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First results of Bentophos®-applications in Germany

- Introduction and Preliminary Application Results

Dr. Said Yasseri / Nicolai Nowak
Phoslock Seminar at POLEKO Poznan
22nd November 2007

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Issues for lake restoration:

- effective nutrient elimination
- sustainable method
- toxic effects
- cost-/benefit-ratio

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Bentophos®

- What is Bentophos®?
- What is lanthanum?
- How effective is the phosphate bond and the the capacity of binding phosphate under real conditions?
- Is lanthanum toxic?
- Applications in Germany?
- Which amount of phosphorus in water bodies has been reduced?
- Can Bentophos® prevent phosphorus release from sediment?
- Can Bentophos® increase the permanent phosphorus-fraction in sediment?

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Bentophos® - technical Data

- base material: bentonite (95 %-by weight)
- modification: enrichment with lanthanum-ions (La^{3+}-Ions)
  - lanthanum-ions (embedded inside the bentonite-layers) as the active component (5 %-by weight)
    highly effective phosphate-bond
- product: clay-like granules
- capacity of binding phosphate:
  - stoichiometric ratio
    $La : PO_4$ is 1 : 1
  - ➢ laboratory study adsorption result:
    1 t Bentophos® contain 50 kg lanthanum
    -> ability to bind/remove 34 kg phosphate
    (=11 kg phosphorus)

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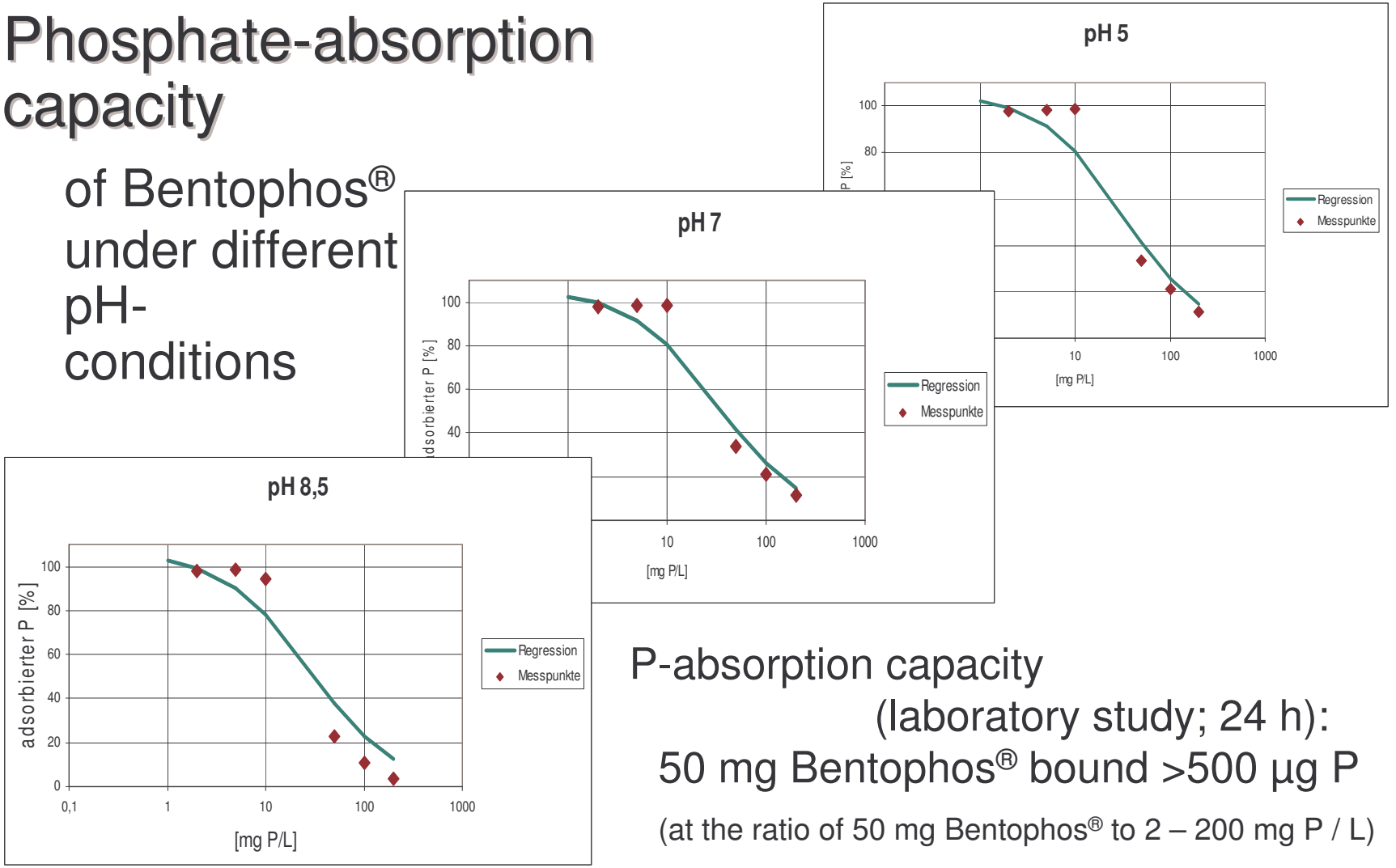
Phosphate-absorption capacity

of Bentophos® under different pH-conditions



P-absorption capacity
(laboratory study; 24 h):
50 mg Bentophos® bound >500 µg P

(at the ratio of 50 mg Bentophos® to 2 – 200 mg P / L)

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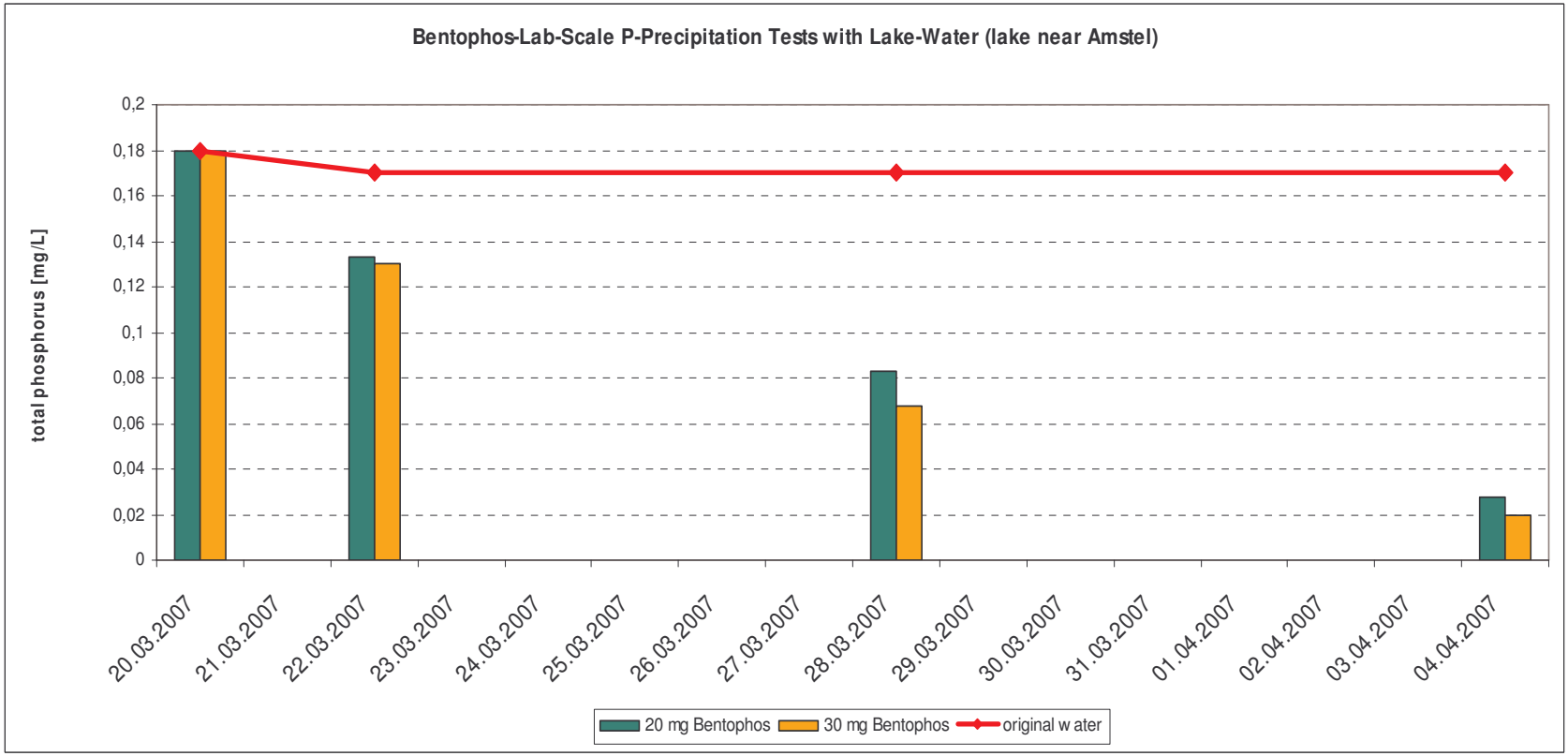
Declining phosphorus concentration in water-column of a alkanity rich water after treatment



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Lanthanum in the environment

- Background concentration of lanthanum in different water body sediments:
  ~ **40** mg/kg dw. (source RIVM, NL)

- Geogenic lanthanum in Elbe river sediments:
  ~ **44** mg/kg dw. (source GKSS, D)

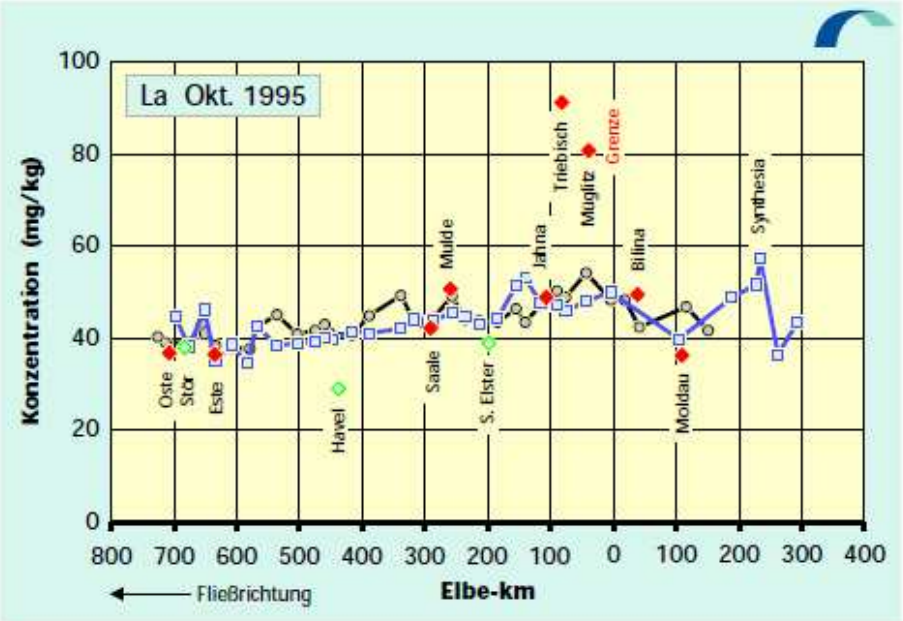
- Own findings: [mg/kg dw.]

Silbersee	**12**
Otterstedter See	**11**
Ellisee	**36**
Webersee	**43**
Bärensee	**21**
Lago di Varese	**14**
Ouderkerkerplas	**24**

Table 5.1. Background concentrations of REEs in surface water, sediment and soil

Element	surface water FRESH[1] (µg/L)	surface water SALT[2] (µg/L)	sediment[3] FRESH (mg/kg d.w.)	sediment[3] SALT (mg/kg d.w.)	groundwater[2,4,5] PH ≥ 6.2 (µg/L)	groundwater[2,4,5] PH ≤ 6.2 (µg/L)	soil[2,6] (mg/kg d.w.)
Sc	<2.80*	0.0007	9.8	12.9	0.001	0.013	0.9
Y	<0.22*	<0.22*	16.8	18.6	0.416	0.077	
Ce	<0.13*	<0.13*	68.9	92.6	0.956	<0.13*	9.0
Pr[7]	<0.08*	<0.08*	8.0	10.9	0.125	<0.08*	
Nd	<0.39*	0.0092	36.0	40.4	<0.39*	1	40

1. Detection limits with ICP-MS (van Son, 1994)
2. Stuyfzand, 1991



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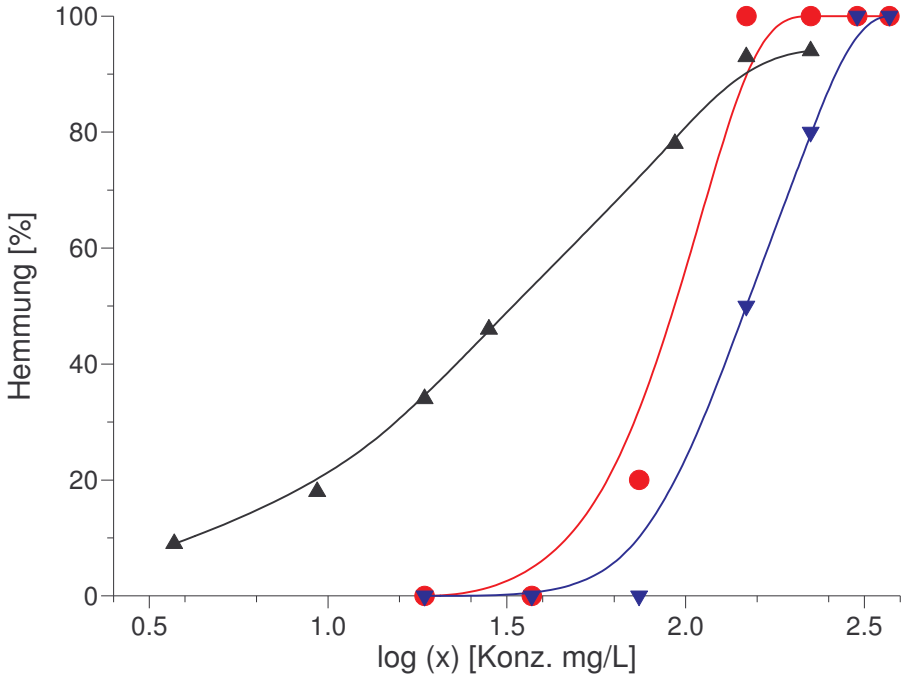
Bentophos® - toxicological Data

Tests regarding the ecotoxicity of lanthanum-ions in water:

Luminiscent bacteria (ISO 11348-3) **EC_{50} = 37 mg La/L**

Daphnia magna (DIN 38412-L30) **EC_{50} = 103 mg La/L**

Fish eggs (DIN 38415-T6) **EC_{50} = 150 mg La/L**



for comparison:

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

in presence of phosphate:
no toxic effect detectable at all

after formation of lanthanum-phosphate:
no more bioavailability

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Uptake of Lanthanum-Ions in different fish tissues

			02.05.2007	02.05.2007	02.05.2007
			Otterstedter See	Otterstedter See	Otterstedter See
	Common eel		**skin**	**muscle**	**liver**
parameter	method	unit			
dryweight	ISO 11465:1996-12	%	**55.8**	**21.5**	**39.6**
copper	DIN 38406-E29:1999-05	mg/kg TS	**2.6**	**1.0**	**120**
zinc	DIN 38406-E29:1999-05	mg/kg TS	**49**	**57**	**182**
cadmium	DIN 38406-E29:1999-05	mg/kg TS	**<0.5**	**<0.5**	**0.5**
mercury	EN 12338-E31:1998-07	mg/kg TS	**0,037**	**0.079**	**0.077**
nickel	DIN 38406-E29:1999-05	mg/kg TS	**2.1**	**<0.5**	**<0.5**
lanthanum	DIN 38406-E29:1999-05	mg/kg TS	**2.9**	**<0.5**	**0.9**
aluminium	ISO 11885-E22:1997-11	mg/kg TS		**<5**	**190**

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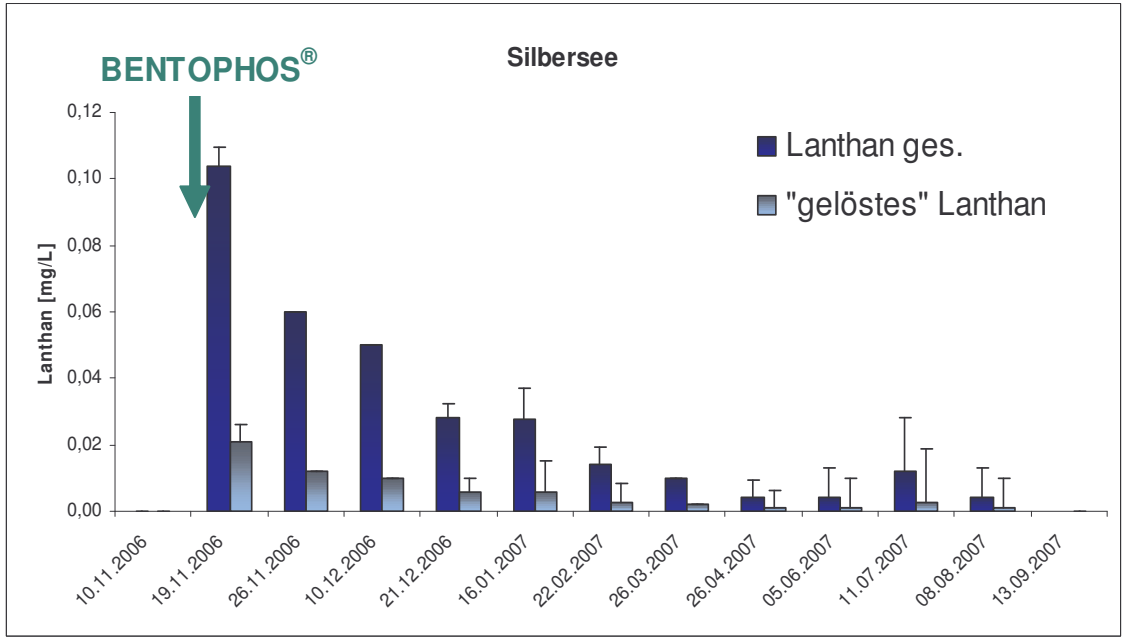
Lanthanum characteristics

- total lanthanum in water decreased from 100 to 0 µg/L
- dissolved lanthanum in water ranged about 20 to 0 µg/L
- lanthanum in sediment increased from 12 to ~135 mg/kg d.w.



21.5 t Bentophos® contain 1075 kg lanthanum. In 350000 m³ lake water result:

BENTOPHOS®

	10.11.06		19.11.06	10.12.06	21.12.06	16.01.07	22.02.07	26.03.07	26.04.07	05.06.07	08.08.07	13.09.07	
La^{3+}	0.00		0.104	0.050	0.028	0.028	0.014	0.010	0.004	0.004	0.004	0.0	mg/L
total La	0.00		36.4	17.5	9.8	9.6	4.9	3.5	1.4	1.4	1.4	0.0	kg

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Applications - Examples

- Silbersee:
  - artificial lake, area 9 ha, max. depth 8 m
  - eutrophied
  - intensive use as a recreational lake
  - regular bathing ban due to massive cyanobacterial blooms during the last years
  - high phosphate concentrations in sediment
  - Bentophos® application dose: 21.5 tons
- Otterstedter See:
  - age 12000 a, area 4.5 ha, max. depth 11 m
  - recreation zone, densely populated
  - eutrophied
  - partly successful removal of deep water, nevertheless repeatedly cyanobacterial blooms
  - aim: prevent Phosphate from being released from the sediment into the water column
  - Bentophos® application dose: 11 tons

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Technical Application - Principles

raw material / granules

preparation of a suspension

spraying on / injecting in the water body

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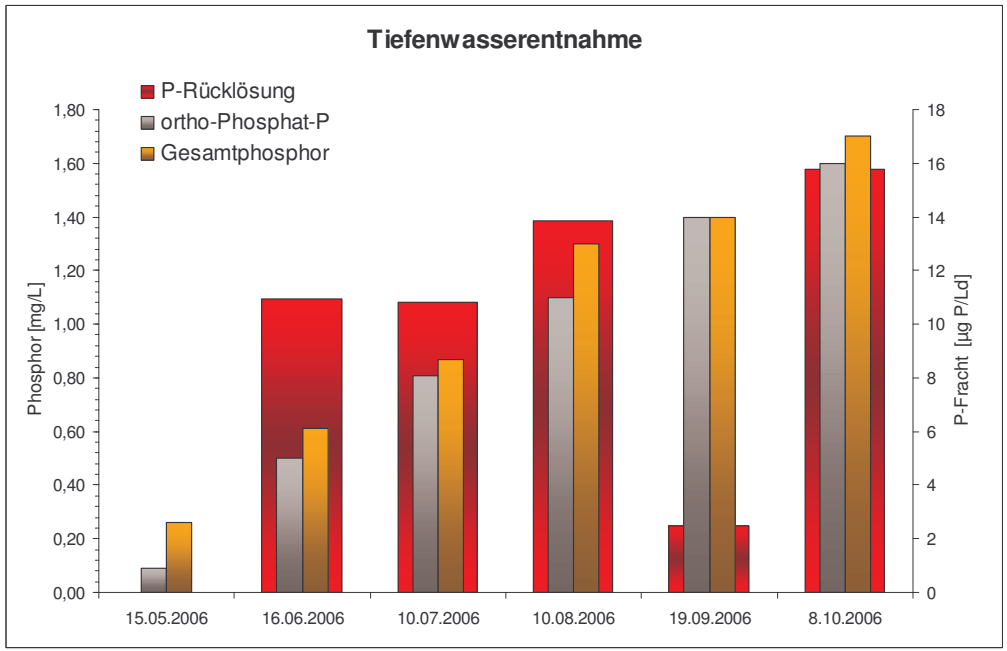
- Silbersee
  - during deep water removal phosphorus-conc. in water increased from 0.29 to 1.70 mg/L
  - ortho-phosphate fraction take share up to 100 % of total phosphorus
  - phosphorus-load from sediment increased up to 16 µg P/Ld (after Bentophos® application phosphorus load has been limited to max. 0.3 µg P/Ld)



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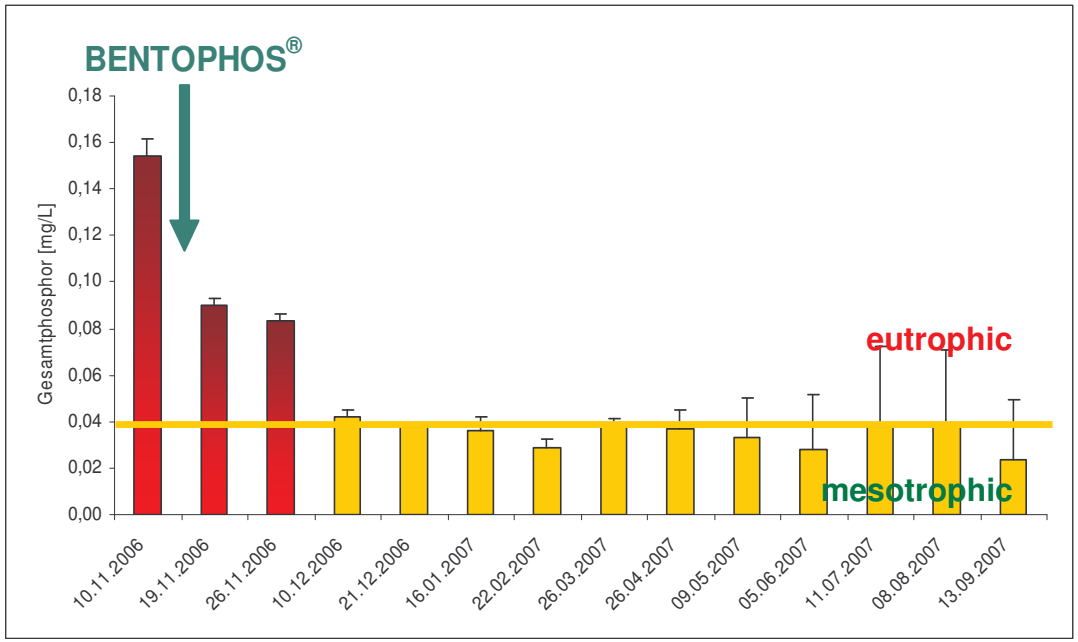
•Silbersee

- ortho-phosphate decreased below detection limit after 3 weeks (<0.01mg/L)
- total-phosphorus content dropped 85 % down to 24 µg/L



•Otterstedter See

- reduction of ortho-phosphate-content below detection limit (<0.01 mg/L)

BENTOPHOS®

mg/L	03.11.06		08.11.06	17.11.06	29.12.06	30.01.07	26.03.07	26.04.07	05.06.07	11.07.07	08.08.07	13.09.07
total-phosphorus	0.050		0.032	0.030	0.033	0.041	0.037	0.038	0.045	0.042	0,065	0.050
ortho-phosphate–p	0.022		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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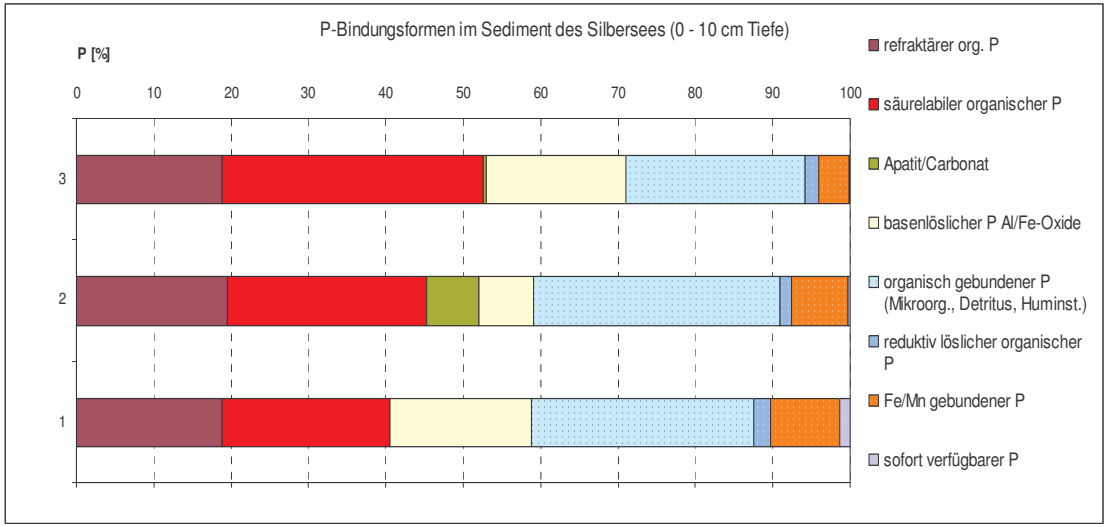
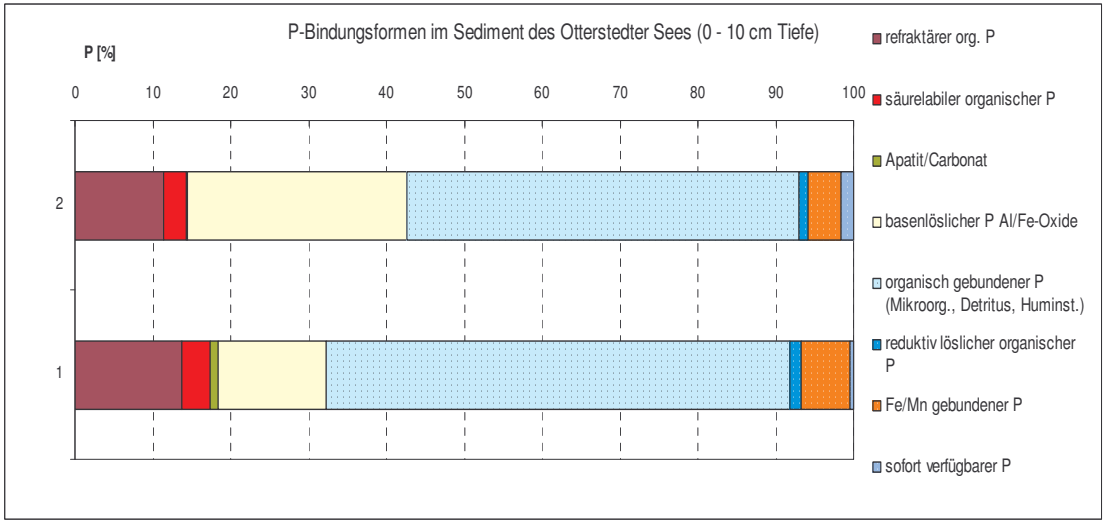
- **Silbersee:**
  - sediment contain approx. 1000 kg phosphorus
  - initially 40 % as biogenic phosphorous available
  - decreased on ~30 % over the observed period



- **Otterstedter See:**
  - sediment contain approx. 700 kg phosphorus
  - initially 70 % as biogenic phosphorous available
  - increase of permanent phosphorus



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•Bärensee:

- artificial shallow lake; 5 ha; max. depth 3.5 m
- eutrophied
- intensive use as a recreational lake
- regular massive blue-green-algae blooms
- chlorophyll-a concentration >80 µg/L (February)
- phosphate permanently in use
- aim: prevent phosphate from being released from the heavy anoxic sediment
- Bentophos® application dose 11.5 tons

BENTOPHOS®

	08.02.2007	11.06.2007		21.06.2007	16.08.2007	17.09.2007	
Secchi-depth	**0,3**	**1,5**		**1,9**	**1,3**	**1,8**	**m**
chlorophyll a	**82,6**	**6,2**		**14,8**	**35,3**	**22,8**	**µg/L**
ortho-phosphate-p	**<10**	**<10**		**<10**	**<10**	**<10**	**µg/L**
total-phosphorus-p (1 m)	**96**	**72**		**45**	**36**	**32**	**µg/L**
total-phosphorus-p (3 m)	**82**	**69**		**120**	**74**	**59**	**µg/L**

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Conclusions

- ✓ lanthanum is a ubiquitary element in sediments
- ✓ fast and permanent binding of ortho-phosphate (PO_4)
- ✓ effective reduction of phosphorus at most water bodies characteristics
- ✓ undiminished effect under anoxic conditions
- ✓ minor ecotoxicological relevance
- ✓ reduce phosphorus-release from sediment
- ✓ increase permanent phosphorus-fraction
- ✓ rather no influence on the water bodies ion equilibrium
- ✓ wide pH range stability of lanthanum-phosphate
- ✓ good cost-benefit ratio

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Roadmap

- further tests on ecotoxicological issues and long-term effectiveness of Bentophos
  - lab-scale / mesocosm projects on sensitive environments
  - full-scale projects on highly eutrophied ecosystems

- Involve and support scientific researchers / organizations in Europe
  - Germany: IGB Berlin, Env. agencies in many Federal States (Niedersachsen, Hamburg, Brandenburg, Baden-Württemberg, Hessen…)
  - U.K.: Center of Ecology and Hydrology (CEH)
  - Italy: ARPA Lombardia, Prov. of Varese
  - Netherlands: Dr. Miquel Lurling (Univ. of Wageningen), Leon Lamers (Univ. of Nijmegen)

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- private limnological Institute
- founded (1972), directed by: *Dr. Karl-Ernst Nowak (*grad. at MPI for Limnology Plön*, Prof. W. Ohle)*
- first studies on Phosphate elimination at a wastewater treatment facility in 1971
- lab for environmental analysys, accreditation in accordance with ISO 17025:2005
- various german registrations (wastewater analysys, drinking water analysys etc.)
- specialized in the analysys of harbour sediments /dredged materials (e.g. german reference lab for the analysis of Organotin-compounds in sediments)
- since July 2006 exclusive licencee of Bentophos® (Phoslock®) in D-A-CH and since 2007 licencee in BENELUX
- limnological consultancy for *Phoslock Water Solutions* and tight cooperation with Phoslock European Office on important projects throughout Europe and Mid-East
  - research regarding enhancement in efficiency of Bentophos®
  - studies regarding the ecotoxicity and the sustainability of Bentophos®
  - development and improvement of application methods
- up-to-date Information on Bentophos ® /Phoslock® :
  - *http://www.bentophos.de*

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