# **WASSERVIRTSCHAFT**

# Biochemically Stimulated Sludge Decompositionin Shallow LakesA Feasibility Study



## **Biochemically Stimulated Sludge Decomposition in Shallow Lakes: A Feasibility Study**

Deposited sludge is frequently a threat to the use of eutrophic shallow lakes and fishponds. Three feasibility studies in which products containing CaO2 were tested as an alternative to dredging showed a significant reduction of sediment thickness and organic matter content. The gradual release of oxygen apparently promotes the transfer of electron acceptors through the confining layer into the sediment and stimulates microbial mineralization there. Negative effects on the lake ecosystems were not detected.

## Kai-Uwe Ulrich, Alice Rau und Thomas Willuweit

## 1 Reason for the Study

The rapid eutrophication of lakes and rivers in combination with massive sediment accumulation, a shortage of oxygen near the bottom, insufficient fixation of phosphate (PO4-species), and a dominance of cyanobacteria continues to be a core global problem with regard to water quality and health [1]. Shallow lakes, which are the most commonly found bodies of fresh water around the world, are particularly vulnerable to these problems [2]. They are common elements of the landscape and contribute to the microclimate, biodiversity, local recreation, and even to the production of food when managed as fishponds. Due to their shallow water depth (<5m), they are frequently polymictic, occasionally with a weather-related temporary stratification.

In contrast to deep lakes, nutrients are recycled quickly and more frequently in shallow lakes, which causes a higher trophic degree [3]. At the median trophic level, the most important primary producers and nutrient pools are macrophytes and floating leaf plants supporting transparent (clear) lake water. With increasing addition of nutrients, the dominance of macrophytes can quickly switch to phytoplankton, causing intensified clouding of the water. Cyanobacteria and intense sedimentation rapidly lead to substantial limitations in the use of eutrophic lakes.

Since a reduction of the trophic degree can take a very long time, due to the well-known hysteresis, even after the nutrient additions are curbed, effective measures for the preservation

## Abstract

- The active substance calcium peroxide stimulated sludge decomposition in three test waters.
- Organic material in the sediment decreased more than stoichiometrically expected.
- The treatment did not have a negative impact on aquatic ecology.

of waters and their use in the sense of a lake therapy are desirable [4]. This usually draws the focus of research to the sediment that is deposited (often as sludge).

The traditional restoration methods for the sediment include dredging, which involves a harsh disruption of established habitats and usually high costs. It also requires moving or depositing the dredged material elsewhere. The dredged material is frequently contaminated with regulated substances in concentrations higher than the legally permissible limits. Several in-situ measures counteract excessive oxygen deficits and/or nutrient releases from the sediment. One established technique is adding nitrate as the electron acceptor to increase the redox potential near the sediment-water confining layer and to stimulate the mineralization in combination with calcium or iron for phosphate precipitation (RIPLOX method) [4]. Even though this method adds a water-soluble nutrient, which can counteract the nitrogen limitation that promotes the growth of cyanobacteria, this can indirectly also increase the phosphor bonding capacity of the sediment [5].

The present study tested the feasibility of a new method in which a nutrient-rich substance mix is used that contains aerobe microbes and releases molecular oxygen over a longer period. This oxygen promotes the aerobe microbial decomposition of organic material (OM) and the potential oxidation of reduced ions. In this paper, we present the results of the accompanying analyses of applications at three test sites, two ponds and one shallow lake in Germany and China.

## 2 Material and Implementation

The active substance used in the feasibility studies is a mix of up to three components and available in specialized retail stores in Germany under the product name SchlixXPlus:

- calcium peroxide (CaO2), active substance (15-75%),
- bentonite (for thinning), CaCO3 and CaCl2 (for buffering) and Ca(OH)2 (as byproduct from the CaO2 production),

 cultivated aerobe bacteria (up to 8 different kinds, freezedried).

Calcium peroxide is a nearly water-insoluble powder (<0.01% solubility at 20°C), which slowly decomposes in non-acidic water over 8 to 10 weeks, releasing molecular oxygen [6]:

$$2 \operatorname{CaO}_2 + 2 \operatorname{H}_2 \operatorname{O} \Rightarrow 2 \operatorname{Ca(OH)}_2 + \operatorname{O}_2 \tag{1}$$

The substance was used as oxygen-releasing compound for the decomposition of pollutants in the soil [7], in sediments of shrimp farms, in treatment walls [8] or for control of P-concentration in water and sediments. It is used in toothpaste, cosmetics, and in the pharmaceutical industry. For simplification, the tested active substance is hereinafter referred to as "stable inorganic peroxide" or (SIP).

Using a special boat equipped with a suspension and dosing system as well as GPS tracking, the SIP was applied on the sediment surface or injected with a lance about 0.5m deep into the sediment. To measure the chemical impact potential, the SIP dose per m<sup>2</sup> required to reduce the loss on ignition by at least 1 percentage point was calculated. Assuming an average biomass according to Gl. 2 [9], 1.56g O2/g OM are required. Thus, 15.6g O2/kg TR (dry residue) are needed to decompose 10g OM/kg TR. For the 0-1 cm thick sediment layer with a dry gross density of 0.045g TR/cm<sup>3</sup> OS (wet original sediment), 450g TR/m<sup>2</sup> require a calculated 7.0g O2/m<sup>2</sup>:

$$C_{106}H_{180}O_{45}N_{16}P + 118,5 O_{2} \rightarrow 106 CO_{2} + 66 H_{2}O + 16 NH_{3} + [PO_{4}] + energy$$
(2)

Given that 1 kg SIP releases 33.3 g O2 in 8-10 weeks, the requirement is calculated for at least 210g/m<sup>2</sup> lake surface. In addition, the released oxygen can also oxidize inorganic reduction agents in the sediment, e.g. Fe(II):

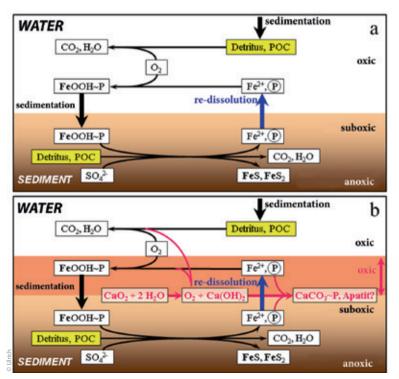
$$Fe^{2+} + 0.25 O_2 + 2.5 H_2 O \rightarrow Fe(OH)_3 + 2 H^+$$
 (3)

A conceptual outline of the interactions and reactions near the water-sediment boundary is shown in **Figure 1**.

## **3 Investigation Area**

## 3.1 Mühlenteich Lake

Mühlenteich Lake (52° 12,027' N, 8° 6m265' E) is located within a flora and fauna nature reserve in the municipality of Georgsmarienhütte near the Oesede Cloister, Lower Saxony. The surface is approx. 10,700 m2 (without a fully dried-up area), the water depth in 2014 was between <0.5 m and 1.1 m. The lake is supplied by precipitation and groundwater, as it does not have a connection to a nearby river. Prior to the first application of the SIP, the entire sediment volume was estimated to be 10,700 m3. SIP was applied four times in dosages of 47g/m<sup>2</sup> (9/2012), 280g/m<sup>2</sup> (7/2013), 140g/m<sup>2</sup> (6/2014) and 62g/m<sup>2</sup> (8/2018). Between August 2012 and June 2019, the sediment thickness was measured again in a comparison to the current and original water level at the marked points P1 to P17 (initially P1 to P5). Sediment samples were taken in linear tubes, homogenized, and analyzed for TR and OM concentrations according to DIN EN 12 880 and DIN EN 15 935. The TR density was calculated based on TR concentration assuming an average solid matter density of 2.5g/cm<sup>3</sup>. The diffuse P-release from the sediment was measured in 10 sediment cores after 48 hours of incubation with



**Figure 1:** Conceptual drawing of biochemical reactions in the phosphor and iron cycle near the water-sediment boundary: a) without addition of SIP, b) after addition of SIP

in-situ temperature and daylight simulation. The lake water quality, phytoplankton, zoo plankton, and macrophyte biocenosis were monitored.

## 3.2Caohai Fish Pond

In a Chinese-German collaboration, a fish pond partially separated from the Caohai pond of the Dian Lake (24° 48'-25° 28'N, 102° 29'-103° 01'E) was chosen for a six-month feasibility study. The relatively old, highly eutrophic shallow lake is located at an altitude of +1 887m NHN in the vicinity of the city of Kunming in the province of Yunnan in southwestern China. Roughly in the center of the approx. 10,000-m<sup>2</sup> large test pond, two acrylic glass tube enclosures with a diameter of 1m and a length of 2m were installed prior to the sediment treatment. Each enclosure covered a sediment surface of 0.8m<sup>2</sup> at ~0.8m sediment depth and encased a water volume of approx. 0.8 m<sup>3</sup>, depending on the water level: In the experimental enclosure (EE) and the test pond, the SIP was injected approx. 0.5m deep into the sludge with a CaO2-dose of 0.2g/ kg sediment as suspension while the reference enclosure (RE) remained untreated.

Prior to the sediment treatment and after six months, sediment samples were taken to determine key features such as water content and dry gross density, organic material as loss on ignition, P-concentration and P-fractions, by means of a sequential extraction according to Psenner et al. [10] and as modified by Hupfer [11]. The sediment thickness was monitored by weekly measurement of the water depth relative to a fixed marker on the outer wall of the enclosure. The School of Life Science of Yunnan University conducted biological monitoring of the phytoplankton, the submersed macrophytes, and the macro-zoobenthos. Phytoplankton monitoring was carried out on two sampling strips. Water biology was monitored prior to the start of the project, and three and six months after the SIP application, respectively.

## 3.3 Kleiner Russweiher Pond

The largest SIP test application in terms of surface took place at Kleiner Russweiher Pond near Eschenbach i. d. OPf, Bavaria. In this shallow lake, 16.9 of 27 ha of the sediment surface were treated with 7.5 t SIP with a dosage of 44g/m<sup>2</sup> in April 2019. The boat tracks were recorded by means of GPS as visualized in Figure 2. Monitoring of effects comprised analyses of lake water, pore water, and sediment properties including sequential P-extraction as well as an inventory of communities of phytoplankton, zooplankton, macro-zoobenthos, and macrophytes.

## 1 Results and Discussion

## 4.1 Mühlenteich Lake

In the Mühlenteich, the initial sediment thickness was 99.8  $\pm$  32.5cm (N = 5). The first low dosage of the SIP addition (47g/m<sup>2</sup>) in the year 2012 led to a reduction of the sediment thickness by 12% on average. In June 2013, due to accumulating seston deposits, an average sediment thickness of 91.4  $\pm$  32.5 cm (N = 5) was measured at P1 to P5 before the second (main) dosage. The data for the sediment properties indicated high variability, which could be reduced by dividing the five initial monitoring points into two groups: Group 1 (P1, P3, P4) and Group 2 (P2, P5). Three months after the second SIP application, the reduction of sediment thickness was even more evident (Figure 3). Based on the initial TR content, a maximum loss of 220 kg/m<sup>2</sup> or a reduction of sediment thickness by 25% was detected.

After the third SIP application, the sediment thickness was further reduced to  $59.8 \pm 16.8$  cm (N = 17). This reduction of sediment thickness by another 20%, when viewed in percentages, resembled the maximum average loss of OM (234 ± 128kg/m<sup>2</sup>) and the reduction of sediment volume by 22%, based on the sediment data measured in October 2013 (N = 15). Due to the accumulation of seston deposits with fresh OM

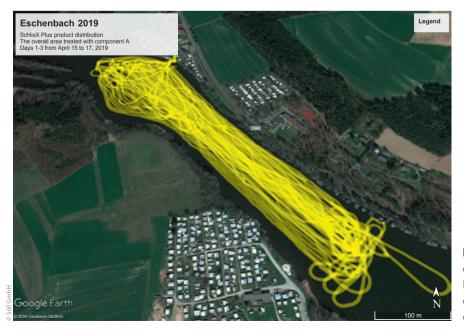


Figure 2: Aerial photo of the western part of Kleiner Russweiher Pond. The yellow line shows the boat tracks in the SIP application across the sediment surface as recorded with GPS. and a persistent portion of residual OM, the sediment samples continued to contain residual OM concentrations after each SIP application. In total, the treatment effect throughout the entire monitoring period from August 2012 to October 2014 saw an average reduction in sediment thickness from  $45 \pm 11\%$  (N = 5). Between October 2018 and June 2019, both sediment volume and OM content were reduced on average by 18% after the fourth SIP application.

The P-release rates that were measured prior to the application were higher  $(13.7 \pm 8.1 \text{mg P}/(\text{m2} \cdot \text{d}))$  than a few months after the application  $(3.9 \pm 9.8 \text{mg P}/(\text{m2} \cdot \text{d}))$ . Meanwhile, 3 of 10 sediment samples even indicated a P-absorption (Figure 4). At the same time, spatial variability was ample and seasonal effects with a P-release higher in early summer than in early spring cannot be ruled out.

Based on the available monitoring reports, ecological monitoring of Mühlenteich Lake showed no negative effects of the treatment on the composition and frequency of the zooplankton and phytoplankton species or the submersed macrophyte vegetation. Since some species reproduced in the fall and effectively consumed phosphate, the observed slight reduction of phosphate content in the lake water could not be ascribed solely to the SIP application. Throughout the SIP application period, Mühlenteich Lake was prevented from drying out completely and ensured that fish could regenerate. Further studies of the effects of SIP on the P-balance are required.

## 4.2Caohai Fish Pond

During the test period, the sediment surface in the untreated reference sample (RE) of the Caohai test pond fluctuated by  $\pm 3$  cm compared to the original surface level. In the

experimental enclosure (EE), the level of the sediment surface was reduced after the SIP application by up to 12cm (or by 24% of the treated layer) (Figure 5). A temporary increase of the sediment surface in June was due to the massive growth of littoral aqueous plants, which occurred both in the RE and the test pond. The massive growth of submersed macrophythes temporarily obstructed concrete depth measurements. A decreasing trend of the sediment surface level was also measured on several marker rods distributed over the test pond surface in comparison to an untreated reference point. The ecological analyses showed a rapid seasonal succession of plant and animal biocenoses characterized by hypertrophic production and decomposition processes, so that with regard to the tested active substance, no definitive interpretable findings could be gained.

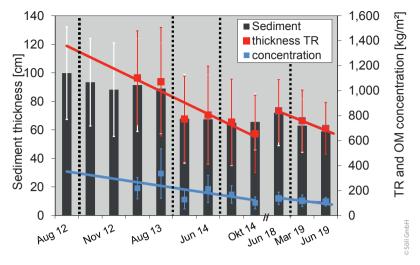
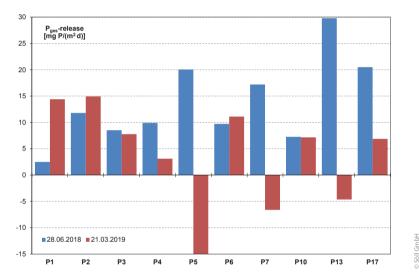


Figure 3: Temporal progression of sediment thickness (left y-axis), concentration of dry residue (TR) and organic material (OM) (right y-axis), influenced by SIP application (dashed lines) at Mühlenteich Lake



**Figure 4:** P-release rates measured in 10 sediment cores that were taken from Mühlenteich Lake before 06/28/2018 and a few months after SIP application

The analysis of the phosphor bond in the sediment using the standard protocol for sequential extraction ([10], [11]) showed significant shifts of the P-fractions, in particular an increase of the P-fraction (BD-P) that is soluble under reduction conditions and of the P-fraction (NaOH-SRP) that is soluble in 1 M sodium hydroxide (Figure 6). These two phosphate pools matched the iron that was extracted at the same time, which suggests that the oxidation of Fe(II) caused an increase in the P-sorption pool of Fe(III) hydroxides.

Therefore, SIP application can support increased P-sequestration for as long as oxic conditions are maintained near the sediment surface. This sequestration effect was more profound in the sediment of the experimental enclosures in the Caohai test pond than it was in the sediment of Kleiner Russweiher Pond, where a similar shift of P-fractions could be found.

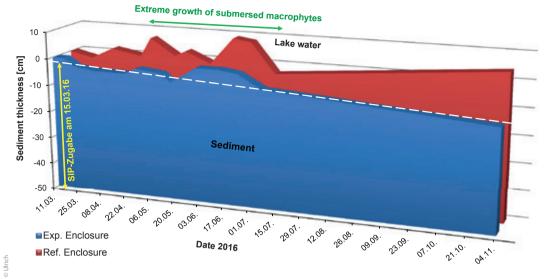
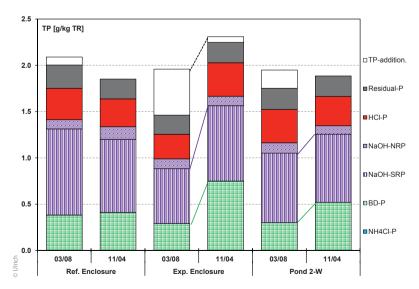
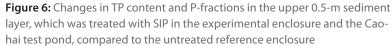


Figure 5: Changes in the sediment thickness within the experimental enclosure of the upper 0.5m layer, which was treated with SIP, compared to the untreated reference enclosure at Caohai test pond of Dian Lake, China

## 4.3 Kleiner Russweiher Pond

NNine weeks after the SIP application at Kleiner Russweiher Pond, the OM concentration of the sediment was reduced by 3-6% at the sample point of the treated section compared to 2.5-4% in the untreated section (N = 4). However, there were indications that a part of the SIP had drifted due to wind with the water current from the treated to the untreated section of the lake. The TR content indicated a slight decrease rather than an increase, which was actually to be expected because of the solid minor components in the SIP. After nine weeks, the sediment decomposition in the treated section was  $2.7 \pm$ 1.5 cm (N = 115) in consideration of the measured gross sedimentation rate. A further measurement after five months showed a total volume reduction by 11,700 m<sup>3</sup> of sediment on a measuring surface of 70,000 m<sup>2</sup>, which equals an average





reduction of sediment thickness by 17 cm. In consideration of the measured sedimentation rate of TR, the average reduction of sediment thickness was  $22 \pm 2$  cm. Obviously, most of the sediment decomposition occurred later than nine weeks after the SIP application, which suggests a longer adaptation time of the mineralizing microorganisms.

## **5** Conklusion

The three independent feasibility studies showed a substantial reduction in sediment thickness and organic material after addition of SIP, which by far exceeded even the stoichiometrically estimated scale of magnitude. Comparable effects were not detectable in the untreated reference areas (e.g. in the reference enclo-

> sure). The data therefore support the postulated mechanism of stimulated microbial decomposition of organic material through release of oxygen from CaO2. This process possibly promoted the transfer of electron acceptors (oxidation agents) from the lake water through the confining layer and increased the activity of the microbial mineralization in the sediment. No undesired side effects of the tested SIP on the lake ecosystems were observed. Seasonal changes in the plankton communities and nutrient content within the lake water (data not presented due to a lack of space) occurred during the monitoring periods but cannot be traced back to the sediment treatment with SIP. The products containing CaO2 seem to be suitable as effective, environmentally friendly, and cost-efficient method for lake treatment. Further projects and studies are recommended to understand the effects on the sediments of small and shallow lakes not only in view of phosphate sedimentation but also concerning the short and long-term ecological effects of lake treatment with SIP.

## Thanks

We would like to extend our special thanks to the towns of Georgsmarienhütte and Eschenbach i. d. OPf and to Environmental Councilors Andreas Möllenkamp and Christian Meyer for their support of the studies. We are also grateful to Andreas Boenert with AgL - Büro für Umweltgutachten for providing the monitoring data and reports. Juliana Valle with Söll GmbH deserves our thanks for her help with the improvement of an earlier draft of this paper.

## Authors

Dr. rer. nat. Kai-Uwe Ulrich BGD ECOSAX GmbH Tiergartenstraße 48 01219 Dresden k.ulrich@bgd-ecosax.de

## Alice Rau

State Dam Administration of Saxony, operations in Oberes Elbtal 01744 Dippoldiswalde alice.rau@ltv.sachsen.de

## **Dipl.-Chem. Thomas Willuweit**

Söll GmbH Fuhrmannstr. 6 95028 Hof willuweit@soelltec.de

## Literature

- [1] Ansari, A. A.; Gill, S. S.; Lanza, G. R.; Rast, W. (Eds.): Eutrophication: causes, consequences and control. Berlin: Springer-Verlag, 2011.
- [2] Downing, J. A.; Prairie, Y. T.; Cole, J. J. et al.: The global abundance and size distribution of lakes, ponds, and impoundments. In: Limnology and Oceanography 51 (2006), 5, p. 2 388-2 397.
- [3] Kumar, D. S.; Sekaran, V.: Nutrient Cycles in Lakes. In: International Journal of Lakes and Rivers 7 (2014), no. 1, pp. 11-24.

## Kai-Uwe Ulrich, Alice Rau und Thomas Willuweit

## Biochemically Triggered Sludge Decay in Shallow Lakes: Feasibility Study

Deposited sapropel often threatens the use of eutrophic shallow lakes and fish ponds. Three independent feasibility studies, in which CaO2 bearing products were tested as soft alternatives, showed considerable decrease of sediment depth and organic matter content. Likewise effects were absent in an untreated control enclosure. The field data support a mechanism of stimulated organic matter decay through the release of oxygen from virtually insoluble calcium peroxide. Obviously this process improved the transfer of electron acceptors (oxidants) from the lake water across the interface and enhanced microbial mineralization in the sediment. Adverse effects of the tested material on the lake ecosystems including macrozoobenthos, fish fauna, zooplankton, phytoplankton and aquatic plants have not been observed. The CaO2 bearing pro-ducts appear suitable as effective, environmentally friendly, lowcost alternatives to conventionally applied remediation measures such as aeration or sediment dredging. However, further research is needed on the potentials to prevent P-release from the sediment and promote P sequestration.

- [4] DWA (Eds.): Grundlagen und Maßnahmen der Seentherapie. [The Basics and Measures of Lake Treatment] In: DWA Leaflet (2006), No. M 606.
- [5] Schauser, I.; Lewandowski, J.; Hupfer, M.: Seeinterne Maßnahmen zur Beeinflussung des Phosphor-Haushalts eutrophierter Seen - Leitfaden zur Auswahl eines geeigneten Verfahrens. [Intra-lake Measures to Influence the Phosphor Balance of Eutrophicized Lakes – Guide to the selection of a suitable method] In: Reports of the IGB (2003), Issue 16.
- [6] Ma, Y.; Zhang, B. T.; Zhao, L. et al.: Study on the generation mechanism of reactive oxygen species on calcium peroxide by chemiluminescence and UV-visible spectra. In: Luminiscence 22 (2007), pp. 575-580.
- [7] Cassidy, D. P.; Irvine, R. L.: Use of calcium peroxide to provide oxygen for contaminant biodegradation in a saturated soil. In: J. Hazard. Mater. 69 (1999), pp. 25-39.
- [8] Chevalier, L. R.; McCann, C. D.: Feasibility of calcium peroxide as an oxygen releasing compound in treatment walls. In: Int. J. Environ. Waste Management 2 (2008), 3, pp. 245-256.
- [9] Uhlmann, D.; Horn, W.: Hydrobiologie der Binnengewässer. [Hydrobiology of Inland Waters] Stuttgart: UTB Verlag Eugen Ulmer, 2001.
- [10] Psenner, R.; Pucsko, R.; Sager, M.: Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten. [The Fractioning of Organic and Inorganic Phosphor Bonds of Sediments] Versuch einer Definition ökologisch wichtiger Fraktionen. [Approach to a Definition of Ecologically Important Fractions] In: Arch. Hydrobiol. Suppl. 70 (1984), pp. 111-155.
- [11] Hupfer, M.: Bindungsformen und Mobilität des Phosphors in Gewässersedimenten. [Bonding Forms and Mobility of Phosphor in Aquatic Sediments] In: Steinberg, C.; Bernhardt, H.; Klapper, H. (Eds.): Handbuch Angewandte Limnologie. [Compendium of Applied Limnology] ecomed Verlag, 1995, pp. 1-22.
- [12] Town of Georgsmarienhütte (Ed.): Natur, Naturschutz [Nature, Nature Conservation]: Mühlenteich - Kloster Oesede (www.georgsmarienhuette.de/stadt/natur/naturschutz/ muehlenteich-kloster-oesede/; retrieval on 01/27/2020).

## Dispringer Professional.de

## Keyword: shallow lakes

Ludewig, C.; Weyer,G.: Entschlammung von Flachseen am Beispiel des Steinhuder Meeres. [Desludging Shallow Lakes by Example of Steinhuder Meer] In: Wasser, Energie und Umwelt. [Water, Energy, and the Environment]

Wiesbaden: Springer Vieweg, 2017. www.springerprofessional.de/ link/12350170

Schuster, H.-H.; Prante, J.; Gade, R.: Sanierung des Dümmer Sees und seines Umlandes. [Rehabilitation of Dümmer Lake and Its Environs] In: Wasser, Energie und Umwelt. [Water, Energy, and the Environment]

Wiesbaden: Springer Vieweg, 2017. www.springerprofessional.de/ link/12350176

## IMPRINT:

Special Edition 2020 in cooperation with Söll GmbH, Fuhrmannstr. 6, 95030 Hof; Springer Fachmedien Wiesbaden GmbH, Postfach 1546, 65173 Wiesbaden, Sitz: Wiesbaden, Amtsgericht Wiesbaden, HRB 9754, USt-IdNr. DE81148419

MANAGING DIRECTORS: Joachim Krieger, Juliane Ritt, Stefanie Burgmaier

HEAD OF CORPORATE SOLUTIONS: Markus Bereszewski

PROJECT MANAGEMENT: Anja Trabusch

COVER PHOTO: © Elenarts / Getty Images / iStock

Q





# <image>

## Highly effective sludge decomposition in natural bodies of water.

Clear, sustainable results while protecting the environment.

In SchlixX Plus, owners, leaseholders or managers of larger bodies of water now have an extremely effective tool against increased silting, which poses a great danger to the animals and plants living in there. In addition to permanent phosphate binding and oxygen release, highly effective microorganisms ensure active decomposition of sludge at the bottom of the lake.

Check out the other water treatment products of OASE PROFESSIONAL – Water Technology as well! Developed jointly with experts in biology, these products have holistic effects – in natural bodies of water, swimming lakes or fish farms.



www.oase-professional.com