

Article

Treatment of Hypolimnion Water on Mineral Aggregates as the Second Step of the Hypolimnetic Withdrawal Method Used for Lake Restoration

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Abstract: The study aimed to assess the usefulness of mineral aggregates in orthophosphate (OP) removal from hypolimnetic water withdrawn from eutrophic lakes. Two low-cost and easily available reactive materials were tested: lightweight expanded clay aggregate (LECA) and crushed limestone (LS). Their performance regarding OP removal and the effect on the pH, Ca²⁺, Mg²⁺, N-NO₃ and N-NH₄ concentrations of treated water were investigated in a column experiment with four-filter beds made of LECA and amended with LS (additions of 0, 25, 50 and 75% of the bed volume). The highest OP removal (>50%) was achieved in LECA beds with high (75% by volume) amendments of LS. Neither LECA nor LS distinctly affected the pH (maximum pH increase, from 7.1 or 7.2 to 7.6, occurred in the case of the LECA bed). In real-life conditions, it is not feasible to install a full-scale bed made of these mineral aggregates on the outflow from a lake due to the large required size of such a bed. At the operation time set for 30 d, the size of a bed would need to reach between 6113.2 and 12,226.4 m³. The proposed bed should be just one of the elements of an integrated treatment system. Constructions consisting of sorption beds ought to be coupled with adequately designed zones of aquatic vegetation. Three conceptional solutions were proposed for in situ treatment of the withdrawn water, differing in arrangement and construction of the potential sorption bed. Application of such solutions should be regarded as a substantial improvement of Olszewski's method, as it can mitigate the pollution of downstream ecosystems.

Keywords: P removal; mineral aggregates; LECA; limestone; hypolimnion withdrawal; Olszewski's method



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1. Introduction

Many lake restoration methods have been developed and implemented [1,2], including the technical engineering methods and the ecological engineering solutions [3,4], often referred to as “methods supporting the proper restoration of waterbodies”. The restoration of waterbodies is always an arduous challenge and is not always successful [5–7]. Therefore, new solutions for sustaining and improving the water quality should develop into ecosystem biotechnology.

The simplest and the least expensive method of lake restoration is to withdraw water from the lake's hypolimnion directly through a pipeline and discharge it into a downstream water body, usually a small river or a creek. The principle of the method is that deoxygenated and nutrient-rich water is removed from the lake together with organic residues settling from the trophogenic zone. Such a technology was developed by Prof. Olszewski and implemented for the first time in Lake Kortowskie (Poland) in 1956 [8,9].

In Poland, Olszewski's method has also been used to restore Lake Rudnickie in Grudziądz and the Pławniowice Reservoir [10]. Due to its simplicity and low cost, this lake restoration solution attracts the most interest in Europe and Northern America [11–13]. However, a serious drawback is the pollution of the receiving river with nutrients [14–16]. A long-term research project dealing with Lake Kortowskie has confirmed that the total phosphorus concentrations at the lake's outflow in the summer varied within $0.37\text{--}1.73\text{ mg P}\cdot\text{dm}^{-3}$, and the levels of orthophosphates (OP) ranged from $0.30\text{ to }0.65\text{ mg PO}_4^{3-}\cdot\text{dm}^{-3}$ [17], whereas mean concentration of ammonium during pipe operation reached up to $1.16\text{ mg N-NH}_4\cdot\text{dm}^{-3}$ [18]. Thus, attempts to reduce these nontarget effects on the downstream ecosystems are needed.

This can be gained by in situ treatment of the hypolimnetic water withdrawn from a lake before it reaches the receiving water body. For this purpose, hydrophyte methods, based on the biological processes used so far in wastewater treatment [19] could be employed. Microorganisms, as well as water and moisture-loving plants (hydrophytes) growing in properly designed facilities (earthen filters or ponds), are flooded periodically or permanently with wastewater. Such systems are highly effective in removing organic substances and ammonium nitrogen (over a 90% removal success) [20]. On the other hand, the reduction of phosphorus concentration by an accumulation in plant tissues can reach 10–40% [21,22]. Despite the numerous advantages of hydrophyte wastewater treatment facilities, the solution presents a major drawback, i.e., a large area it needs to cover to be efficient [23]. An alternative option is to couple biological processes with sorption in specially designed abiotic–biotic systems involving mineral aggregates [24,25]. The application of mineral aggregates can help to reduce substantially the area dedicated to water pretreatment while simultaneously raising the efficiency of phosphorus removal. Currently, sorption materials of natural origin are widely used in wastewater treatment technologies, which results from their high effectiveness in the removal of pollutants and low costs [26,27]. An example is an aggregate called lightweight expanded clay aggregate (LECA), consisting mainly of clay minerals. With its high sorption capacity, water-permeability and porosity, LECA are employed in hydrophyte wastewater treatment facilities with both vertical and horizontal wastewater flows [28–30]. An additional benefit is that the surface of LECA can be overgrown with a biofilm, where the development of microorganisms favors the nitrification and denitrification processes, as well as dephosphatation. This property endows LECA with the capacity to remove effectively both phosphorus and nitrogen [27,31–33]. Carbonate minerals, such as dolomite and calcite, are another group of sorption materials widely used in the removal of phosphorus from water. They are applied as crushed carbonate rocks (dolomite or limestone, LS) to fill sorption beds in hydrophyte wastewater treatment plants and in earthen and plant systems developed to purify wastewater [27,34,35], river waters [36,37] and in biogeochemical barriers used in the pretreatment of groundwater [38,39]. The research conducted thus far has focused on the assessment of the sorption capacity of small-grained ($<10\text{ mm}$) mineral aggregates at high-concentration OP solutions, usually found in wastewater ($5\text{--}200\text{ mg}\cdot\text{dm}^{-3}$) [40–43]. Only a few studies [44,45] have assessed adsorption capacity of mineral aggregates under relatively low OP concentrations typically found in freshwater ecosystems. Therefore, information about the removal of OP under lake-specific OP concentrations and ionic composition is still limited. On the other hand, it is also extremely important to assess the efficiency of the removal of pollutants under dynamic flow conditions, as the efficiency of phosphorus removal in static studies (batch type) is not necessarily repeatable in semitechnical or technical flow-through experiments [29,46].

Hence, the objective of this study was to determine the possibilities of using mineral aggregates in different volumetric ratios in sorption beds to remove phosphorus compounds from hypolimnetic water discharged to a downstream water body. Our analysis included LECA and calcite-based aggregate (limestone) with grain sizes of 10–30 mm. Dynamic flow column experiments were performed using natural water from the lake's hypolimnion. The research focused on the effectiveness of the process and on the impact

the applied sorption materials had on the pH and the concentrations of Ca^{2+} , Mg^{2+} , N-NO_3 and N-NH_4 in treated water. The results can provide valuable information that may allow us to improve Olszewski's method; in addition to which, they might serve as a basis for developing innovative engineering solutions for the betterment of the surface water quality. The reported study responds to the tasks defined in the Water Framework Directive 2000/60/EC of 25 October 2000, which obligates all European Union member states to achieve a good environmental status of all waters until 2027.

2. Materials and Methods

2.1. Reactive Materials

Two reactive materials were used in the study: LECA and limestone (LS), both having grain sizes of 10–30 mm. As already mentioned, these aggregates were chosen from among four low-cost and easy available materials tested in a previous study for OP removal from hypolimnetic water in static sorption experiments [44]. According to the X-ray diffraction (XRD) analysis, LECA consists mainly of clay minerals (91%), mostly aluminum silicates, including smectite, illite and chlorite, accompanied by quartz, calcite and dolomite. The material is characterized by a very high porosity of 78% and surface area of $51.2 \text{ m}^2 \text{ g}^{-1}$ (determined with the N_2 adsorption (BET) method). Limestone is crushed sedimentary rock, originating from deposits in Southwestern Poland, and it contained mainly calcium carbonate in the form of calcite (96%). Its surface area was $1.3 \text{ m}^2 \text{ g}^{-1}$. The main metallic components of LECA are silicon, aluminum and calcium, whereas limestone contains mainly calcium (Table 1).

Table 1. The pH and compositions of the reactive materials (%) (manufacturer data) (LS: limestone and LECA: lightweight expanded clay aggregate).

Reactive Material	pH	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	SiO_2	MnO	Na_2O	K_2O	TiO_2	P_2O_5
LECA	8.2	10.76	3.20	8.31	15.82	0.04	56.26	0.01	0.59	3.58	0.64	0.23
LS	7.5	53.33	0.61	0.27	0.38	0.13	2.60	0.01	-	-	-	-

“-” – not detected.

2.2. Experimental Design

Four columns made of PVC (diameter of 0.07 m and length of 1 m) were filled with reactive materials (total volume of the materials was 0.004 m^3). One column was filled with LECA only (variant 1, V1), and three columns were filled with LECA previously mixed with LS (V2–V4) (Figure 1). The addition of LS made up 25%, 50% and 75% of the total bed volume (V2–V4, respectively), which corresponded to LECA and the LS volumes to volume ratios of 3:1, 1:1 and 1:3, respectively. Hypolimnetic water continuously flowed onto the filter bed under constant flow conditions (the water discharge was regulated using a valve in the column outlet (Figure 1)). The water discharge in the column inlet was $0.017 \text{ m}^3 \text{ h}^{-1}$. The experiment was performed in a temperature-controlled room at 10°C . The effluent from each column was sampled at 28 min steps as long as the recorded reduction rate of the phosphate concentrations was $\geq 10\% \pm 1\%$. The following parameters were measured in the effluent: the pH and concentrations of phosphate, calcium, magnesium, nitrates and ammonium.

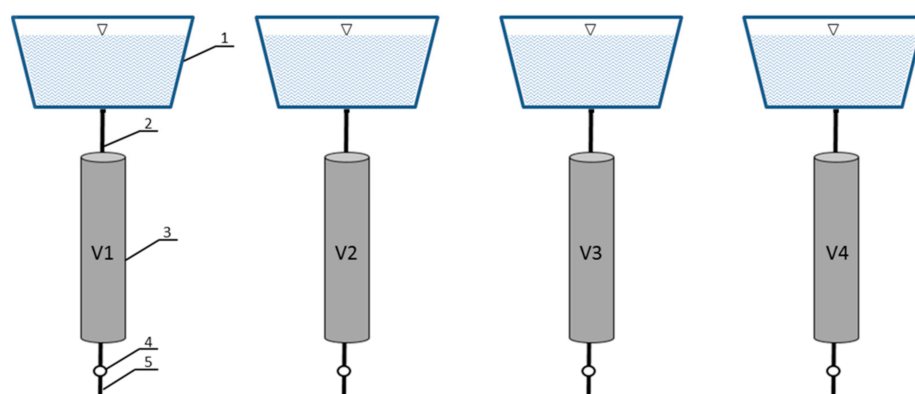


Figure 1. Setup of the column experiment: (1) hypolimnetic water reservoir, (2) alimenting pipe, (3) column bed, (4) regulating valve and (5)–discharge tube. V1: column filled with lightweight expanded clay aggregate (LECA) only, and V2–V3: columns filled with LECA and limestone (LS) (volumetric share of LS: 25%, 50% and 75%, respectively).

2.3. Hypolimnetic Water

Hypolimnetic water was sampled from the outlet of the hypolimnion withdrawal pipeline operating in Lake Kortowskie, a water body situated in Olsztyn, Poland (Figure 1). The sampling took place in late July 2017, as the middle of summer represents a period of the highest near-bottom nutrient concentrations in stratified lakes due to organic matter sedimentation and decay, as well as internal nutrient loading from sediments. Hypolimnetic water sampled for the experiments was characterized by low temperature, nearly neutral pH and OP concentrations of 0.41–0.46 mg PO_4^{3-} dm^{-3} (Table 2).

Table 2. Properties of the hypolimnetic water used in the experiments.

Parameter	Variant			
	V1 (100% LECA)	V2 (75% LECA + 25% LS)	V3 (50% LECA + 50% LS)	V4 (25% LECA + 75% LS)
Temperature ($^{\circ}\text{C}$)	9.9	10.1	10.0	9.9
pH	7.13	7.17	7.08	7.07
PO_4^{3-} (mg dm^{-3})	0.46	0.43	0.41	0.44
N-NO_3 (mg dm^{-3})	0.06	0.07	0.07	0.07
N-NH_4 (mg dm^{-3})	1.85	1.95	1.94	1.81
Ca^{2+} (mg dm^{-3})	67.0	67.3	67.0	67.4
Mg^{2+} (mg dm^{-3})	10.6	11.1	10.9	11.3

2.4. Chemical Analysis

The pH was measured potentiometrically using a standard multimeter (MultiLine P4, WTW, Weilheim, Germany). The OP concentration was determined using the molybdenum blue method according to the standard protocols (PN-EN ISO 6878) at the wavelength of 880 nm and optical path length of 50 mm on a Nanocolor UV/Vis spectrophotometer (Macherey-Nagel, Düren, Germany). Ionic concentrations (Ca^{2+} , Mg^{2+} , NO_3^- and NH_4^+) in the hypolimnetic water were determined by high-performance liquid chromatography (HPLC) chromatography (Shimadzu analyzer, Prominence System, Tokyo, Japan).

3. Results

3.1. Orthophosphate (OP) Removal Efficiency

OP retention was recorded on all column beds (Figure 2). Irrespective of the experimental variant, the highest reduction of OP concentration took place in the very initial stage of the experiment (within 0.5 h (28 min; Figure 2). Afterwards, the OP concentration

slowly increased, reaching the assumed saturation level (minimum OP removal rate of $10 \pm 1\%$) after about 2–7.5 h, depending on the column bed filling (Figure 2 and Table 3).

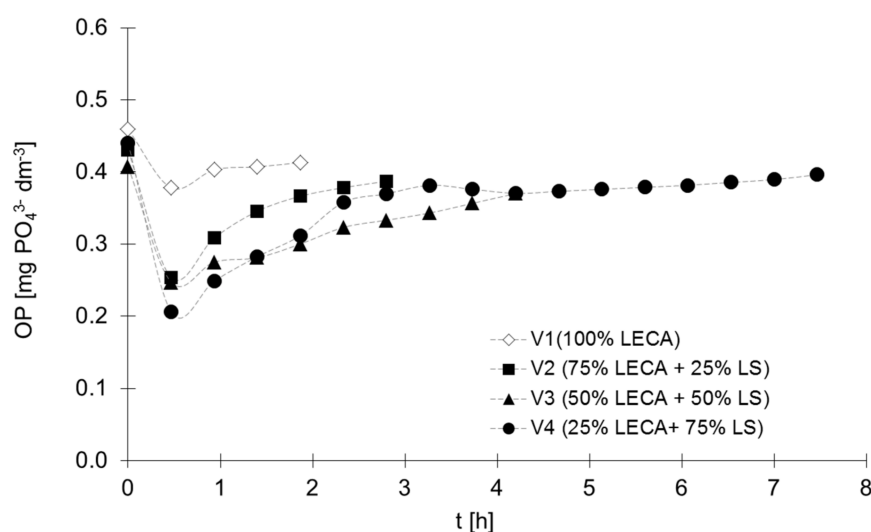


Figure 2. Orthophosphate (OP) removal from the hypolimnetic water during treatment on column beds (LS: limestone); dashed lines were used for better visibility of the trend. Results were presented for the time of effective sorption (OP removal rate of $\geq 10 \pm 1\%$).

Table 3. Parameters of the orthophosphate (OP) removal onto LECA/LS beds (effective sorption defined as a OP removal rate of $\geq 10 \pm 2\%$).

Variant of Bed Composition	Time of Effective Sorption	Volume of Water Treated (dm ³)	P Removed (mg PO ₄ ^{3−})
V1 (100% LECA)	1 h 52 min	335	19.7
V2 (75% LECA + 25% LS)	2 h 48 min	508	45.5
V3 (50% LECA + 50% LS)	4 h 12 min	762	70.1
V4 (25% LECA + 75% LS)	7 h 28 min	1348	122.3

The OP removal rate increased with the increasing LS volume in the bed. After 0.5 h of the column operation, the OP concentration dropped to $0.38 \text{ mg PO}_4^{3-} \text{ dm}^{-3}$ in the column filled with LECA only (V1), which corresponded to the OP removal rate of 17.8% (Figure 2). Within the same time, in beds amended with LS (V2, V3 and V4), the decrease was 2.2–3 times higher and accounted for 41.0%, 39.3% and 53.2%, respectively (the achieved OP concentrations were 0.25, 0.25 and $0.21 \text{ mg PO}_4^{3-} \text{ dm}^{-3}$; Figure 2). Thus, no important difference was detected between variants V2 and V3 (25% and 50% LS), whereas the further addition of LS (75%, V4) resulted in an obviously higher sorption. After a longer time of the bed operation, the OP concentrations continued to increase, indicating a decreasing OP removal (Figure 2). However, in the column V3 (50% of LS), this decrease in OP removal was slower as compared to the other beds amended with LS (V2 and V4), and thus, a slightly higher removal of OP was recorded after two to three hours in V3 (50% LS) than in V4 (75% LS), which is contrary to the pattern observed after 0.5h (Figure 2). At the same time, the OP removal on column V3 (50% LS) was distinctly higher as compared to V2 (25%LS) (the OP removal rates after about two to three hours were 16–26% and 9–15%, respectively; Figure 2).

In the column filled with LECA only (V1), an OP removal rate of at least 10% was maintained for 1 h 52 min (Figure 2 and Table 3). During this time, the LECA bed (V1) treated 335 dm^3 of the hypolimnetic water, which corresponded to a total load of 152 mg PO_4^{3-} and removed 12.9% of this load ($19.7 \text{ mg PO}_4^{3-}$) (Table 3). In the case of columns with LECA and limestone (V2–V4), the duration of the effective OP removal ($\geq 10\%$) was 1.5, 2.3 and

four times longer, respectively, than on the LECA bed (V1). The most efficient column V4 (the highest addition of limestone) treated 1348.4 dm^3 of the hypolimnetic water, which corresponded to a load of 593 mg PO_4^{3-} and fixed 20.6% of the load ($122.3 \text{ mg PO}_4^{3-}$).

After the removal rate dropped below 10%, all the beds continued to reduce the OP concentration in the hypolimnetic water by about 8% (V1 and V2 for at least four hours, whereas V3 - for six hours). This is a valuable observation for a potential field construction of such beds, as it shows prolonged OP fixation.

3.2. pH and Concentration of Ca^{2+} and Mg^{2+} in the Hypolimnetic Water after Treatment

All the tested filter beds raised the pH of the hypolimnetic water, but the pH remained nearly neutral to slightly alkaline throughout the entire experiment (Figure 3). The most pronounced pH change was recorded during the initial stage of the experiment (after 0.5 h of the bed operation): the pH increased from 7.1–7.2 (before treatment) to 7.5 (V1), 7.6 (V2), 7.3 (V3) and 7.4 (V4). However, the pH dropped to the level of 7.2–7.4 during the continued operation of the filter beds (Figure 3).

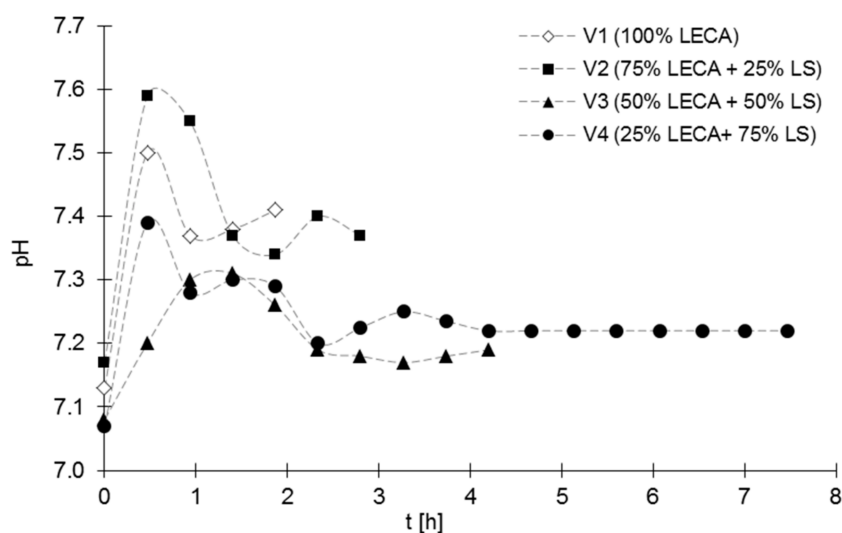


Figure 3. The pH of the hypolimnetic water during treatment on the column beds (LS: limestone); dashed lines were used for better visibility of the trends. Results were presented for the time of effective sorption (OP removal rate of $\geq 10 \pm 1\%$).

The treatments on the LECA and LECA/LS beds also affected the ionic composition of the hypolimnetic water (Figure 4a,b). Similar to the pH, the contents of the calcium and magnesium increased sharply during the initial stage of the experiment. After 0.5 h, the concentrations of Ca^{2+} and Mg^{2+} rose by $22.7 \text{ mg Ca}^{2+} \text{ dm}^{-3}$ (33.9%) and $16.1 \text{ Mg}^{2+} \text{ dm}^{-3}$ (145.0%) after treatment on the LECA bed (V1), as compared to untreated water. The supply of Ca^{2+} was much higher in the columns enriched with LS (51.1%, 55.4% and 65.0% in the variants V2, V3 and V4, respectively) and increased with the increasing share of this material in the bed volume (Figure 3). A contrary effect was recorded for magnesium: the increase in its concentration was the higher the lower the LS volume. For example, after 0.5h, the concentration of Mg^{2+} after treatment on the columns V2 and V3 was 150% and 73% higher (as compared to the nontreated water, respectively), whereas, after treatment on V4, the difference was only 4%.

During the subsequent bed operation, the concentrations of Ca^{2+} and Mg^{2+} tended to decrease and remain relatively stable, although some slight fluctuations took place. The concentrations of both cations showed very similar trends in all variants and remained in the range typically found in freshwater.

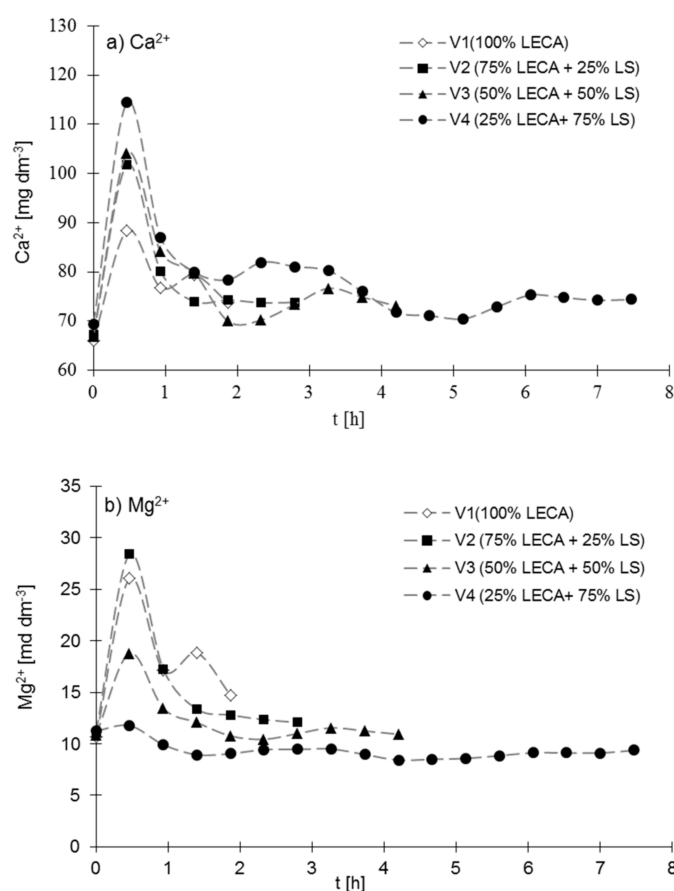


Figure 4. Concentrations of Ca^{2+} (a) and Mg^{2+} (b) in the hypolimnetic water during the treatments on the column beds (LS: limestone); dashed lines were used for better visibility of the trend. Results were presented for the time of effective sorption (OP removal rate of $\geq 10 \pm 1\%$).

3.3. Inorganic Nitrogen in the Hypolimnetic Water after Treatment

After treatment on the column filled with LECA only (V1), the concentration of the nitrates sharply dropped after 0.5 h and further increased, reaching nearly the level of not treated water (Figure 5a), whereas the concentrations of N-NH_4 clearly increased throughout the time of the column operation (Figure 5b,c). The concentrations of N-NH_4 at the end of the column operation were 10.5% and 9.8% (respectively) higher as compared to the water not subjected to treatment.

After contact with column beds containing 25% and 75% LS (V2 and V4) the same trend can be seen for the nitrates, with a sharp drop after just 0.5 h (28 min) of the treatment and a subsequent increase (Figure 5a). In the variant V3 (50% LS), the concentrations of the nitrates initially also decreased (reaching a level about two times lower as compared to the other columns with LS; Figure 5a) but remained relatively stable afterwards (Figure 5a). However, for ammonium, treatments on columns with LS resulted in an opposite change as compared to the column filled with LECA only (V1). In the initial stage of the column operation (up to 1 h 24 min for V2, 1 h 52 min for V3 and 2 h 20 min for V4), N-NH_4 slightly decreased (by 7.6–10.6%, 16.9–20.3% and 6.9–12.1%, respectively) as compared to the hypolimnetic water without treatment (Figure 5b). Afterwards, the concentration of N-NH_4 started to increase but remained lower as compared to the hypolimnetic water before treatment (V2, 25% LS), remained relatively stable (V3, 50% LS) or further dropped (V4, 75% LS).

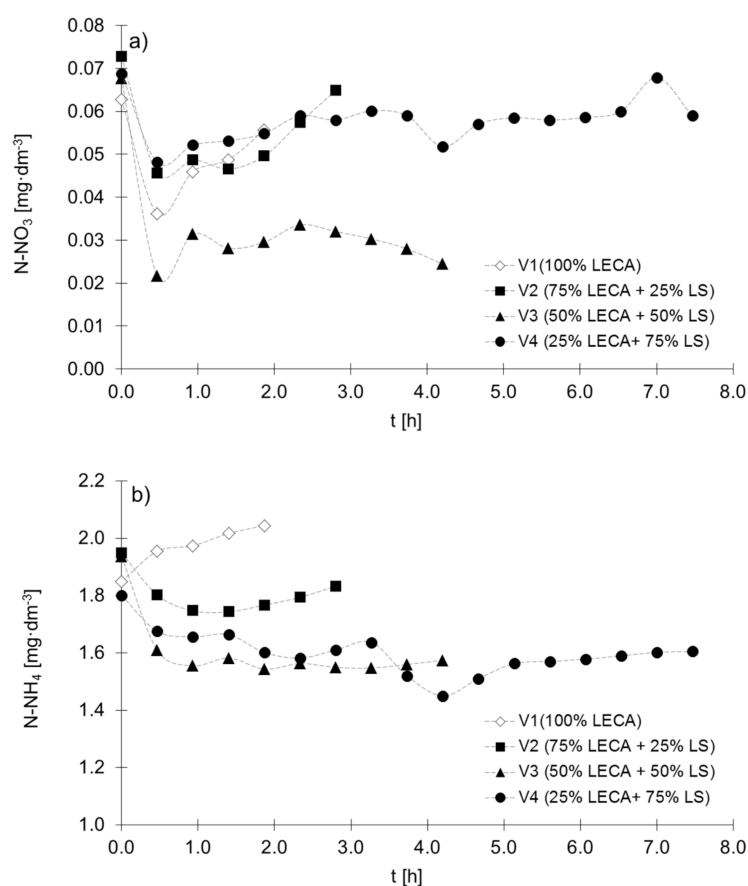


Figure 5. Concentrations of nitrates (a) and ammonium (b) in the hypolimnetic water during the treatments on column beds (LS: limestone); dashed lines were used for better visibility of the trend. Results were presented for the time of effective sorption (OP removal rate of $\geq 10 \pm 1\%$).

4. Discussion

4.1. OP Removal Efficiency

The results showed that a similar pattern of OP removal in time was observed irrespectively on the composition of the sorption bed, with the most pronounced P sorption in the very initial stage of the experiment (up to 0.5 h) and its continued decrease during the column operations (Figure 2). This indicates that the surface areas of the reactive materials were gradually exhausted, leading to a drop in the OP fixation. Interestingly, at the beginning of experiment, a substantial rise in the pH and concentrations of Mg^{2+} and Ca^{2+} also took place (Figures 3 and 4), which points at the flushing of calcium and magnesium from the alkaline components of the sorbents. The increase in pH from nearly neutral to slightly alkaline must have reduced, to some extent, the sorption of OP onto LECA, as its adsorption ability decreases with the alkalization of the solution [44,45] due to the change in the ligand type being replaced with OP [45]. In the case of the same LECA as investigated in the current study, a pH rise from 7.0 to 7.5 at the temperature of 10 °C resulted in a 10% lower OP fixation [44]. An increase in pH in the range observed after 0.5 h could also affect the performance of LS, as it generally enhances OP sorption onto calcite, most likely by changes in phosphate speciation [46,47]. Furthermore, the adsorption of OP onto LS was probably positively affected by the elevated concentrations of Ca^{2+} and Mg^{2+} , as they also enhance the OP adsorption onto calcite [47–49]. Therefore, it can be concluded that, during the initial stage of the experiment, the highest OP removal in the beds with LS was mainly due to the highly reactive surface available for adsorbing phosphate ions and was supported by pH rise and the $\text{Ca}^{2+}/\text{Mg}^{2+}$ supply. In the further stages of the experiments, OP retention decreased with time, which, in case of LS, was not

only due to the gradual saturation of the reactive surface with phosphate ions, but also due to the decreasing pH and $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentrations. Naturally, these new components (additional pool of Ca and Mg) were fast removed from the system due to the continuous water flow. However, random measurements of the pH and concentrations of Ca^{2+} and Mg^{2+} revealed that these parameters were substantially raised already after one minute of the bed operation (data now shown). Thus, as water flowed down the column, its pH and Ca/Mg contents gradually increased due to contact with the sorbents, which must have affected the sorption taking place in the lower part of the column (that was reached by water with an already raised pH and metal concentrations).

Generally, the performance of columns in OP retention was the better the higher the volume of LS in the sorption bed (Figure 2). However, enhancement of the OP removal due to the LECA replacement with LS was not proportional to the LS addition. This can be seen when comparing variants V2 and V3 (25% and 50% of LS), as only slight difference in OP removal were observed (39% versus 41%, accordingly; Figure 2). One likely reason for that is the relatively low pH observed in the variant V3 (Figure 3). Only a minor increase in OP removal in V3 as compared to V2 in the initial stage of the experiment could therefore be due to a relatively low pH in V3 (in V2, the OP retention was probably enhanced thanks to the distinct pH increase, whereas this supporting effect was not involved in V3). Moreover, only a minor rise in the Ca^{2+} concentration was recorded when the LS share in the bed increased from 25% to 50% (V2 versus V3; Figure 4a), showing the same pattern as OP (Figure 2). A relatively low supply of Ca^{2+} in V3 could be another reason for an only slightly increased OP retention in V3 as compared to V2 during the initial stage of the experiment.

A relatively low pH and low Ca^{2+} leaching in V3 as compared to V2 during the initial stage of the experiment (0.5 h) suggests that, despite the higher addition of LS in V3 (50% of LS by volume), only slightly more calcite was dissolved as compared to V2 (25% of LS by volume), which might result from the nonhomogeneous water flow through the bed (preferential paths). This is another factor potentially explaining an only minor increase in OP removal at a higher share of LS in V3 as compared to V2 (Figure 2). However, changes in the pH during the continued bed operation show that the pH rise in V3 was somehow delayed as compared to the other variants (the highest pH value was recorded after 1–1.5 h in V3 and after 0.5 h in the other variants) (Figure 3). Hence, it can be assumed that, at this time, the remaining volume of the column was available for the flowing water (which did not get into contact with the water earlier), resulting in a pH change, although this is not confirmed by Ca^{2+} (Figure 4a). The same reason is likely to be valid for the slower decrease in OP removal in V3 as compared to the other variants (Figure 2).

Irrespectively of the above-described observations, the research outcomes showed that LECA and LS, if applied in an adequate volumetric ratio, can be an effective sorption material for the removal of OP from hypolimnetic water. The addition to LS making up 25%, 50% and 75% relative to LECA improved the effectiveness of the OP removal from hypolimnetic water by 4.8%, 16.4% and 19.2%, respectively, since the moment the presumed saturation of the bed was achieved ($\leq 10\%$) (Table 3). LS added to the sorption bed also resulted in a three- to five-fold longer operating time compared with the time attained by the LECA bed (Table 3). This confirms that the addition of LS to highly porous LECA can distinctly enhance the effectiveness of the OP removal and longevity of the filter bed. The reason for that is the slightly higher adsorption capacity of the LS. Both materials were tested in our previous study [44]. In hypolimnion water, the maximum adsorption capacity of the LS was about 18% higher as compared to the LECA [44]. Drizo et al. [50] also reported higher P sorption onto the limestone as compared to the LECA. However, the presence of LECA in a filter bed is important because of its high porosity and hydraulic conductivity, ensuring efficient water flow through the system [26]. Thus, a combined bed made of LECA and LS at a volumetric ratio of 1:3 is recommended as a treatment method for the purification of hypolimnetic water.

Despite the high effectiveness of the removal of OP in the experimental study, a fully dimensional bed filled with a LECA-LS mixture in real-life conditions is not possible to

design because of its large size. Our calculations revealed that, for the hydraulic conditions employed, i.e., a water discharge of $0.017 \text{ m}^3 \text{ h}^{-1}$, retention time of 28 min and bed volume of 0.004 m^3 , the OP removal rate was from 3.18 to $6.36 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (depending on the type of bed) [51]. Therefore, at a reduction of the OP concentration from $0.4 \text{ mg} \cdot \text{dm}^{-3}$ (concentration determined in the hypolimnetic water) to a value below $0.1 \text{ mg} \cdot \text{dm}^{-3}$ at the operation time set for 30 d, the size of the bed would need to reach between 6113.2 and $12,226.4 \text{ m}^3$ [51]. For this reason, the removal of nutrients from hypolimnetic water on LECA-LS beds should be just one of the elements in an integrated water pretreatment system. Potential solutions to be applied in the field are discussed in Section 4.4.

4.2. Effect on pH, Ca^{2+} and Mg^{2+}

For the protection of receiving waters, it is important that LECA/limestone beds do not substantially affect the physiochemical properties of the treated water. The maximum increase in pH relative to the initial value was 0.4 (V2; Figure 3). It occurred in the first phase of the experiment and was followed by a decreasing tendency (Figure 3), so that the pH remained approximately the same as in the natural water of the hypolimnion. This is due to the relatively low pH of the used materials: LECA– 8.2 and LS– 7.5 , and nearly neutral pH of the hypolimnetic water (7.1 – 7.2 , Table 2). The source of the pH rise must have been caused by a slight dissolution of the alkaline components of the sorbents bearing Ca and Mg, as their concentrations also increased (Figure 4), as previously discussed. In general, a higher supply of calcium in the case of LS and magnesium in the case of LECA were observed. This probably reflects the mineral compositions of the mineral aggregates: LS contains about five-fold more calcium than LECA (due to the dominance of calcite), and LECA contains about five-fold more magnesium than LS (Table 1). However, the concentration of magnesium was higher after the treatment of hypolimnetic water on the sorption beds with a higher share of LECA after about 1.5 h of treatment, whereas in the initial stage of the experiment, it was slightly higher in variant V2 than in V1, despite the lower LECA share in V2 (Figure 4b). This difference was, however, only minor (1.7 mg/L after 0.5 h , of which 0.5 mg/L was due to the difference in the initial concentrations; Table 2; after 1 h , no actual difference was recorded). This suggests that the replacement of 25% of LECA with LS by volume (V2,) actually did not change the rate of Mg^{2+} supply from the sorption bed. One reason for that could be the different solubilities/dissolution rates of the Mg-bearing minerals present in the LECA (mainly clay minerals (smectite, chlorite and illite) and dolomite) and LS (probably Mg-calcite and/or dolomite; only calcite was detected in LS).

This study demonstrated that the pH and concentrations of calcium and magnesium increased due to the hypolimnetic water treatment on all the sorption beds, mainly during the initial stage of the experiment. As previously discussed, an increased pH and supply of Ca^{2+} and Mg^{2+} can, to some extent, enhance the OP removal efficiency by LS by supporting the adsorptive OP binding onto calcite [46,47,49], but this effect would probably be limited to the initial phase of the bed operation. An increase in Ca^{2+} concentration due to sorbent dissolution can also contribute to dissolution-induced phosphate precipitation with calcium on the mineral surface, a consequence reported, for example, by Wang et al. [52] and Kłasa et al. [53] for calcite surfaces, as the supply of calcium and corresponding pH increase both enhance the saturation with respect to the calcium phosphates. This process, due to the low solubility of calcium-phosphate phases and their stability under a wide range of environmental conditions [54,55], is believed to improve the long-term performance of P-reactive materials [26,35,56,57]. A similar effect can be due to the Mg^{2+} supply [58]. However, precipitation processes are likely under high OP concentrations, so their importance in the treatment of hypolimnetic water would probably be minor.

The results of our experiments are also valid in terms of the potential applicability of pretreatment systems, especially because numerous studies carried out before on the potential use of P-reactive materials in wastewater pretreatments demonstrated a strong alkalization of the environment, depending on the applied sorption products. For example, Polonite[®], which is calcium silicate rock heated at 900°C , proven to be a highly effective

P sorption material, caused an increase in the pH up to 10.8 in permeable reactive barriers [38] or even up to >12 in a wastewater filtration system [59]. Filtralite-P, LECA heated at 1200 °C, raised the pH to 10.7 [27]. Although these materials are much more efficient in P removal than LECA [60] and LS [38], their highly alkaline properties and strong effects of the pH of the effluent bring up questions of their applicability in natural water bodies, as that would necessitate an additional solution to decrease the pH back to the levels of the natural values. Another non-target effect potentially influencing downstream water bodies is the modified composition of the hypolimnetic water in terms of increased concentrations of calcium and magnesium. Higher Ca^{2+} concentration may contribute to enhanced calcite precipitation in receiving water bodies. As phosphate is co-precipitated with calcite, this process is seen as an important self-purification mechanism in lakes and rivers [61–64].

4.3. Effect on Inorganic Nitrogen

Changes in the concentrations of nitrogen compounds did not show a clear dependency on the material filling the column bed, except for the fact that a decrease in the N- NH_4 concentrations took place only after treatment on the beds containing LS (V2–V4; Figure 5b), whereas they increased after the treatment on the column made of LECA (V1). The highest and stable reduction of ammonium and nitrate concentration was recorded in the column V3 (50% LS) (Figure 5a,b). Nevertheless, the loss of nitrates was observed for all the columns (Figure 5a).

The hypolimnion water was initially anoxic or hypoxic (some nitrates were present, Table 2). In the initial stage of the experiment, the removal of N- NH_4 by nitrification could be therefore excluded from our experiment, which was confirmed by the fact that the concentrations of N- NO_3 dropped at the same time (Figure 5a,b). The loss of ammonium could have been caused by the anammox process (leading to NH_4^+ oxidation into N_2 under anaerobic conditions using nitrites as terminal electron acceptors [65]). The temperature of hypolimnetic water (about 10 °C) and its pH during treatment (7.2–7.6) should not hinder the process, as both laboratory and commercial-scale experiments have proven that this process can occur at lower temperatures, i.e., from 10 °C [66], and the water pH within 7.5–8.5 [67]. However, the concomitant depletion of nitrates in the initial stage of the column operation (Figure 5a) suggests that the denitrification could also proceed at the same time.

During the later stage of the experiment an increase in N- NO_3 concentrations was recorded (the exception was column V3, where N- NO_3 was relatively stable; Figure 5a). This must have been an effect of oxygenation of the hypolimnetic water and resulting NH_4^+ nitrification. Oxygenation of the hypolimnion water is unavoidable in a treatment system under real-life conditions, so the nitrification of ammonium should be expected. However, the increase in N- NO_3 was much smaller than the loss of N- NH_4 (Figure 5a,b), so also some other factors had to be responsible for the persistent N- NH_4 drop.

The question is why N- NH_4 was lost only after the treatment on LS-containing beds (V2–V4), whereas its concentration slightly increased after the treatment on the column bed made of LECA only (V1) (Figure 5b). This is very surprising, as LECA has been proven to be able to remove NH_4^+ by sorption processes [68]. Moreover, the effect of LS on NH_4^+ removal seems to be confirmed also by the fact that the initial decrease in the N- NH_4 concentrations lasted the longer, the higher was the LS share in the column (1 h 24 min for V2, 1 h 52 min for V3 and 2 h 20 min for V4 (Figure 5b)). If microbial processes are assumed to dominate in the N transformations in our experiment, the results suggest that the presence of LS had a somehow promoting effect on the microbial activity. On the other hand, some depletion of N- NH_4 in the very first stage of the experiment (Figure 5b) could have been due also to the pH increase as the importance of NH_4^+ decreases in favor of ammonia ($\text{NH}_{3\text{aq}}$) as the pH rises above 7. However, taking into account that only a slight pH change took place (from 7.1 or 7.2 (no treatment) to 7.6 (V2), 7.3 (V3) and 7.4 (V4); Figure 3), the N- NH_4 loss by up to 20% (Figure 5b) could not be related to the pH rise only (at pH = 7.5, ammonia constitutes about 5% of the ammoniacal species). Moreover,

that highest loss occurred due to the treatment on the column V3 (50% LS), and no loss occurred in column V1 (LECA only), where the pH was very similar to that recorded after the treatments on the other columns (Figure 3).

Thus, the complex mechanism of the observed depletion of ammonium during the bed operation could not be directly explained within this study; still, the results seem to suggest some importance of LS in NH_4^+ loss, even though the NH_4^+ loss was only slight. The removal of nitrogen compounds on the sorption beds is mainly related to the microbial activity, as the surfaces of aggregates promote the development of a bacterial biofilm [31–33], so an increased efficiency in terms of N removal can be expected after biofilm development. Nevertheless, even the little and short-term removal of inorganic nitrogen from the treated water, as observed in our study, is important for the protection of the downstream water as water withdrawn from the hypolimnion is usually rich in ammonium.

4.4. Potential Solutions for the Treatment of Bed Construction in the Field

As previously stressed, the removal of nutrients from hypolimnetic water in LECA-LS beds should be just one of the elements in an integrated water pretreatment system. To achieve the prolonged removal of OP, sorption beds should be coupled with systems where vascular plants are used. Numerous studies have identified a group of plants with a high affinity to nitrogen and phosphorus accumulation, such as common reed (*Phragmites australis*), sweet flag (*Acorus calamus*), broadleaf cattail (*Typha latifolia*), acute sedge (*Carex acuta*), yellow iris (*Iris pseudacorus*) and reed mannagrass (*Glyceria maxima*) [39]. The construction of abiotic systems in the form of sorption beds would be used in the form of gabions placed in the river channel receiving hypolimnetic waters directly at the hypolimnion discharge. Below, a few solutions for the implementation are presented.

The placement of gabions longitudinally, along the river/creek banks, would be the easiest solution (Figure 6). Directly at the outlet of the withdrawal pipeline, gabions with high shares of limestone mixed with LECA (75% and 25%, respectively) should be used as filter materials due to their higher sorption capacity, as revealed.

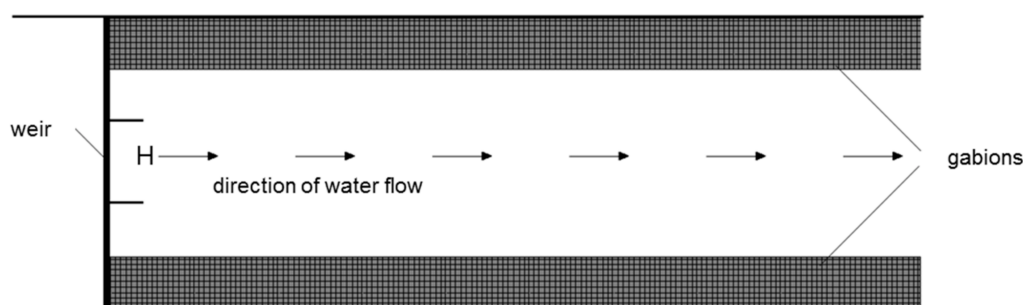


Figure 6. Longitudinal arrangement of a treatment system for hypolimnetic water using reactive materials. H: outlet of the hypolimnion withdrawal pipe.

Another solution would be lying the gabions crosswise in the riverbed (Figure 7). Alternately, the gabions should be placed on both riverbanks. This solution enhances the reactive area of the filter materials and their volume, which, together with a longer retention time, will result in a higher P removal. Limestone and LECA should be involved the same way as proposed for the previous solution, with a higher limestone volume in the front section of the system.

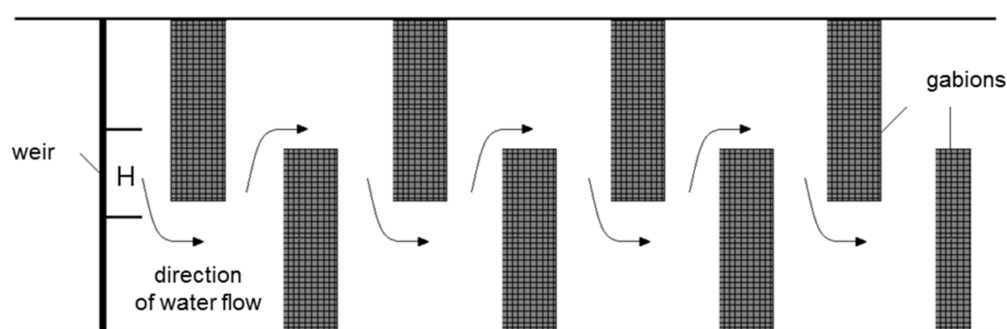


Figure 7. Crosswise arrangement of the treatment system for hypolimnetic water using reactive materials. H: outlet of the hypolimnion withdrawal pipe.

In both described arrangements, the placement of the reactive materials in the riverbed will result in a reduced river width and, thus, increased water level. To avoid flooding of the surrounding area, it is necessary to properly design the height of the gabions. Moreover, the designed structures should not be wider than 75% of the riverbed width to maintain fish migration [69]. A disadvantage of the described solutions is that probably only part of the material volume in gabions will be available for the flowing water, due to limited penetration, and some of the reactive surface will not be used, especially in the inner part of the gabions.

The induction of more intense water flowing through the gabions is possible by spraying the hypolimnetic water over the filter bed (Figure 8). For this purpose, discharged water must be directed onto the bed. This requires the placing of the filter bed out of the river, possibly close to the hypolimnion discharge. A mixture of LECA and limestone (50%:50%) should be used to ensure the high hydraulic conductivity of the treatment bed. Drainage tubes located at the bottoms of the gabions will collect the treated water and re-direct it into the river. The retention time may be adjusted by the size of the filter bed.

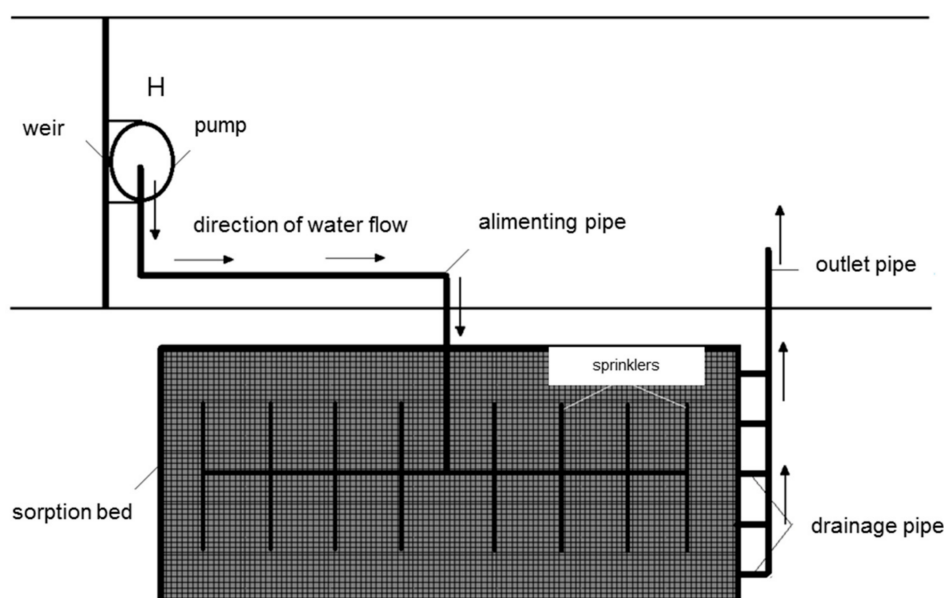


Figure 8. Separate filter bed for the treatment of hypolimnetic water using reactive materials. H: outlet of the hypolimnion withdrawal pipe.

The proposed solutions differ in gabion arrangements, which affects the contact time of the treated water with the reactive materials and the sorption of P. However, in such systems, on a technical scale, other processes of P removal are also involved, including microbiological transformations in biofilms developed on the filter bed [40]. The efficiency of

the treatment is also affected by meteorological conditions (temperature and precipitation) and the composition of the treated water. It is recommended to design integrated water pretreatment systems that will employ both abiotic (sorption materials) and biological processes (aquatic plants). The natural environment is a sensitive ecosystem, where the implementation of any water treatment method must involve a detailed analysis considering both the effectiveness of the process and its influence on the aquatic environment.

The results presented in this study and the concept of different solutions for hypolimnetic water treatment are the first stage of the research. A full confirmation of the effectiveness of the proposed solutions will be possible after a study on a technical scale.

4.5. Possible Reuse of Reactive Materials

The reuse of once-used reactive materials is an important issue in terms of circular economy, as it could help avoid the generation of waste materials. Another urgent point is P recycling, as it could reduce the pressure on nonrenewable P resources. These two problems have received more and more attention, and the need to develop reuse and/or recycling strategies has been recognized [25,70–73]. Reuse and/or recycling is especially desirable in the case of materials whose production involves high-energy inputs, such as LECA [73].

The recovery of P requires its separation from the reactive material. Chemically adsorbed OP can be desorbed from LECA and LS. The desorption of OP from LECA to distilled water can be as high as 42% [45], whilst the desorption of OP from calcite (main component of LS) reaches 100% in calcite-equilibrated solutions [47,49]. However, OP precipitation with Ca is another possible mechanism of OP removal onto Ca-bearing mineral aggregates due to the dissolution of Ca compounds serving as the Ca source [58,74], although it typically requires high OP concentrations and a long contact time [35]. In that case, P recovery would probably require the use of a strongly acidic extraction agent (to dissolve Ca-PO₄) and further chemical P precipitation from the obtained solution. However, under freshwater-relevant OP concentrations, the amount of P sorbed by the mass of the medium is relatively low [44,45]; hence, the P elution from these sorbents after the treatment of hypolimnetic water is a rather unlikely option for efficient and cost-effective P recovery [71]. Therefore, their direct reuse is probably a more reasonable approach. This seems to be valid mainly for LECA, as this medium is widely applied as a soil conditioner for improved soil aeration and moisture retention. LECA enriched with previously sorbed P could offer an additional fertilizing effect. The reuse of LECA for fertilization and soil amendment for acidic soils has been suggested by previous studies [26,27]. However, the plant availability of P sorbed by LECA is very limited due to a strong OP fixation by Al/Fe oxides [70]. Ca-bound P shows a wide range of plant availabilities, depending on the type of calcium-phosphate formed [75], and their fertilization efficiency is mainly reported in acidic soils [76,77]. Hence, limestones and Ca-rich LECA materials represent some options for reuse as acid soil fertilizers, but this application will also unavoidably raise the soil pH, limiting, to some extent, the P availability for plants. Moreover, a direct application of LS is not possible due to the coarse grains of the material, so its processing by crushing would be required, increasing the time and expenditures needed to make it suitable for use in soils. The direct application of P-enriched LECA (without further processing) for its conventional use as soil amendment seems to be the most likely to implement in practice, even though its fertilizing role would probably be minor.

The reuse of reactive materials previously applied for the treatment of hypolimnetic water by their application in the environment seems to be less restricted as compared to reactive materials used for wastewater treatment. In the latter case, the risk of heavy metals and other pollutants or pathogens (such as *Escherichia coli*) presence in the sorbent is somehow the limiting factor [73]. In natural waters, such as lakes' hypolimnion, this should not be the case. Even though *E. coli* is often present in the surface layers of lakes during bathing season, this does not influence the sanitary status of the hypolimnion due to

thermal stratification. Heavy metals can be problematic in hardly contaminated water bodies, as metals often accumulate in sediments and can be released to the hypolimnion.

5. Conclusions

Our study revealed that the treatment of hypolimnetic water on sorption beds made of LECA and LS can be a useful method of OP removal. The highest OP removal success (>50%) was achieved when the LECA beds were amended with a high volume of LS (75%). Thus, a combined bed made of LECA and LS at a volumetric ratio of 1:3 is recommended as a treatment method for the purification of hypolimnetic water. The fact that the tested sorption materials did not cause negative effects on the pH of the water suggests that these materials can be safely employed for potential application in the environment. A slight removal of nitrogen can be also gained on sorption beds made of LECA and LS. According to our calculations, in real-life conditions, it is not feasible to install a fully dimensional bed on the outflow from a lake due to the large size required for satisfactory OP removal. Hence, the proposed bed should be just one of the elements of an integrated treatment system consisting of abiotic (sorption materials) and biotic (aquatic plants similar to constructed wetlands) elements. The performance of a potential treatment system based on LECA and LS needs further investigations on a technical scale. The results of the study are an important contribution to innovative solutions for the improvement of the ecological state of water ecosystems. This is in accordance with the Water Framework Directive of the European Union, which requires the achievement of the good ecological status of water bodies in all the member countries by 2027.

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