Elk Lake Sediment Analysis

A summary of results and implications for Phoslock treatment

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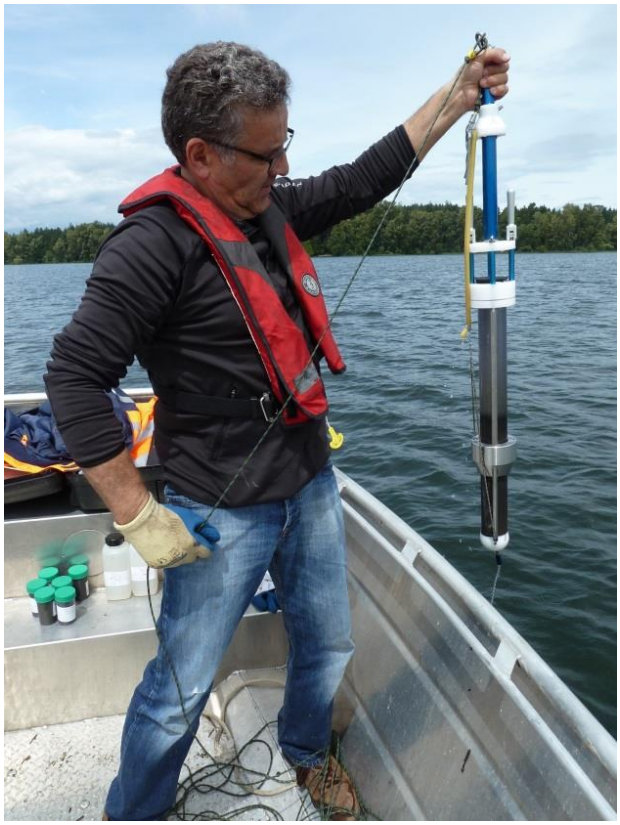
1 Introduction

Elk Lake (2.46 km^2) is a large lake on the outskirts of the City of Victoria in British Columbia that experiences cyanobacterial blooms in the winter. A recent study by Nurnberg and La Zerte (2016) determined that internal phosphorus loading from sediments was the main phosphorus (P) source in the lake and recommended a potential Phoslock treatment aimed at capping the sediments and reducing the nutrients available for cyanobacteria.

As no specific information on the P fractions in the sediments was available that could support any dosing and ultimately price estimate for a Phoslock treatment, the BC Ministry of Environment recently commissioned the Institut Dr Nowak (IDN) to collect sediment cores from the lake and undertake Psenner based sediment P fractionation on the collected cores.

Sediment sampling took place on the 1st of June, 2016 and was undertaken by staff from the Institut Dr Nowak and Phoslock Water Solutions Ltd. Logistical support (including the provision of a boat) was kindly provided by two employees from the Ministry of Environment. Based on the recommendations of Dr Gertrud Nurnberg, sediment samples were taken from seven different locations across the lake and analysed according to the Psenner method to determine the "potentially releasable" phosphorus fractions in the sediment. Two water samples were also collected and analysed for a number of basic water quality parameters so that a complete picture of the situation of the lake could be obtained at the time of sampling.



This report summarizes the work that was undertaken and presents the results of the analyses undertaken in our laboratories outside the city of Bremen in Northern Germany during July 2016. The results presented in the report contain sufficient information to allow an application strategy and dosing plan for Phoslock to be developed.

2 Methods

2.1 Sampling

2.1.1 Sediment

Sediment samples were collected using a Mondsee corer which had been brought from Germany for the sampling. The corer is shown in the picture on the previous page. This sampler is an Austrian made, specially designed sediment corer, ideal for the collection of undisturbed sediment cores. The sample locations are shown in Figure 1 and the grid reference in Table 1. Only the top 5 cm of sediment were sampled in all locations, with the exception of Location 6 where two depths of sediment were sampled (0-5 cm, 5-10 cm). The top 5 cm is generally considered to be the most active sediment layer in terms of phosphorus release to the overlying water column and, in many cases, is the sediment layer taken into account when calculating Phoslock dosages.

All samples were kept cool to limit bacterial activity, but not frozen (to prevent damage to organic material and leaching of cell content). Following the sampling, the samples were transported to the IDN labs in Germany for analysis.

2.1.2 Water

Water samples were taken using the Mondsee corer that was used to take sediment cores. The samples were taken at Locations 2 and 3 as shown in the diagram below. A surface sample (from 1m depth) was collected at Location 2 while a 16m sample was collected at Location 3. The two different depths were sampled so that a comparison could be made between water chemistry in the epilimnion and hypolimnion.

2.2 Analysis

Analysis of both water and sediment parameters were performed according to either the applicable international (ISO) or European standards (EN) or the German equivalent (DIN). Further information on analysis methods can be provided upon request.

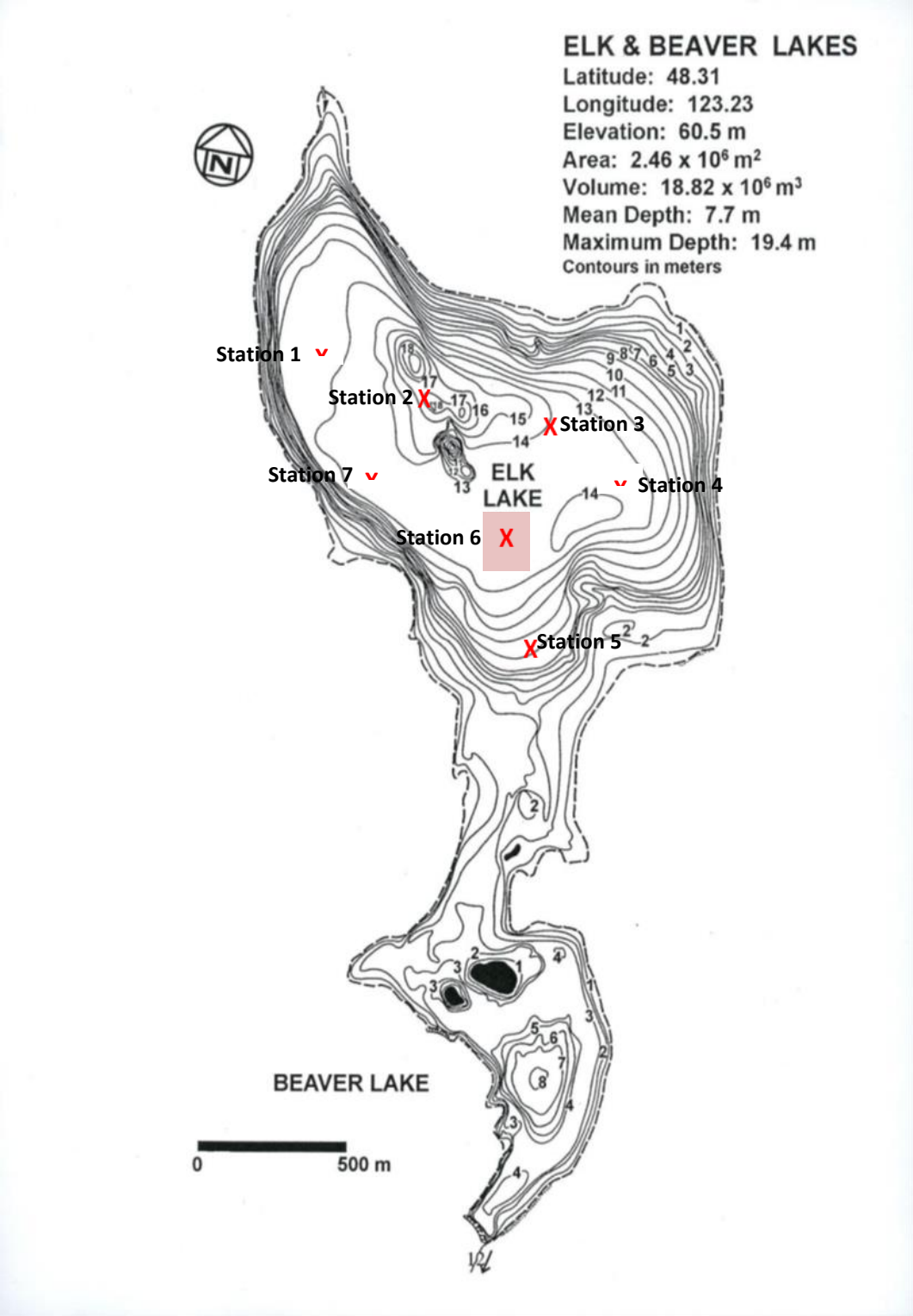


Figure 1: Bathymetric map of Elk lake with the location of the sampling stations

Table 1: Grid reference for sampling locations

Sampling location	N	W
1	48° 32.037	123° 24.450
2	48° 31.966	123° 24.193
3	48° 31 942	123° 23.905
4	48° 31.809	123° 23.568
5	48° 31.577	123° 23.823
6	48° 31.772	123° 23.887
7	48° 31.766	123° 24.163

2.3 Fractionation

The fraction of sediment phosphorus that is bio-available (or potentially bio-available) was determined using a simplified fractionation method based on the procedure described in *Psenner 1984* and the modifications described in *Hupfer 2009*. In this method, each sediment sample is sequentially exposed to different solutions that are able to dissolve different fractions of phosphorus.

In the first step of the Psenner procedure, oxygen free water is used to extract easily releasable, or labile, phosphorus from the sediment, while in the second step, the sample is mixed with a bicarbonate dithionite solution to create reducing conditions. In the third step, phosphorus is extracted from the sediment sample through the use of a sodium hydroxide (high pH) solution, while in the fourth step, the solution is mixed with hydrochloric acid. In the final step, the remaining phosphorus is analysed through complete digestion of the sample (using aqua regia) according to ISO 11885-E22:2009-09. In the first four steps, the total phosphorus and ortho-phosphate concentrations in the supernatant are determined after centrifugation and filtration though a 0.4µm filter (using the methylene blue method ISO 6878-D11:2004-09). The derived concentrations are presented as mass phosphorus per mass dry weight of the analysed sediment sample (typical: mg P/kg DW).

The potentially releasable phosphorus fraction (and therefore the fraction of phosphorus that should be taken into account when calculating a Phoslock dosage) is the proportion of the total phosphorus in the sediment which comprises the loosely bound and immediately available phosphorus (Step 1), the Iron and Manganese bound phosphorus as well as the reductive releasable organic phosphorous (Step 2) and the phosphorous bound within organic structures such as microorganisms, detritus and humic substances (Step 3).

During our analysis of the Elk Lake samples, only the first three of the five steps in the procedure were executed as the information collected in these three steps is sufficient to allow a determination of bio-available phosphorus to be made. Phosphorus released into the solutions in the fourth and fifth steps is considered to be not releasable under naturally occurring conditions. Further details about the method used can be found in *Hupfer 2009* or provided on request.

3 Results

In this section, the results that were obtained through our analysis of the water and sediment samples are presented. The significance of the results is discussed in Section 4. .

3.1 Water quality

The water quality results are shown on the following page in Table 2.

Table 2: Water quality parameter

		Date	01.06.2016	01.06.2016
		Location	Elk Lake station 2	Elk Lake station 3
		Depth	1m	16m
Parameter	**Method**	**Unit**		
Water sampling technique	DIN 38402-A11:1995-12			
pH-Value	ISO 10523-C5:2012-04		8.07	7.59
Conductivity (25°C)	EN 27888-C8:1993-11	µS/cm	183	186
Total Phosphorus	ISO 6878-D11:2004-09	mg/l	0.059	0.77
ortho-Phosphat-Phosphor (PO4-P)	ISO 6878-D11:2004-09	mg/l	<0,005	0.38
Ammonium-Nitrogen (NH4-N)	ISO 11732-E23:2005-05	mg/l	<0,04	0.74
Nitrate-Nitrogen (NO3-N)	ISO 13395-D28:1996-12	mg/l	<0,02	0.03
Total Nitrogen	EN 12260-H34:2003-12	mg/l	0.41	1.2
TOC	EN 1484-H3:1997-08	mg/l	6.9	6.8
Sulfate	ISO 10304-1-D20:2009-07	mg/l	7.8	6.3
Chloride	ISO 10304-1-D20:2009-07	mg/l	11	11
Calcium	ISO 11885-E22:2009-09	mg/l	19	21
Magnesium	ISO 11885-E22:2009-09	mg/l	4.3	4.5
Iron	ISO 11885-E22:2009-09	mg/l	0.03	1.0
Manganese	ISO 11885-E22:2009-09	mg/l	<0,02	0.61
Aluminium	ISO 11885-E22:2009-09	mg/l	0.03	0.11
Lanthanum	ISO 11885-E22:2009-09	mg/l	<0,002	<0,002

3.2 General sediment quality

Prior to undertaking the Psenner fractionation of the sediment samples, each sample was analysed for a range of general parameters. The parameters that were analysed and the results obtained are shown below in Table 3.

Table 3: Sediment quality parameters
(LOI: loss on ignition, is the weight % that is lost when dried material is exposed at the indicated temperature; TC: total carbon; TOC: total organic carbon)

		Location	Elk Lake Station 1	Elk Lake Station 2	Elk Lake Station 3	Elk Lake Station 4	Elk Lake Station 5	Elk Lake Station 6 (a)	Elk Lake Station 6 (b)	Elk Lake Station 7	Elk Lake Station 6 (a)	Elk Lake Station 6 (b)
		Depth	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	5-10cm	5-10cm
Parameter	**Method**	**Unit**										
Sediment sampling	ISO 5667-13-S1:1998-02											
Dry Weight	ISO 11465/EN 14346	%	7.7	7.8	11	7.7	9.3	7.7	7.7	7.9	9.6	9.4
LOI 550°C	DIN 38414-S3/EN 15169	% DW	26.8	25.4	20.9	26.4	23.9	26.6	26.8	25.9	27	26.2
LOI 800°C	DIN 38414-S3:1985-11	% DW	28.2	26.6	22	27.9	25.1	28.2	28.4	27.4	28.7	27.7
Total Phosphorus	ISO 11885-E22:2009-09	mg/kg DW	1370	2500	1480	1580	1510	1580	1230	1480	1440	1280
Total Nitrogen	ISO 11261:1997-05	mg/kg DW	16000	16000	13000	15000	14000	16000	16000	15000	15000	15000
TC	ISO 10694:1996-08	% DW	14.3	13	10.9	14.2	12.8	14.1	14.4	13.8	14.5	14
TOC	ISO 10694:1996-08	% DW	14.2	12.8	10.9	14.1	12.7	13.9	14.3	13.8	14.3	13.8
Iron	ISO 11885-E22:2009-09	mg/kg DW	29400	28600	28700	31200	30900	32600	31200	33700	30100	30100
Manganese	ISO 11885-E22:2009-09	mg/kg DW	800	770	760	760	820	780	640	720	690	690
Aluminium	ISO 11885-E22:2009-09	mg/kg DW	35200	30000	32300	35600	36600	34900	33900	35000	31800	33200
Calcium	ISO 11885-E22:2009-09	mg/kg DW	11200	9170	11800	11200	12200	10900	10800	11100	10000	10300
Magnesium	ISO 11885-E22:2009-09	mg/kg DW	7050	6480	7300	7720	8490	7400	7140	7420	6720	7060
Sodium	ISO 11885-E22:2009-09	mg/kg DW	880	750	930	960	1030	970	840	950	860	830
Potassium	ISO 11885-E22:2009-09	mg/kg DW	3650	3390	3750	4040	4340	3860	3600	3890	3500	3590
Lanthanum	ISO 11885-E22:2009-09	mg/kg DW	9	7	10	9	10	9	9	9	8	8
Sulphur	ISO 11885-E22:2009-09	mg/kg DW	7700	5810	4910	7480	5090	10400	11600	11400	10200	9850

3.3 Sequential phosphorus extraction from sediment

Table 4 summarizes the results of the sequential phosphorus extraction.

Table 4: Results of the reduced sequential phosphorus extraction (according to Psenner methodology)

Fraction (unit: mg P/kg DW)	Location	1	2	3	4	5	6a	6b	7	6a	6b
	Depth	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	5-10cm	5-10cm
Step 1											
Water labile P	TP	1.2	6.1	1.3	0.7	0.5	1.2	0.6	0.7	2.9	0.5
Step 2											
Fe/Mn bound P and reductive releasable org-P	TP	190.7	505.1	281.6	305.1	247.1	341.6	268.4	258.4	223.7	160.6
Step 3											
Base releasable P, Al/Fe oxides (pH 14)	SRP	250.7	956.6	362.2	315.9	249.8	371.1	264.2	249.5	239.0	208.1
Organic bound P (Microorg., detritus, humic substances)	NRP	384.8	528.0	425.8	554.4	404.4	484.5	341.8	326.7	455.8	341.6
Available P (TP step 1 + TP step 2 + NRP step 3)		**576.6**	**1039.2**	**708.7**	**860.3**	**652.1**	**827.2**	**610.7**	**585.7**	**682.4**	**502.7**
TP (measured by ICP)		**1370**	**2500**	**1480**	**1580**	**1510**	**1580**	**1230**	**1480**	**1440**	**1280**
% available P		42.1	41.6	47.9	54.5	43.2	52.4	49.7	39.6	47.4	39.3

4 Discussion

4.1 Water

At the time of sampling, the pH was slightly basic, with values of 8.07 and 7.59 in the 1m and 16m samples respectively. These values are nevertheless within the normal pH range. Higher pH values can indicate the presence of an algal bloom.

At 183-186 µS/cm, conductivity was relatively low, indicating low overall concentration of ions in the water.

Total phosphorus in the surface layer was high at 0.059 mg P/L high, indicative of eutrophic conditions. The bottom waters were hypertrophic with a concentration of 0.77 mg P/L. Concentrations above 0.1 mg P/L are indicative of hypertrophic conditions and therefore the hypolimnetic water of Elk Lake greatly exceeded this threshold at the time of sampling. The low orthophosphate-phosphorus (PO_4-P) concentrations in the surface water (below the detection limit of 0.005 mg P/L) are not surprising given that the sampling took place in early summer when algae and bacteria in the water column actively scavenge any available PO_4-P. The high PO_4-P concentration in the bottom water layer is indicative of sediment P release and shows the potential for an algal bloom once this ortho-phosphate pool moves to the epilimnion. While the PO_4-P remains in the hypolimnion, however, algae will be unable to immediately utilize this pool of readily available phosphorus due to the absence of light at these depths and the likely presence of a thermocline preventing mixing between the top and bottom water layers. Most probably, most of the PO_4-Pin the hypolimnion was previously bound to iron in the sediments but released due to the development of anaerobic conditions. This would also explain the difference between the moderate concentration of iron in the surface water (0.03 mg Fe/L) and the high concentration of iron in the bottom layer (1 mg Fe/L). Another indicator for this is the high manganese concentration at the bottom (0.61 mg Mn/L) and low concentration (below detection limit) at the surface, as well as the high ammonium concentration at the bottom (0.74 mg NH_4-N/L).

4.2 Sediment

The data in Table 3 show that the sediments of Elk Lake are relatively homogeneous across the different sampling locations, with most parameters having comparable values. This can also be seen in Table 5, where the averages and standard deviations of the different parameters are given. The main exceptions to this homogeneity are: 1) the total phosphorus concentration at sampling station 2 which is much higher than the concentration at the other sampling locations and 2) the sulphur concentrations at sampling stations 6 and 7 which are also much higher than other sampling locations.

On average, the sediment has a relatively low dry weight, meaning that the majority of the sediment consists of pore water.

With Total Organic Carbon (TOC) being only slightly lower that Total Carbon (TC), the majority of the carbon in the sediment is of organic origin.

Table 5: Average values, standard deviation and relative standard deviation (= standard deviation/average *100%) over all sampled stations with equal weight given to each sample

Parameter	Unit	Average	Standard deviation	Relative standard deviation (as % from average)
Dry Weight	%	8.58	1.2	13.6
LOI 550°C	% DW	25.59	1.9	7.4
LOI 800°C	% DW	27.02	2.1	7.6
Total Phosphorus	mg/kg DW	1545	355.2	23.0
Total Nitrogen	mg/kg DW	15100	994.4	6.6
TC	% DW	13.6	1.1	8.1
TOC	% DW	13.48	1.1	8.0
Iron	mg/kg DW	30650	1631.1	5.3
Manganese	mg/kg DW	743	56.4	7.6
Aluminium	mg/kg DW	33850	2020.0	6.0
Calcium	mg/kg DW	10867	874.5	8.0
Magnesium	mg/kg DW	7278	554.4	7.6
Sodium	mg/kg DW	900	82.9	9.2
Potassium	mg/kg DW	3761	281.4	7.5
Lanthanum	mg/kg DW	8.8	0.9	10.4
Sulphur	mg/kg DW	8444	2576.5	30.5

4.3 P-fractionation

The potentially biologically available phosphorus quantity (= available P) is the amount of phosphorus that could be released from the sediment under naturally occurring conditions. As described earlier, it is composed of different fractions that are released into the overlying water column under different conditions. The water labile P is immediately available. The iron and manganese bound P can become available under anaerobic conditions. Organic bound P is released due to biological activity such as bacterial degradation. The residual phosphorus is considered inert under naturally occurring conditions.

The results of our fractionation (from Table 4) are graphically represented in Figure 2 and Figure 3. Figure 2 shows the proportion of phosphorus contained in each fraction and demonstrates that, on average, about 40% of the phosphorus in the Elk Lake samples is present in the potential bio-available fractions. Figure 3 allows a comparison to be made of the different “releasable” P-fractions. This second graph clearly shows that the quantity of water labile P in the samples was negligible, while, in most samples, there was slightly more organic bound P than reductive releasable P (Fe/Mn bound and reductive releasable organic P).

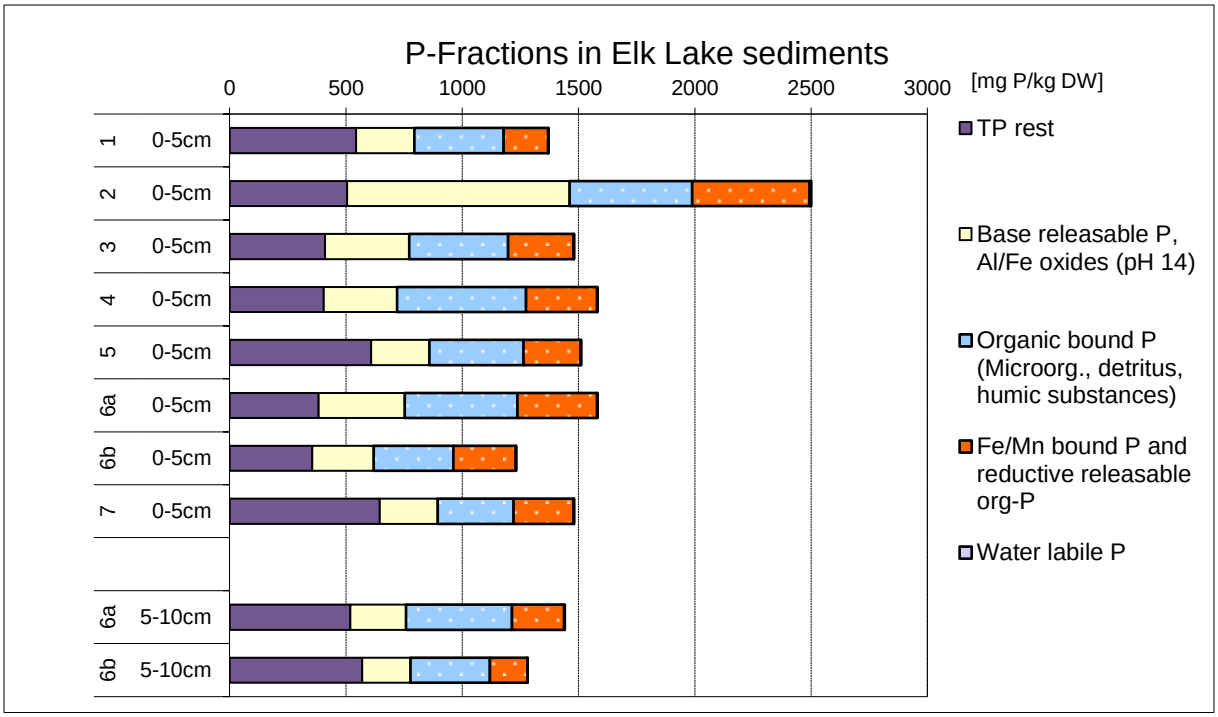


Figure 2: All P-fractions in Elk lake sediments

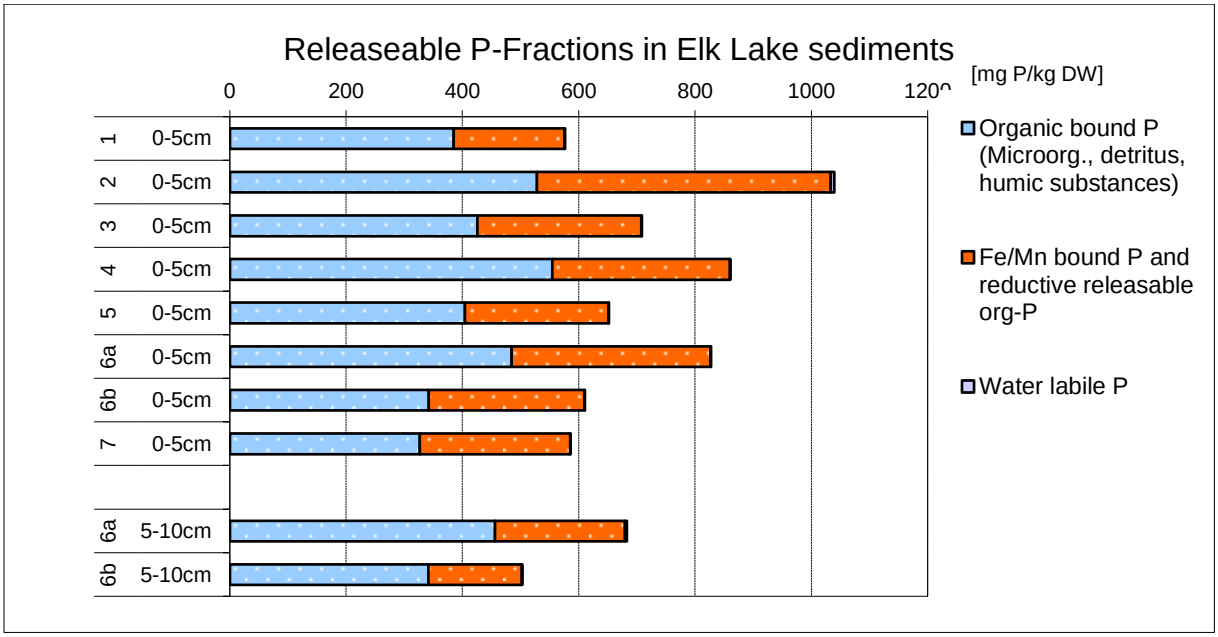


Figure 3: Potential biologically available P-fractions in Elk lake sediments

The results of the sequential phosphorus extraction contained in Table 4 (as well as the dry weight in Table 3) can be used to calculate the total amount of phosphorus that can be potentially released from the Elk Lake sediments, which in turn allows a calculation of the total dosage of Phoslock that would be required in order to immobilize this releasable P pool. The total releasable P pool can be calculated as follows:

- Firstly, available P per kg DW is converted to available P per m^3 WW (wet weight) by multiplying the available P in mg P/L (derived from Table 4) with the percentage dry weight (which is expressed as the 100%*(kg DW/kg WW)) and the specific weight. As the exact specific weight is unknown, a rule of thumb value of 1.1 kg WW/L WW is used;
- This value is then multiplied by the total sediment volume;

The results for each sampling location are given in Table 6. The table shows the available P content per litre of sediment sample. The measured dry weight is then used to convert this to the quantity of available P per cubic metre of sediment and per square metre of sediment over the 5 cm sediment depth.

Table 6: Calculations of the total amount of "releasable" phosphorus at each of the sampling locations at Elk Lake

		1	2	3	4	5	6a	6b	7		6a	6b
		0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm	0-5cm		5-10cm	5-10cm
Available P	mg P/L	**576.6**	**1039.2**	**708.7**	**860.3**	**652.1**	**827.2**	**610.7**	**585.7**		**682.4**	**502.7**
DW (=kg DW/kg WW)	%	7.7	7.8	11	7.7	9.3	7.7	7.7	7.9		9.6	9.4
Available P	g P/m^3	48.84	89.16	85.75	72.87	66.71	70.07	51.73	50.90		72.06	51.98
Available P (over 5 cm depth)	g P/m^2	2.44	4.46	4.29	3.64	3.34	3.50	2.59	2.55		3.60	2.60

A weighted average for the available phosphorus concentration can be obtained by multiplying the above results for each sampling location with a weighting corresponding to the percentage of the total surface area that has the type of sediment obtained at that sampling location. The relative surface areas were estimated from the bathymetric map shown in Figure 1 and are shown in Table 6 below. The table uses this weighting to calculate the available P (per 5 cm of sediment) for each sediment location. (Note: As there were two samples for sampling location 6, the weighting for each sample is multiplied by 0.5)

Table 7: Calculation of weighted average available P in top 5 cm sediment (weighted P= % of area for station * available P of station; weighted average = sum of weighted P for all stations)

Calculating weighted average over top 5 cm		1	2	3	4	5	6a	6b	7
Depth at sampling station	m	12	16	14	13	9	13	13	13
Estimated % representative of total area	%	14	8	14	14	16	9	9	16
Available P (over top 5 cm)	g P/m^3	48.8	89.2	85.7	72.9	66.7	70.1	51.7	50.9
Weighted P	g P/m^3	6.84	7.13	12.0	10.2	10.7	6.31	4.66	8.14

weighted average
66.0

The total amount of potentially bio-available phosphorus can be calculated based on these weighted averages. In Table 8, we have calculated various dosage scenarios based on the recommendations of Dr Nurnberg (e.g. treating only the area of the lake that is deeper than 9 m, deeper than 7 m and the entire surface area). The Phoslock dosages are based on the principle that each kg of Phoslock has the theoretical ability to bind 10 g of P. We have calculated both the quantity of available P in the top 5 cm for each of these dosing scenarios, as well as the additional quantities of Phoslock that would be required, should a decision be made to dose for a deeper sediment depth (e.g. up to 10 cm). Each scenario is based on the area treated and the depth of sediment that is taken into account. As the difference between the sediment in the top 5 cm and the 5 to 10 cm at sampling location 6 was only minimal, the same weighted average of available phosphorus concentration was used in this calculation.

We hope that the information provided in Table 8 can be used as a basis for further discussion by the BC MOE, the Elk Lake stakeholders and other experts in the determination of an appropriate dosing strategy for a Phoslock application to Elk Lake.

Table 8: Dosage estimation based on sediment area treated

		Depth <9m		Depth <7m		Total surface	
		Top 5 cm	Top 10 cm	Top 5 cm	Top 10 cm	Top 5 cm	Top 10 cm
Surface area	ha	110.8	110.8	126.4	126.4	186.6	186.6
Sediment volume	m3	55390	110780	63220	126440	93300	186600
Weighted average available P conc in sediment	g P/m3	66.0	66.0	66.0	66.0	66.0	66.0
Amount of available P in sediment	kg P	3653	7307	4170	8339	6154	12307
Phoslock dosage	ton Phoslock	365.3	730.7	417.0	833.9	615.4	1230.7

The results show that a minimum Phoslock dosage would require at least 365.3 tonnes. A more generous dose, in which the whole lake surface and the top 10cm sediment are treated, would require 1,230 tonnes Phoslock. A variety of dosage strategies may be considered for Elk Lake and careful consideration should be given to different options. In addition to strategies based on dosage only to areas below a certain depth contour (e.g. > 7 m or > 9 m depth), an alternative strategy may be to treat all available P in the top 10 cm of the deepest areas of the lake and only the available P in the top 5 cm for the rest of the lake. Dividing the application into two applications could also be considered – one targeting P in the top 5 cm of sediments and a second application in some years for phosphorus contained in the 5-10 cm layer in the deeper areas of the lake.

5 Literature

Hupfer, M., Zak, D., Roßberg, R., Herzog, C., Pöthig, R., 2009 Evaluation of a well-established sequential phosphorus fractionation technique for use in calcite-rich lake sediments: identification and prevention of artifacts due to apatite formation, Limnology and Oceanography: Methods 7, 399–410

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Psenner, R., Puesko, R. and Sager, M.: 1984, 'Die Fractionierung Organischer and Anorganischer Phosphorverbindungen von Sedimenten Versuch einer Definition Okologisch Wichtiger Fractionen', Arch. Hydrobiol. 10, 115–155