Supporting constructed wetlands in P removal efficiency from surface water
Agnieszka Bus and Agnieszka Karczmarczyk

ABSTRACT
The research investigated the implementation of suspended reactive filters to support the phosphorus (P) removal efficiency of constructed wetlands (CWs). The reactive material (RM) used in this study was autoclaved aerated concrete (AAC). The laboratory experiment consists of four plastic boxes filled with the volume of 10 L of artificial P solution with three variants of RM mass to volume ratio: 1:1 (g:L), 5:1 (g:L), 10:1 (g:L), and the blind probe 0:1 (g:L) as a reference. AAC of different weights (10, 50 and 100 g) was wrapped in a filter bag, put into boxes, and suspended. After 30 days of the laboratory experiment, AAC was able to reduce the P-PO₄ concentration from 2.972 mg·L⁻¹ to: 0.341 mgPO₄-P·L⁻¹, 0.006 mgPO₄-P·L⁻¹ and 0.004 mgPO₄-P·L⁻¹ for 10 g, 50 g and 100 g mass variant, respectively. This concentration reduction corresponds to unit sorption of: 2.53 mgP-PO₄·g⁻¹, 0.58 mgP-PO₄·g⁻¹ and 0.30 mgP-PO₄·g⁻¹ for 10 g, 50 g and 100 g, respectively. Based on the obtained data, the CW supporting filter was dimensioned to reduce the outflow P concentration to 0.01 mg·L⁻¹. P removal efficiency prediction was calculated for Cetynia River, Poland.

Key words | autoclaved aerated concrete, box experiment, constructed wetland, phosphorus removal, suspended reactive filters

INTRODUCTION
Wetlands are one of the most valuable parts of the landscape, often known as a ‘kidney of the landscape’, filtering and purifying the water (Jørgensen et al. 2010). Vymazal (2010) defined constructed wetlands (CWs) as engineered systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils, and the associated microbial assemblages to assist in treating wastewaters. The main aim of designing CWs is to take advantage of exactly the same processes that occur in natural wetlands but in a more controlled environment. Mitsch et al. (2015) found that water purification is one of the most important ecological services that CWs fulfil.

The more likely removal mechanisms for phosphorus (P) in wetland treatment systems include vegetation uptake, or other biological processes such as bacterial immobilization, adsorption, and precipitation (Crites et al. 2006; Ballantine & Tanner 2010). CWs have a wide array of applications such as treatment of different kinds of sewage, landfill leachate, agricultural runoff and surface runoff from roads (Vymazal 2007; Lu et al. 2009; Obarska-Pempkowiak et al. 2010; Vymazal 2010; Johannesson et al. 2015).

In all types of CWs, P accumulation is low, but it should be considered that P removal is not the primary target of the treatment (Vymazal 2010). Studies on P cycling in CWs have showed that soil bed filling in major long-term observations works as a P sink (Vymazal 2010). The main P removal mechanisms in sub-surface flow CWs are adsorption and precipitation. However, the sands, washed gravel, crushed rock or peat CWs bed fills are characterized by short-term and low P sorption capacity (Vymazal 2007).

Macrophytes remove nutrients but, on the other hand, dead plants are an additional source of P. What is more, the amount of contamination uptake by macrophytes is limited by their growth rate, the nutrient concentration in the treated water or sewage, the potential biomass accumulation, the range of ecological tolerance for different contaminants and the length of the growing season (Obarska-Pempkowiak et al. 2010; Vymazal 2010). If the wetland is not harvested, P returns to the water in the system through decomposition processes. In these cases, the harvested vegetation might account for 20 to 30% of
the applied P (Crites et al. 2006). In contrast, the vegetation typically used in wetland systems is not considered to be a significant factor for P removal, even if harvesting is practised (Crites et al. 2006).

The way to increase CWs’ system efficiency for removing P is to apply reactive materials (RMs). Such materials should contain Ca, Fe and Al that in a chemical and physical way remove P from water or wastewater during adsorption and precipitation processes (Klimeski et al. 2012).

Previously, some attempts have been made to apply RMs into CWs as an additional step to remove and increase P removal in such systems. Some studies have been based at laboratory scale (Heal et al. 2005; Ballantine & Tanner 2010) and even full scale working system applications (Heal et al. 2005; Leader et al. 2005; Žibiene et al. 2015).

The chosen P-sorbing material for full scale experiments should fulfill some basic criteria and requirements: it should have moderate to high affinity for P removal; be readily available at low cost (e.g. industrial by-products or wastes); be relatively abundant and easily accessible; be non-toxic to the environment; available locally to reduce transport costs; be suitable for reuse with no risk to soil or water quality in either the short or long term; and be a renewable and natural material (Ballantine & Tanner 2010). Not all P-RMs are able to meet these criteria, but is important to fulfill as many as possible.

The novelty of this study is the use of RMs in the form of filters suspended in the water. Suspended reactive filters (SRFs) are a system of curtains consisting of filter bags filled with P RM and suspended in the treated water. Such filters can be implemented in slight as well as still water flow conditions. The idea is to implement SRF curtains in many reduplications located along the length of the water body. The advantages of SRF filter technology are: (1) direct contact of the RM with the water being treated; (2) lack of interference in the structure of ditches or ponds; (3) no need to change the shape of the bottom and banks; (4) no need to use by-passes to direct the flow; (5) easy installation without using heavy equipment; (6) easy replacement for the RM; (7) the possibility of seasonal use in periods of increased input of pollutants; (8) the adjustable length of string enables customization to the depth and level of water; and (9) construction made of unattractive materials prevents theft. The SRF technology has been granted a patent application in Poland (P. 403571).

The aim of the study is to increase of CW phosphorus removal efficiency using RMs implemented in the form of suspended filters.

### METHODS

#### Material

Autoclaved aerated concrete (AAC) is a popular lightweight material used in civil engineering. Quartz sand, lime or cement and water are used as a binding agent. The material structure of AAC is characterized by its porosity and low density. The main compounds are SiO₂ (57%) and CaO (25%). From a mineralogical point of view, the dominant component of AAC is tobermorite, which is a calcium silicate hydrate mineral with the chemical formula: Ca₅Si₆O₁₆(OH)₂·4H₂O. Table 1 presents more physical and chemical parameters of AAC. In this study, mechanically crushed material was used.

#### Experiment design

The experiment was performed indoors, at room temperature (~20 °C). One row of four plastic boxes (Figure 1) were each filled with a volume of 10 L synthetic P-PO₄ solution prepared by dissolving KH₂PO₄ with three variants of RM weight (w) to volume (v) ratio: 1:1 (w/v), 5:1 (w/v), 10:1 (w/v), and the blind probe 0:1 (w/v) as a reference. RM of different weights (10, 50 and 100 g) was wrapped in a filter bag made of polyester textile with a 1 mm mesh, then put into boxes and suspended. This means of RM application

### Table 1 | Physical and chemical parameters of AAC

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>57.24</td>
</tr>
<tr>
<td>CaO</td>
<td>24.62</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.96</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.35</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.52</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.48</td>
</tr>
<tr>
<td>Mineral composition</td>
<td>[%]</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>39</td>
</tr>
<tr>
<td>Quartz</td>
<td>38</td>
</tr>
<tr>
<td>Calcite</td>
<td>20</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>3</td>
</tr>
<tr>
<td>Grain size (mm)</td>
<td>2–5</td>
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<td>pH</td>
<td>8.5</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>83.75</td>
</tr>
<tr>
<td>Bulk density (kg m⁻³)</td>
<td>300</td>
</tr>
</tbody>
</table>
has been named SRF (Karczmarczyk et al. 2016). The mean P-PO$_4$ concentration of the box experiment was 2.972 mg·L$^{-1}$ ± 0.120. Such a high P concentration is corresponding to strongly polluted surface water (Mosiej & Bus 2015). During the experiment, boxes were covered to limit evaporation and penetration of light. Samples for analyzing the P-PO$_4$ concentration were taken from each box every second day after pH measurement, then were filtered through a 0.45 μm filter. The PO$_4$-P concentration was analyzed using flow injection analysis by FiaStar 5000. The pH was measured in unfiltered samples by LF-340 pH meter. The experiment lasted 30 days, and during this time 15 samples from each box were collected to observe the behavior of P in contact with RM.

RESULTS AND DISCUSSION

Suspended filters experiment results

Changes in pH and PO$_4$-P concentrations with the percentage reductions in different w/v ratios in the box experiment are shown in Figure 2. The decreasing values of P-PO$_4$ concentration with increasing weight of the applied material are shown. In contrast, the pH values increased with increasing weight of the material.

At the end of the experiment (after 30 days) the PO$_4$-P concentrations were decreased and equaled: 0.341 mgPO$_4$-P·L$^{-1}$, 0.006 mgPO$_4$-P·L$^{-1}$ and 0.004 mgPO$_4$-P·L$^{-1}$ for 10 g, 50 g and 100 g, respectively (Figure 2). The experiment resulted in total reduction of 88.0% for 10 g, 99.8% for 50 g and 99.9% for 100 g of material. The fastest and most rapid P reduction were observed with 50 g and 100 g of AAC. However, both the 50 g and 100 g experiments reached equilibrium after 12 days. The pH values increased in the experiment time from 7.10 to 7.15 at the beginning to 9.25 for 10 g, 9.57 for 50 g and 9.75 for 100 g, which is a result of the material’s alkalinity (Table 1). In the case of 10 g of AAA, there is seen to be a gradual increase in pH value during the experiment. With 50 g and 100 g of AAC, the observed pH values start to gradually reduce after P achieves equilibrium. Similar observations have also been observed by Agyei et al. (2002), who reported that P removal efficiency decreased as the solution pH increased up to pH 9, above which P removal started to increase. The box experiment with SRFs is a kind of long-term kinetic study. However, the constant flow condition (without any shaking) differentiates it from typical batch test, which also influence the sorption. A typical batch test lasts from a minute to as much as 2 or 3 days (Jia et al. 2013). In contrast, the box experiment was conducted over 30 days.

Comparing the box experiment reduction result with typical bath tests gives comparable results. Jia et al. (2013) found a 94% reduction of P after eight hours of shaking. Prolonging the contact time did not bring a significant increase in sorption capacity. To test the powder fraction of AAC, it was used with an initial P-PO$_4$ concentration of 25 mg·L$^{-1}$ and a w/v ratio of 5 g/1 L. Kang et al. (2017) also tested AAC for P removal capacity under typical batch conditions. They reached 97% reduction after 20 min. of contact time. However, the tested initial concentration (50 mg·L$^{-1}$) as well the mass to volume ratio of 1 g/30 mL used was high. The prolongation of contact time to 24 h did not give any results. On the other hand, Karczmarczyk et al. (2014) observed a 95% P-PO$_4$ reduction after 48 hours for an initial concentration of 0.56 and 1.00 mgP-PO$_4$·L$^{-1}$. After 10 hours’ contact time, the reduction was around 70%. What is more, there were no significant differences in reduction between the initial concentrations of 0.25; 0.56 and 1.00 mgP-PO$_4$·L$^{-1}$. The AAC used in that research is characterized by a 1–6 mm fraction and w/v ratio of 1 g/100 mL. SRF reduction after 48 hours equals
29%, 57% and 79% for 10 g, 50 g and 100 g, respectively. Karczmarczyk et al. (2014) calculated maximum sorption capacity by the Langmuir isotherm to 78.8 mg·g⁻¹ at 24 h contact time.

The observed pH increase is a result of releasing Ca(OH)₂ after the reaction between tobermorite and water (Berg et al. 2006). Egemose et al. (2012) also observed that the pH value increases as long as tobermorite is available and for that reason the pH is a good indicator of the long-term efficiency of AAC and can be used as an indicator of the available Ca for P binding. It is also seen that the most rapid pH increment is for 50 g and 100 g of AAC variants. The pH value is regarded as an important factor of hydroxyapatite (HAP) formation in P removal (Egemose et al. 2012; Li et al. 2015; Kang et al. 2017). Li et al. (2015) claim that at a pH of 4–10, H₂PO₄⁻ and HPO₄²⁻ are the elementary phosphate groups in solution that are able to connect with Ca²⁺ and form calcium phosphate compounds such as CaHPO₄. When the pH ranged from 10–12, the phosphate removal rate increases and the high pH caused P-PO₄ to precipitate as a calcium phosphate which is hard to dissolve (Li et al. 2015). They claim that the AAC reducing mechanisms of P include both physical adsorption and crystalline precipitation of HAP. Dissolved calcium, which is one of the components of AAC, combines with P-PO₄ and OH⁻ to form HAP. Also, Kang et al. (2017) observed a final increase of pH to 9–10, resulting in a sharp increase in phosphate adsorption by formation of calcium phosphate precipitates.

In the case of SRFs, total P-PO₄ loads removed have a good correlation (R² = 91%) with the applied mass of AAC. The highest cumulative load was noted in the case of 100 g AAC and it equals 29.95 mg P-PO₄. 50 g and 10 g of AAC removed 29.10 mg P-PO₄ and 25.26 mg P-PO₄, respectively. However, converting the full loads into unit sorption gives opposite results. The highest unit sorption of P-PO₄ was retained in the case of 10 g of AAC (2.53 mgP·g⁻¹). The unit sorption of 50 g and 10 g equals 0.58 mgP·g⁻¹ and 0.30 mgP·g⁻¹, respectively.

Figure 2 | P-PO₄ concentrations with P-PO₄ reduction and pH variation in different w/v variants of synthetic P solution experiment: (a) 10 g of AAC; (b) 50 g of AAC; (c) 100 g of AAC.
The unit sorption at a 1 g:1 L ratio is about four times higher than 5 g:1 L, and eight times higher than 10 g:1 L. Such an observation indicates oversizing of the mass of RM used in the experiment.

P removal by RMs in natural water can differ significantly from laboratory tests. Among the factors are hydrological conditions (stagnant or slight water flow conditions, retention time) temperature, grain size of RM, microbiological transformations, water characteristics e.g. pH, salinity or redox potential influence on RM P capacity. The specific sorption of some inorganic anions (silicate), heavy metals (Ba, Cr, Cu, Ni, Zn) and organic compounds (humic acids) can lead to lower sorption and even desorption of P (Cucarella & Renman 2009). Kang et al. (2017) tested the influence of raw and thermally treated AAC on the P sorption properties of anions such as nitrate, sulfate and bicarbonate. They observed that P sorption decreased with the increase in the concentration of all anions (from 1 to 10 mM). The competing anions’ effect on P sorption is as follows: HCO$_3^-$ > SO$_4^{2-}$ > NO$_3^-$. In contrast, Buránek et al. (2015) tested the influence of Vltava river water on P removal by typical batch test experiments. The removal efficiency of AAC with an artificial P solution ranged from 63.92% to 89.50%. The removal efficiency achieved by the same fraction (0.125-0.250 mm) of AAC with river water was characterized by a lower removal rate than the model water of only around 2-3%.

**P-removal prediction by CW with AAC implementation – case study**

The Cetynia River is a small, low land river located in the western part of Mazowieckie voivodeship, Poland. The river is highly polluted both by wastewater effluent from municipal treatment plants and agricultural runoff. The P-PO$_4$ concentration determined from August 2013 to August 2015 ranged from 0.005 to 3.485 with an average of 0.730 mgP·PO$_4$·L$^{-1}$ (Mosiej & Bus 2015). To reduce the P concentration, the CW removal efficiency prediction was calculated (Lu et al. 2009). The average concentration is 0.730 mgP·PO$_4$·L$^{-1}$ and the water flow at the proposed wetland location is 398 m$^3$·d$^{-1}$. The analyzed catchment area for the wetland location section covers 5,500 ha.

The most popular and also commonly used model for P removal prediction by CWs is the areal k-C* Kadlec & Knight model (Brix et al. 2000).

Knowing the average water flow ($Q = 398$ m$^3$·d$^{-1}$) and P-PO$_4$ inflow concentration ($C_0 = 0.730$ mg·L$^{-1}$), the wetland area ($A$) allows to reduce P-PO$_4$ concentration to 0.01 mg·L$^{-1}$ ($C_e$) is able to calculate by Obarska-Pempkowiak et al. (2010) model that is based on Kadlec & Knight ones.

The hydraulic load retention is:

$$H_{LR} = \frac{b \cdot Q}{A}$$

where $b$ is a conversion factor (100 cm·m$^{-1}$), $Q$ is the average flow of the river (m$^3$·d$^{-1}$) and $A$ is the assumed wetland area (10,000 m$^2$). Then, we are able to calculate the P-PO$_4$ outflow concentration of system:

$$C_e = (C_0) \cdot \exp \left[ - \left( \frac{K_p}{H_{LR}} \right) \right]$$

where $K_p$ is a constant equal to 2.73 cm·d$^{-1}$. Knowing the HLR (5.98 cm·d$^{-1}$) and $C_e$ (0.568 mg·L$^{-1}$) values, the essential object surface area to reduce P concentration to 0.01 mg·L$^{-1}$ is calculated as follows:

$$A_s = \frac{b \cdot Q \cdot \ln(C_0/C_e)}{K_p}$$

Based on that calculation, the required wetland area which is predicted to remove the P-PO$_4$ concentration to 0.01 mg·L$^{-1}$ is 6.25 ha, and it corresponds to 0.11% of the catchment. The ratio between wetland and catchment area ($A_w:A_c$) is 0.11.

Previous studies have not identified the clear rule of an optimum $A_w:A_c$ ratio, and the selection ratio area depends on the effect that we want to achieve: clean water in the outlet (as mg·L$^{-1}$) or a high area specific retention (as kgP·ha$^{-1}$·yr$^{-1}$). Too high $A_w:A_c$ ratio (around 2%) is able...
to give satisfactory P retention results, but at the expense of excluding the land from agricultural usage. Wetlands of smaller ratios (0.05–0.38%) have a high load and higher area specific P retention than larger ones (Johannesson et al. 2015).

Based on Equation (3), changing the \( C_e \) concentration from 0.01 mg·L\(^{-1}\) to 0.730 mg·L\(^{-1}\), the relationship between mass of AAC and wetland area was designated (Figure 4). To determine the required mass of AAC, the sorption obtained in the suspended filter box experiment was used. The observed unit sorption of 1 g:1 L variant gave the most promising result (2.53 mg·g\(^{-1}\)) and from an economical point of view, is the most cost and mass effective. For faster reduction of P, the applied mass of AAC should be greater. The main aim of the presented relation is fixing such a mass of AAC and CW area to decrease the outlet P concentration to 0.01 mg·L\(^{-1}\). For example, to design a 3.0 ha area CW, 5,000 kg of AAC should be applied in the form of suspended filters to achieve a desirable concentration of P additionally. Such a construction solution allows us to select the optimum removal method based on the accessible CW area or mass of material.

The SRF technology was created to reduce the P concentration in the place of its occurrence. A single filtration curtain consists of filtration bags filled with RM and suspended in the water being treated. The number of bags at the single curtain as well as the number of curtains may increase depending on the P concentration. The SRF type of filter can be used both in cases with slight water flow (small streams or ditches) and still water (small water reservoirs). The conditions of stagnation or slight water flow are favorable to increasing the contact time with purified water, which has an effect on P sorption. In the case of SRF application, they can be applied at CWs located directly on the river (in the case of smaller rivers and streams) or as bypass CWs (in the case of bigger rivers to slow down the water flow and extend the retention time). The filter curtains can be located below a jetty or other communication elements (at bigger objects) or hung across the CW in the case of smaller ones.

More studies concerning increasing P removal efficiency by supporting CWs with RMs have been conducted. A vertical flow CW with dolomite chippings as an addition to a reed filter was used to treat domestic wastewater (Žibiene et al. 2015). The filter contains two layers: a bottom layer (0.4 m) made of dolomite (2–5 mm) and an upper layer (0.4 m) made of coarse sand (0.6–2.0 mm). Both layers are separated by a 0.1 m layer of gravel as a reverse filter. The bed filter (160 m\(^2\)) was planted with Phragmites australis. The hydraulic load of the dolomite-reed filter was 0.03 m\(^3\)/m\(^2\)/d. After one year of operation the system has had satisfactory results. Total P removal efficiency ranged from 94.7% to 96.6%. In the case of phosphate, the removal efficiency was 80.0–95.6% (Žibiene et al. 2015).

On the other hand, Heal et al. (2005) reported different results with an ochre filter. A separate tank filled with ochre was installed at the inlet of a horizontal subsurface CW. The filter was filled with 1,200 kg of ochre initially.

**Figure 4** | Relationship between CW area and mass of AAC required to achieve an outlet concentration of 0.01 mg P·L\(^{-1}\).
Then, the mass of the filter was reduced by around 400 kg. The surface area was 175 m² with a gravel substrate planted predominantly with *Phragmites australis*. Based on the presented data, the wetland inlet, outlet and tank outflow total P concentrations showed that the most of the P removal in the system is occurring in the wetland rather than in the ochre filter. In contrast, the laboratory results were much better than the field ones. The retention time in the ochre filter was calculated at 18 minutes and over the same time the laboratory batch experiment had 90% reduction of P.

To treat municipal wastewater and dairy manure, Leader et al. (2005) used two different kinds of material: lime and iron drinking water treatment residuals. The systems were a combination of batch-fed co-treatment reactors (0.23 m²) with either iron or lime in series with vermifilters. Once the laboratory batch experiment had 90% reduction of P. over the same time the laboratory batch experiment had 90% reduction of P. After 52 operational weeks, the P-PO₄ removal from municipal wastewater equalled 95% and 98% for lime or iron co-treatments, respectively. For the dairy wastewater, the P-PO₄ reductions were 16% and 22% by the systems treating diffuse farm runoff: a review. New Zealand Journal of Agricultural Research 53 (1), 71–95.

The P removal in the system is occurring in the wetland and keeping in mind that sorption and precipitation are saturable processes and the sorption properties of the material decrease over time. As a result, the increase in the unit sorption. Faster and more rapid P removal but probably does not increase P removal in CWs. The best sorption was observed for planted soils and dissolved organic carbon concentration.

CONCLUSIONS

Using AAC in the form of SRFs gave good results in P removal efficiency and sorption properties. It confirms the statement that RMs can be used as an additional step for P removal in CWs. The best sorption was observed for 1 g:1 L mass to volume ratio because of the high sorption per unit (2.53 mg·g⁻¹) and economic efficiency. Increasing the weight of RM to the volume of treated water results in faster and more rapid P removal but probably does not influence the increase in the unit sorption.

In the case of Cetyinia River, to increase the P removal efficiency of the surface water treatment process to 0.010 mg·L⁻¹, a 3.0 hectare CW should be supported by 5,000 kg of AAC used as an SRF. However, it should be remembered that for different case study objectives the river flow and inflow concentration are changeable. It should also be considered that ex-situ results may widely vary from in-situ implementation efficiency because of hydraulic conditions, and the presence of other water pollutants occurring in the surface water, and keeping in mind that sorption and precipitation are saturable processes and the sorption properties of the material decrease over time.

REFERENCES


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