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Report on the Application of Bentophos on the Silbersee

Introduction

The Silbersee is an approximately 40 year old lake near Stuhr that was formed from a gravel pit used for the construction of the A1 Motorway, which passes directly to the north of the lake. The lake is popular as a swimming lake for the town of Stuhr and the surrounding area, but is also used for fishing and general relaxation. The lake is bordered on the southwestern side by a camping area. Two beaches with lawns for sunbathing areas are located on the northern and southern shores of the lake. The lake, which is approximately 7 ha in size, is surrounded by trees. Fields used for agriculture extend from the southern and eastern shores of the lake (Photo 1). The lake has a maximum depth of 8 metres and the sediment has a very high loading of nutrients caused by direct inputs, fish and flooding (Photo 2). Phosphorus in the sediment was measured to be approximately 1,000 mg P / kg DW prior to the treatment in 2006. About 40% of this was bio-available P (Figure 1)

Photo 1: The Silbersee and the surrounding area

Following the reduction of nutrients in the Silbersee through the removal of deep water, the Institut Dr. Nowak was commissioned by the Stuhr community to effect a permanent reduction in nutrient levels by removing the phosphate. During 2005 about 18 kg of phosphorus was removed by pumping up and discharging water from the deepest parts of the lake. However, large quantities of phosphate are deposited in the sediment of the lake. These can only be reduced very slowly by water removal. A permanent reduction of the phosphate level to the degree required would have taken many years. Removing the deep water was also out of the question as the resulting reduction in the water level, particularly in the summer, could effect the recreational use of the lake. Dryness in the fringe zones could also damage the natural coverage and destroy the habitats of birds, fish and insects.

Photo. 2: Water flowing into the lake in the late nineties as a result of flooding

Between the 14th and the 15th of November 2006, 21.5 tonnes of Bentophos were applied to the Silbersee in order to immobilise the phosphorus. The aim of this measure was to bind phosphorus in the sediment and water column and minimize the release of sediment P that could otherwise be used in biological processes. In so doing, it was anticipated that the intensive blooms of blue green algae that had occurred in previous years could be prevented.

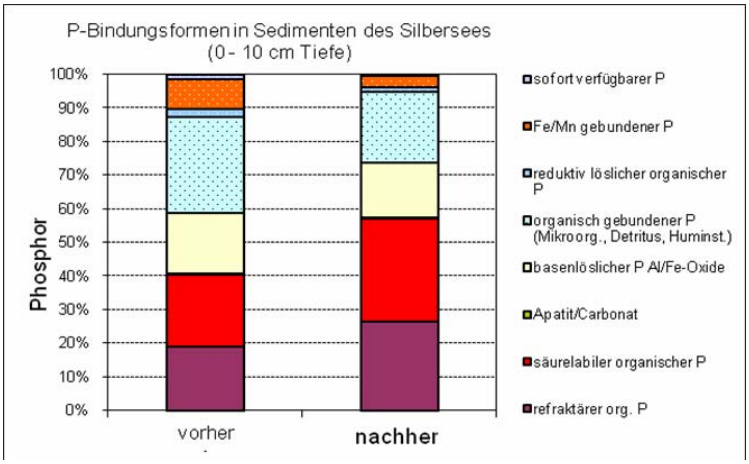

Figure 1: Phosphorus fractions in the sediment of the Silbersee before and after the application (according to Psenner). The dotted areas of each column represent bioavailable phosphorus

Situation during the treatment period

In the period before the application of Bentophos, the water was visibly stratified. Below 5 metres, anaerobic conditions had formed (Figure 2). Prior to the application, destratification commenced as a result of strong winds and by the time of the application the Silbersee was completely mixed. Aerobic conditions extended to the bottom of the lake at 7 m and the pH became stable at a value of 7.6.
This created favourable conditions for the removal of phosphate because a large part of total phosphorus existed as orthophosphate and was distributed evenly over the entire water column. Upon applying Bentophos, it was therefore possible to achieve the maximum phosphate binding efficiency during the slow settling phase through the water column (*Figure 3).*

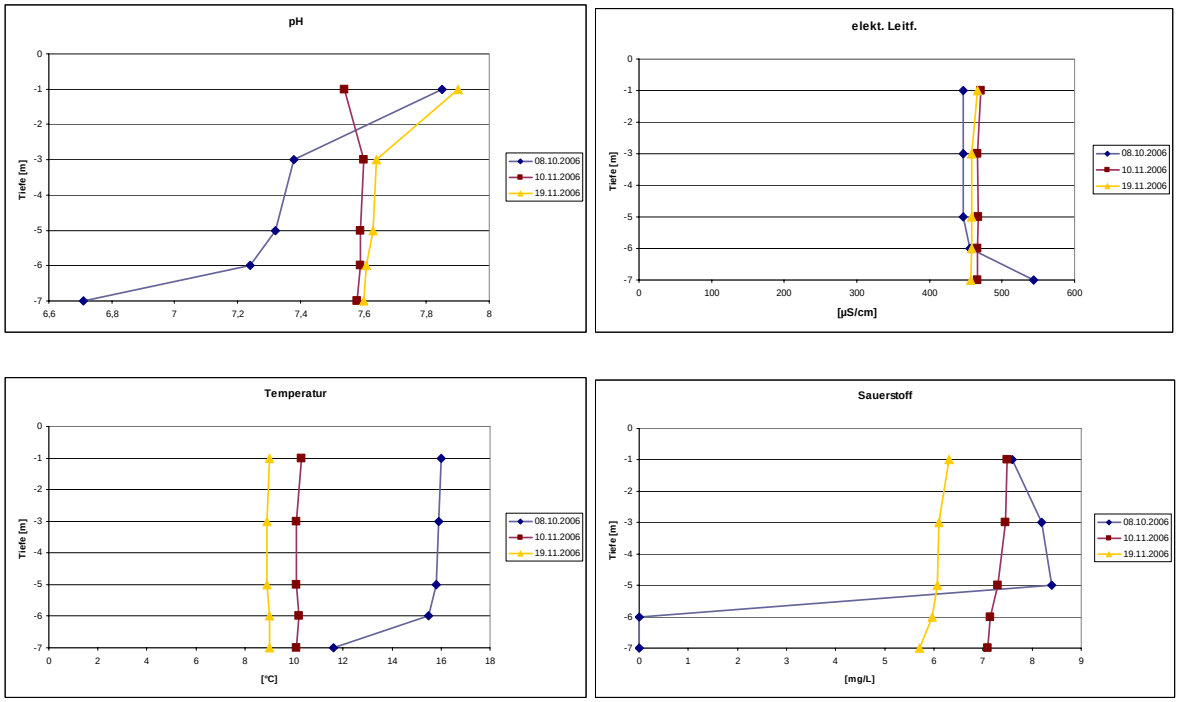

Figure 2: Water chemistry parameters pH, conductivity, temperature and dissolved oxygen

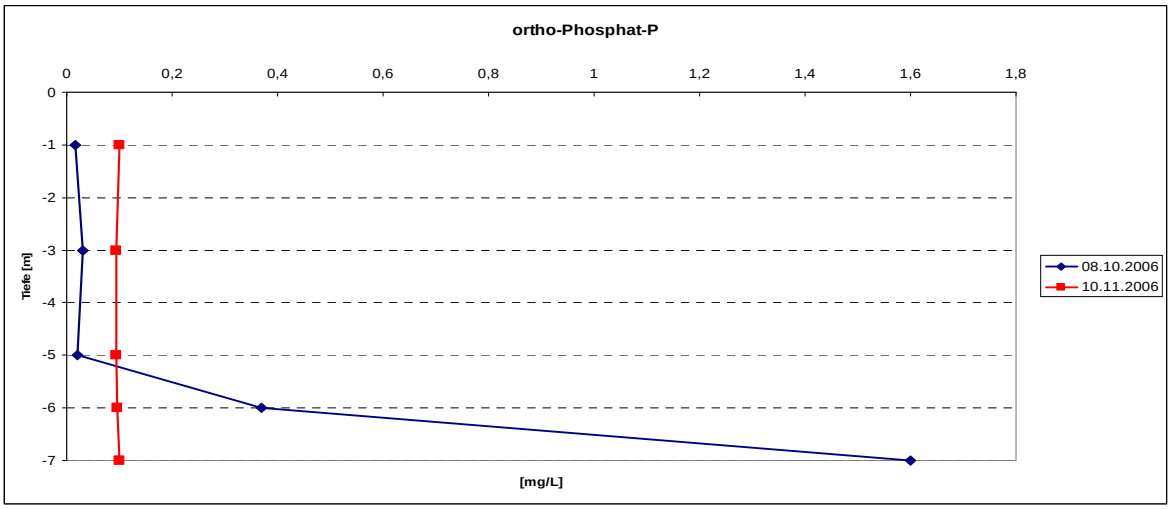

Figure 3: Distribution of ortho-phosphate within the water column before the application of Bentophos on the 14th and 15th of November 2006

Phosphorus concentrations following the application

The lake's water was monitored regularly following the application of Bentophos. One month after the application, orthophosphate in the water column had fallen below detection levels. Total phosphorus concentrations in the lake's water were also reduced by 80% and are currently 30 µg P/L (*Figure 4*).

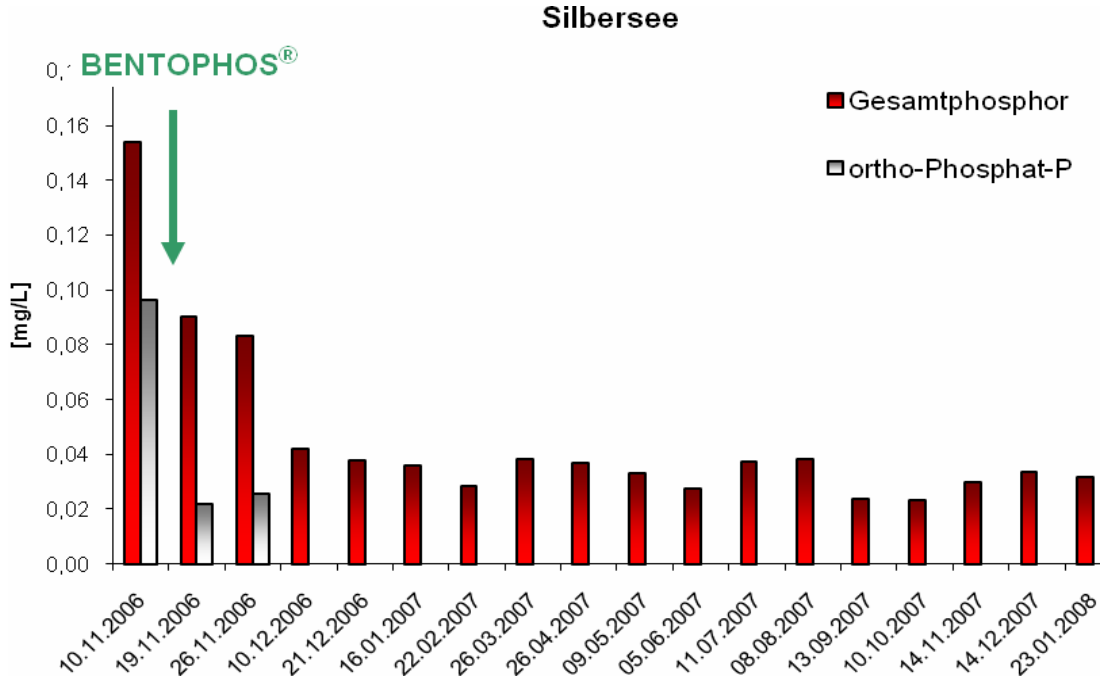

Figure 4: Trends in the concentrations of Total Phosphorus (Gesamtphosphor) and Orthophosphate (PO_4-P –) in the lake water

Sediment testing following the application indicates a very stable situation in relation to phosphorus. As a result, it is not expected that the bound phosphate will be re-released from the sediment.

Lanthanum concentrations in the lake water and in fish

Total lanthanum concentrations in the lake water were measured at 100 µg/L following the application. These dropped during the monitoring period to 4 µg/L (*Table 1 and Figure 5*). Despite the very windy period after the Bentophos® application with winds of more than 9 Bft, no resuspension of the material in the lake has been observed. This also means that both lanthanum and phosphate have been deposited solidly in the sediment.

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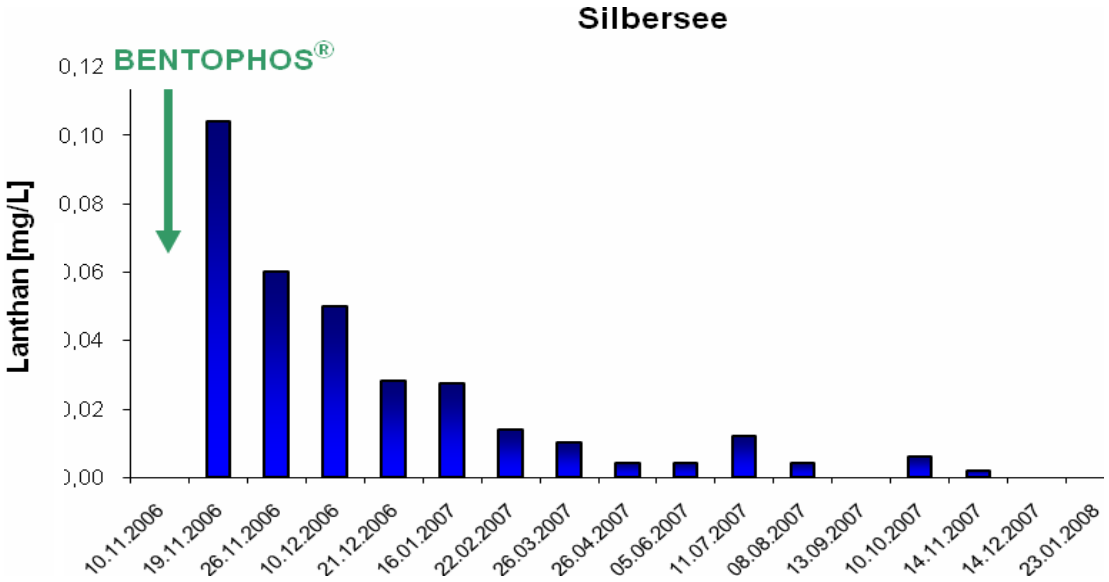
Table. 1: Lanthanum concentrations in the Silbersee following the application (DIN 38406-E29:1999-05)

			26.03.07	26.04.07	09.05.07	05.06.07	11.07.07	08.08.07	13.09.07	10.10.07	14.11.07
Depth	1 m	mg/l	0,01	< 0,01	n.b.	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
	3 m	mg/l	0,01	< 0,01	n.b.	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	0,01
	6 m	mg/l	0,01	0,01	n.b.	< 0,01	0,03	< 0,01	< 0,01	< 0,01	< 0,01
	7 m	mg/l	0,01	0,01	n.b.	0,02	0,03	0,02	< 0,01	0,03	< 0,01



Figur 5: Lanthanum concentrations in the lake water following the application

Table. 2: Lanthanum concentrations detected in fish on the 26.03.2007

Number	Type		Organ	La^{3+} [mg/kg DW]
15	Perch*		Liver	**2,30**
			Skin	**2,30**
			Tissue	**0,12**
1	Pike		Liver	**0,32**
			Skin	**2,20**
			Tissue	**0,03**

*The perch were spawned in the same year (last year) and had a length of up to 10 cm

In order to control lanthanum accumulation by fish in the Silbersee, tissue and organs from fish caught in the lake following the application were tested in the laboratory. As shown in Table 2, lanthanum was detectable. More lanthanum was measured in the skin of perch (which scavenge for nourishment at the lake bottom) than in the tissue. More lanthanum was also detectable in the liver and tissue of the perch than in that of the pike, which hunts for its food. Livers are detoxification organs and lanthanum, which is also purged by humans through the

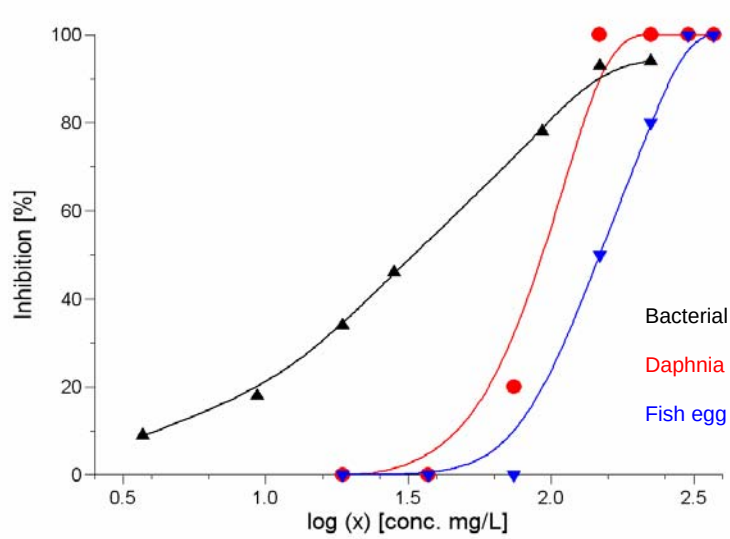
liver, was therefore detectable in the livers of the tested fish. Unfortunately, no tests were undertaken on fish prior to the application and therefore we do not know how high the natural concentrations of lanthanum in lake biota are (The sediment of the Silbersee was measured to contain 12 mg lanthanum / kg DW prior to the application). As a result, fish from a similar lake were examined for comparison purposes (Table 3). The Institut Dr Nowak is currently unable to measure lanthanum concentrations in solids below 5 mg/kg DW. Efforts are currently underway to locate other nearby laboratories with lower detection limits, however to date, these efforts have not been successful. As soon as a suitable laboratory is located with a lower detection limit, the data will be updated.

Table. 3: Metals in Tissue and Organs of Fish from a Reference Lake taken 01.10.2007

			Perca fluvialis			**Rutilus rutilus**			**Abramis brama**			
Parameter	**Method**		Liver	Tissue	Skin	Liver	Tissue	Skin	Liver	Tissue	Skin	Ave
Test												
Dry substance	ISO 11465:1996-12	%	24,9	21,1	44,5	24,4	21,6	40,9	24,8	20,6	32,9	26,8
Aluminium	ISO 11885-E22:1997-11	mg/kg TS	30	100	70	100	50	80	90	40	80	130
Copper	DIN 38406-E29:1999-05	mg/kg TS	12	2	5	41	2	5	32	2	5	3
Zinc	DIN 38406-E29:1999-05	mg/kg TS	109	27	107	160	31	150	88	24	130	150
Cadmium	DIN 38406-E29:1999-05	mg/kg TS	0,3	<0,2	<0,2	0,2	<0,2	<0,2	<0,2	<0,2	<0,2	<0,2
Mercury	EN 12338-E31:1998-07	mg/kg TS	0,36	1,1	0,09	0,14	0,45	0,08	0,07	0,16	0,06	0,15
Nickel	DIN 38406-E29:1999-05	mg/kg TS	2	<1	<1	6	<1	<1	<1	<1	<1	<1
Lanthanum	DIN 38406-E29:1999-05	mg/kg TS	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5

Ecological toxicity assessment of lanthanum

In order to properly assess the use of a material containing lanthanum in bodies of water, ecological toxicity examinations were carried out in the institute in relation to the acute toxicity of lanthanum. To do this, the effective concentration, in which lanthanum has a toxic effect on the test organisms, was measured in accordance with the guidelines of the DIN standards for the appropriate tests. In parallel, tests were also undertaken with lanthanum and a corresponding concentration of phosphate.



For comparison:

Lanthanum concentrations in the water body after Bentophos®:~20 µg/L (factor of 1000 lower)

When phosphate is present, no toxic effects were detected (i.e. lanthanum is no longer bio-available after the formation of lanthanum phosphate)

Bacterial luminescence test (ISO 11348-3) EC_{50} = 37 mg La^{3+}/L

Daphnia magna toxicity test(DIN 38412-L30) EC_{50} = 103 mg La^{3+}/L

Fish egg toxicity test (DIN 38415-T6) EC_{50} = 150 mg La^{3+}/L

Figure 6: Dosage to effectiveness relationship between lanthanum and the corresponding test organism

Table. 4: Fish Egg Tests (according to DIN 38415 Part 6, modified as "Contact"-Test)

Bentophos /Cavity [mg]	pH	O_2 [mg/L]	Coagulated eggs (N)	No somites (N)	Tail not separated from yolk (N)	Heart beat not detectable (N)	Sum of dead embryos (%)
5	7	"	/	/	/	/	0
10	7	"	/	/	/	/	0
25	7	"	/	/	/	/	0
50	7	"	/	/	/	/	0
75	7	"	/	/	/	/	0
100	7	"	/	/	/	/	0
125	7	"	/	/	/	/	0
150	7	"	/	/	/	/	0
175	7	"	/	/	/	/	0
200	7	"	/	/	/	/	0
Internal Controls	6,8	9,5	/	/	/	/	0
External Controls	6,8	11,7	9	/	/	/	9

Note: external controls: 3,7 mg/L 3,4-Dichloanilin Solution, N=Number

Results:
The effective concentrations for the test organisms (EC_{50}) were at least 1000 times higher in the investigations than the highest lanthanum quantity measured in the lake water of the Silbersee (*Figure 5*). With the addition of phosphate, which is present in the Silbersee in the corresponding quantities, no toxic effect was detectable at all. The modified fish egg test shows that there is no effect on sensitive water organisms, even with direct contact to up to four times higher quantities than the standard Bentophos dosage (Table 4). After combining with phosphate, the lanthanum is not bioavailable. The quantity of lanthanum used in the Silbersee therefore has no toxic effect on the organisms in the lake.

Evaluation

The results from the investigation after the Bentophos application provide a positive image about the development in the Silbersee. The objectives of the restoration measures have been completely achieved to date:

- Within a month of the application of 21.5 t of Bentophos to the Silbersee, 100% of ortho-phosphate and 80% of total phosphorus was removed from the water column
- Since the application, ortho-phosphate levels have remained below detection limits and total phosphorus levels have remained constant at around 30 µg/L, despite the rise in temperature in the water column, the stratification of the lake and the development of anoxic conditions in the hypolimnium. This indicates that the re-release of phosphorus from the sediment has been almost completely prevented.
- There have no effects on the flora and fauna in the Silbersee through the use of lanthanum.
- In relation to its phosphorous content, the trophic status of the lake changed from a strongly eutrophic to a mesotrophic condition within a period of two months.

The application did not result in the complete disappearance of blue green algal blooms from the lake, however the blooms that did occur were substantially smaller than in previous years and it was not necessary to close the lake to swimming. Although summer 2007 was cooler than summer 2006 and direct comparisons are somewhat difficult, the Institute Dr Nowak is very satisfied with the results of the application. Unlike 2006, the average temperatures in spring 2007 were very high and this accelerated the growth processes in the lake

The condition of the lake will be monitored further in 2008. Anoxic conditions did develop in the hypolimnion of the lake during the summer of 2007 and this situation is likely to continue in the future. Bacteria in the sediment first use dissolved oxygen in the water for the decomposition of organic materials. When oxygen is no longer available, they switch their respiratory processes to nitrate. This leads to a reduction in nitrogen levels with the result that nitrogen becomes the limiting nutrient for primary production. This in turn limits the growth of algae such as green algae and diatoms, however blue green algae, on the other hand, are able to fix nitrogen from the atmosphere and are not dependent on the availability of nitrogen in water, which is present in the form of ammonium or nitrate. Under such conditions, blue green algae have enormous advantages over other forms of algae and are able to form huge blooms.

On-going control of the phosphorus pool is therefore very important. When the phosphorus pool decreases, the microbial decomposition of organic substances also decreases. This in turn results in shorter anoxic periods and a deterioration in the conditions in which blue green algae can grow. In the Silbersee, there are already signs that this is occurring. After the temperature of the water at the surface of the lake dropped in autumn 2007, oxygen reappeared in the hypolimnium within a short period of time. This process took considerably longer in 2005, before the application of Bentophos. In other words, the Biological Oxygen Demand is lower in 2007 than in previous years. The reduction in BOD can only be attributed to a significant reduction in the phosphorus pool.