4 m	µg/l	30,4	-	-	-	17,7	
Acid buffercapacity at pH 4,3							
DIN 38409-H7:1979-05							
1 m	µg/l	2,18	2,24	2,20	2,35	2,15	2,06
3 m	µg/l	-	2,25	2,26	2,31	-	2,06
4 m	µg/l	2,23	-	-	-	2,25	
Alkalic buffercapacity at pH 8,2							
DIN 38409-H7:1979-05							
1 m	µg/l	vervalt	vervalt	0,056	vervalt	vervalt	0,024
3 m	µg/l	-	0,020	0,092	0,040	-	0,036
4 m	µg/l	0,009	-	-	-	0,170	
Acid buffercapacity at pH 8,2							
DIN 38409-H7:1979-05							
1 m	µg/l	0,06	0,16	vervalt	0,18	<0,01	vervalt
3 m	µg/l	-	vervalt	vervalt	vervalt	-	vervalt
4 m	µg/l	vervalt	-	-	-	vervalt	
Sulfate							
ISO 10304-2-D20:1996-11							
1 m	mg/l	44,0	44,0	42,0	41,0	42,0	33,0
3 m	mg/l	-	42,0	44,0	39,0	-	34,0
4 m	mg/l	45,0	-	-	-	40,0	
Iron							
ISO 11885-E22:1997-11							
1 m	mg/l	0,21	0,24	0,25	0,33	0,60	0,40
3 m	mg/l	-	0,39	0,54	0,46	-	0,56
4 m	mg/l	0,61	-	-	-	1,30	
Manganese							
ISO 11885-E22:1997-11							
1 m	mg/l	0,08	0,08	0,23	0,06	0,08	0,07
3 m	mg/l	-	0,09	0,29	0,07	-	0,07
4 m	mg/l	0,12	-	-	-	0,71	
Lanthanum							
ISO 11885-E22:1997-11							
1 m	mg/l	<0,002	0,028	0,018	0,019	0,027	0,016
3 m	mg/l	-	0,026	0,023	0,022	-	0,022
4 m	mg/l	0,003	-	-	-	0,057	
Aluminium							
ISO 11885-E22:1997-11							
1 m	mg/l	0,16	0,25	0,24	0,37	0,70	0,38
3 m	mg/l	-	0,40	0,48	0,50	-	0,60
4 m	mg/l	0,59	-	-	-	1,40	
Calcium							
ISO 11885-E22:1997-11							
1 m	mg/l	44,0	44,0	46,0	40,0	39,0	37,0
3 m	mg/l	-	45,0	46,0	41,0	-	38,0
4 m	mg/l	45,0	-	-	-	41,0	
Magnesium							
ISO 11885-E22:1997-11							
1 m	mg/l	6,2	6,2	7,1	6,5	6,6	6,9
3 m	mg/l	-	6,3	7,0	6,8	-	7,0
4 m	mg/l	6,2	-	-	-	6,6	

Appendix 2: Analysis of sediment samples

Appendix 2a: Result summary for sediment samples

parameter	method	unit	13/12/2007	16/04/2008	22/05/2008
Loss due to heating at 550°C	DIN 38414-S3:1985-11	%	8	8,20	5,40
Ash content at 800°C	DIN 38414-S3:1985-11	%	83,6	83,1	85,9
Total Organic Carbon	ISO 10694:1996-08	% DW	3,5	3,20	2,80
Total Inorganic Carbon	ISO 10694:1996-08	% DW		2,6	3,7
Total Carbon	ISO 10694:1996-08	% DW		5,5	5,5
Nitrogen (total-N)	ISO 11261:1997-05	mg/kg DW		4100	4100
Dry Weight (DW)	ISO 11465:1996-12	%	28	27,7	30,4
Mercury	EN 12338-E31:1998-07	mg/kg DW		0,23	0,21
Chrome	ISO 11885-E22:1997-11	mg/kg DW	62	310	71
Nickel	ISO 11885-E22:1997-11	mg/kg DW	36	40,0	41,0
Copper	ISO 11885-E22:1997-11	mg/kg DW	40	48,0	39,0
Zinc	ISO 11885-E22:1997-11	mg/kg DW	350	2900	360
Cadmium	ISO 11885-E22:1997-11	mg/kg DW	2,5	3,90	2,40
Lead	ISO 11885-E22:1997-11	mg/kg DW	74	78,0	51,0
Iron	ISO 11885-E22:1997-11	mg/kg DW	28000	32800	33100
Manganese	ISO 11885-E22:1997-11	mg/kg DW	910	950	980
Sodium	ISO 11885-E22:1997-11	mg/kg DW	680	710	670
Potassium	ISO 11885-E22:1997-11	mg/kg DW	8400	8600	8700
Magnesium	ISO 11885-E22:1997-11	mg/kg DW	4900	5200	5200
Calcium	ISO 11885-E22:1997-11	mg/kg DW	88000	83900	86000
Aluminium	ISO 11885-E22:1997-11	mg/kg DW	35000	36700	40000
Phosphorus	ISO 11885-E22:1997-11	mg/kg DW	1700	1900	1700
Lanthanum	ISO 11885-E22:1997-11	mg/kg DW	23	24,0	200
Pore Water					
Ammonium-Nitrogen (NH4-N)	ISO 11732-E23:1997-09	mg N/l	4,1	5,7	8,7
Total Organic Carbon	EN 1484-H3:1997-08	mg C/l	12	11	17
Phosphorus (P)	ISO 6878-D11:2004-09	mg P/l	1	0,53	0,14
ortho-phosphate (as PO4-P)	ISO 6878-D11:2004-09	mg P/l	0,75	0,39	0,02
ortho-phosphate (as PO4)	ISO 6878-D11:2004-09	mg PO4/l	2,3	1,2	0,071

Appendix 2b: Sediment P fractionation:

date	16/04/2008	22/05/2008	16/04/2008	22/05/2008
	%	%	mg P/kg DW	mg P/kg DW
Immediate releasable P	0,0	0,0	0,4	0,2
Reductive soluble organic P	2,7	2,5	41,8	36,6
Fe/Mn bound P	11,6	10,8	180,5	157,3
Organic bound P (Micro-organisms, detritus, humic acids)	12,9	10,8	200,0	158,0
Base releasable P Al/Fe-oxides	39,2	32,6	608,0	476,0
Acid unstable organic P	0,9	1,1	14,4	16,7
Apatite/Carbonate	17,9	23,6	277,1	344,7
Refractonal organic P	14,8	18,5	230,0	270,0
Releasable	27,2	24,1	422,7	352,1
Total	100	100	1552	1460