Removal of phosphorus using suspended reactive filters (SRFs) – efficiency and potential applications
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ABSTRACT
The removal of phosphorus (P) from agricultural runoff is essential to reduce the threat of eutrophication in bodies of water. In this study, an alternative method of applying P reactive materials (RMs) in the form of suspended reactive filters (SRFs) is presented. The SRF method enables P which has already entered a body of water to be caught. In this study, an autoclaved aerated concrete (AAC) was used as the SRFs. The experiment was carried out in a laboratory in a hydraulic block of 1 m in width and 2 m in length. Three curtains, consisting of eight suspended bags filled with the AAC, were used. The ratio of RM mass to water volume in the hydraulic block was 3:1 (g:dm\(^3\)). The initial concentration of P amounted to 1.335 mg P-PO\(_4\)·dm\(^{-3}\). The results demonstrated the successive reduction of P in the water over the experiment duration and the number of cycles in which water passed through the system of curtains. SRFs filled with AAC decreased the level of P-PO\(_4\) in the solution to 0.190 mg·dm\(^{-3}\). The highest removal efficiency (50% overall P reduction) was observed at the beginning of experiment, when the average unit sorption amounted to 0.192 mgP-PO\(_4\)·g\(^{-1}\).

INTRODUCTION
The transportation of phosphorus (P) in streams draining from agricultural areas is dynamic, with peak concentrations connected to high water flows (Johannesson et al. 2015). In rural areas, P in surface waters mostly comes from runoff, subsurface drainage and diffuse pollution, e.g., septic systems. Dissolved reactive phosphorus (DRP) leaching from subsurface drains in clay soils ranged between 0.40 and 0.97 kg·ha\(^{-1}\)·yr\(^{-1}\) with a mean value of 0.60 kg·ha\(^{-1}\)·yr\(^{-1}\); this represents 27% of total phosphorus leaching (Ulén et al. 2016). In Poland, the total annual phosphate load from loam and clay soils ranged from 0.1 to 2.0 kg·ha\(^{-1}\)·yr\(^{-1}\) (Szejba et al. 2016). DRP can be efficiently removed from water by applying P reactive materials (RMs) in the form of different structures, e.g., ditch filters, confined bed runoff filters, riparian runoff filters, surface inlets, pond filters, subsurface drainage filters or bio-retention cells (e.g., Penn et al. 2016). P removal structures are intended to treat ‘hot spots’ of periodic flow of water containing high dissolved P concentrations before they reach surface waters, rather than treating a constantly flowing water source with relatively lower concentrations of P, such as a stream or canal (Penn et al. 2016). Even if they are efficient, some of the dissolved P will reach surface waters. Drainage ditches in particular inevitably receive the discharge of nutrients, particulate matter and other agrochemicals, and they are the dominant pathways for agricultural pollution to be transported to aquatic ecosystems further downstream (Liu et al. 2015). In this study, we propose the innovative method of ‘harvesting’ P from polluted bodies of water, which can be used alone or together with other P control measures, e.g., surface flow constructed wetlands (CWs).

Among the methods of treating a ditch water with the use of P sorbing materials, Penn et al. (2007) have pointed out spreading or dosing them directly to the water or construction of flow-through structures. RMs that are spread or dosed in ditches are difficult or impossible to collect once they become saturated with phosphorus; this means that P will remain within the ditch system. Flow-through structures allow the removal of RMs when they become saturated.
saturated with P; however, they interfere with the shape of the ditch and may be difficult to implement in some settings (Penn et al. 2007). Suspended reactive filters (SRFs) are a system of curtains consisting of filter bags filled with P RMs and suspended in the water. They can be implemented in ponds as well as in flowing water, e.g., drainage ditches or streams. The concept is to implement SRF curtains in many different locations (systematic approach) along the length of the body of water (Figure 1). The main advantages of the SRF solution are: (1) direct contact of the RM with the polluted water, (2) lack of interference in the structure of a ditch or a pond, (3) no need to change the shape of the bottom and banks, (4) no need to use bypasses to direct flow, (5) easy installation without using heavy equipment, (6) easy replacement of RMs, (7) the possibility of seasonal use in periods where the input of pollutants is higher, (8) adjustable length of string enabling it to be customized to the water’s depth and level and (9) construction using unattractive materials prevents theft. The patent for this technology was granted in Poland in 2013 (P. 403571) (Figure 1). Such SRFs located in small agricultural catchments can be low-cost and effective measures to limit loads of P for the main receivers.

The aim of the study was to assess the efficiency of autoclaved aerated concrete (AAC) when used in SRFs for its potential application in P removal from small bodies of water that receive P from diffuse pollution sources.

**MATERIAL AND METHODS**

AAC is a common lightweight construction material. AAC is manufactured from calcareous materials (cement and lime) and siliceous materials (quartz sand) with a trace of Al as the foaming agent. They are mixed, moulded and autoclaved at 180–200°C under a saturated steam pressure of 1.02–1.59 MPa (Isu et al. 1995). The structure of AAC is highly porous and low in density (Karczmarczyk et al. 2014). The main compounds are SiO2 and CaO (Table 1). In this study, manufactured AAC brick crushed and sieved into pieces measuring between 2 and 6 mm in diameter was used. The main advantage of using this common construction (prefabricated) material is that its properties are unified, and there is no need to test the P sorption potential of each lot as is necessary for RMs of a natural origin (e.g., Shilton et al. 2005). Crushed AAC, acting as a RM, can also originate from the demolition of buildings. The efficiency of recycled AAC in the removal of P has been proved, e.g., by Li et al. (2015).

The experiment was conducted on a hydraulic block (S12-MkII Advanced Hydrology Study System). The system consists of upper tank, lower tank and the pump. The upper tank measures 2 m in length and 1 m in width. The depth of the water in the upper tank was maintained at 14 cm in the inlet and 16 cm at the outlet (Figure 2). Three parallel suspended filter curtains, with eight filters in each row, were filled with 50 g of AAC. In total, 24 filter bags were used with a total weight of 1,200 g of RM. An upper and lower
tank were filled with a solution prepared from KH₂PO₄ and tap water. The initial concentration of P-PO₄ in the solution amounted to 1.335 mg·dm⁻³. This value corresponds to the phosphorus concentration encountered in polluted surface waters in Poland. There were 41 sampling events in the 34 days the experiment lasted. Samples were taken at two control points (inlet; outlet) and between the curtains, and were analysed for phosphates P-PO₄ (FiaStar 5000) and pH (LF-340). The average water flow was 240 dm³·h⁻¹. The installed pump enabled the recirculation of water between the upper and lower tanks. The total volume of water in the system was maintained at 400 dm³, in order to keep the ratio of RM mass to solution volume at 3:1 [g:dm³]. A ratio of between 1:1 and 5:1 is optimal for AAC in the case of low (0.5–1.5 mg·dm⁻³) concentrations of P-PO₄ in the solution (estimated based on unit sorption of P under large scale static batch conditions using the AAC in SRFs) (Bus & Karczmarczyk 2017). The experiment setup, with a thermal image proving even water flow through the curtains of the SRFs, is described in Karczmarczyk et al. (2016).

RESULTS AND DISCUSSION

Phosphate concentration, removal rates and pH

The experiment performed simulates the work of the SRF system located in a small stream carrying DRP (Figure 1).
From the initial concentration of 1.335 mg P-PO₄·dm⁻³ to the remaining 0.190 mg·dm⁻³, the successive reduction of P from the water has been observed. The linear alignment of P concentrations over the experiment duration shows a high correlation (R² 0.865). Within 30 days and 1,295 cycles of the water passing through the curtain system, the SRFs removed 85.8% of the DRP from the water. P sorption can be described in three phases, which are related to the pH changes (Figure 3). At the beginning of the experiment (first phase, Figure 3) the AAC was more ‘active’, which is also reflected by the total unit sorption. However, the considerable variability of P-PO₄ concentrations in this phase suggests that, to be effective in removing P, SRFs must be implemented as a system of many curtains spread along streams draining off agricultural land. AAC’s high sorption efficiency in the first phase was related to an increasing pH (from 7.61 to 8.72). The maximum pH value reached 8.98 (second phase) and then decreased systematically, reaching its initial value by the end of the experiment (third phase). The unit sorption of P within the first week varied significantly, but an average of 0.192 mg P-PO₄ was sorbed by 1 g of RM, giving a 50% reduction in the overall unit sorption of P. The process of P removal also occurred in the second and third phases of the experiment, which was related to the stabilization and lowering of the pH level. In total, 0.382 mg P-PO₄·g⁻¹ was sorbed by SRFs using AAC (Figure 3). Comparing this value with AAC’s apparent P sorption capacity (16.87 mg P-PO₄·g⁻¹) estimated in the 30 minutes of contact time in the batch test (Table 1), the SRFs used only a small part of it. This suggests that SRFs filled with AAC could work for much longer if necessary. In natural conditions, high water flows in agricultural ditches are followed by low flows, resulting in an increased contact time between the water and the SRFs. For longer contact times (24 hours), the sorption capacity of similar sized grains of AAC has been estimated for.
78.80 mg P-PO₄·g⁻¹ (Karczmarczyk et al. 2014). According to Cucarella & Renman (2009), materials with a P sorption capacity of above 10 mg g⁻¹ are classified as ‘very high’ sorption capacity RMs.

In general, the rate at which RMs can remove P increases with pH, amount of calcium, contact time, material to solution ratio and temperature (Shilton et al. 2005; Cucarella & Renman 2009; Li et al. 2013). The rate is also inversely proportional to the particle size of the material (Cucarella & Renman 2009). In the case of the results presented here, only the influence of pH on AAC’s removal of P can be discussed, as the other factors, e.g., grain size (2–6 mm), temperature (24°C), material to solution ratio (3:1 g·dm⁻³) and CaO content (25%) were fixed. In the pH range of 4–10, H₂PO₄ and HPO₄²⁻ are the primary phosphate groups in the solution (Holtan et al. 1988). They can combine with Ca²⁺ to form calcium phosphate compounds such as CaHPO₄. At higher pH levels, P-PO₄ can precipitate as crystallized alkaline hydroxyapatite Ca₅(OH)(PO₄)₃. Hydroxyapatite, once formed, could not be easily released in a short period of time due to its low solubility (Li et al. 2015). In our experiment, the pH of the treated water reached 8.98. A similar pH value was reported by Li et al. (2015). In their study, recycled crushed AAC with a CaO content of 28.59% was used, which is comparable in composition to the AAC used in this study (Table 1). Jia et al. (2013), who used recycled cement with a CaO content of 53.50%, reached pH values of 11.0–12.0 just after adding the RM to the P solution. The high CaO content (63.0%) of the crushed concrete used in a stormwater treatment full scale filter was the reason for which acid dosing was necessary to limit the pH level of the effluent to 8.5 (Sønderup et al. 2015). Calcium hydroxide is released naturally from concrete and induces a pH increase in the water. As calcium phosphate gradually covers the surface of the concrete, the release of Ca is reduced and a gradual decline in the pH level occurs (Sønderup et al. 2015), as was observed in the present study.

Factors promoting and inhibiting the removal of P from surface waters by RMs

In natural water, the prolonged use of filters can cause a biofilm to form on the RM and, once this has happened, it reduces the P sorption capacity (Herrmann et al. 2013). The typical characteristics of RMs, e.g., high porosity, specific surface area, etc. (Ge et al. 2016), promote the development of a biofilm on the grains of RMs. The form and content of organic matter can also inhibit or promote P sorption (Ge et al. 2016). In the pH range of 8–9, humic substances can inhibit the precipitation of Ca-phosphates by a combination of humic substances with Ca and the blocking of active growth sites on newly nucleated Ca-phosphate precipitates by organic matter. Organic matter retained in the filters may also contribute to the formation of the biofilm layer on the filter particles (Herrmann et al. 2013). Moreover, the presence of algae in natural water corresponds with an enhanced efficiency of phosphate removal, as the algal activity can elevate the pH (Shilton et al. 2005). Algae can also remove P from water at rates of between 1.30 (Chlorella vulgaris) and 20.83 (Scenedesmus intermedius) mg P dm⁻³·d⁻¹ (Aslan & Kapdan 2006). The question of how to remove phosphorus from water taken up by micro algae is, however, problematic. Keeping in mind the fact that laboratory scale experiments using an artificial P solution cannot fully reflect natural conditions, SRFs using AAC were recognized as a promising technology which needed full-scale testing.

Application guidelines

This technology should be applied in periods during which P outflows from agricultural non-point sources are short and connected with high water flows. The occurrence of these spates can be predicted based on historic meteorological data and the identification of the catchment. It can be a basis for determining periods during which and locations at which SRFs should be implemented. The answer to the question of the life span, potential for reuse and, eventually, the disposal of the RM used for the SRFs is strictly connected with the type of RM used. For AAC, we observed that after being dried it can be efficiently used again, as its apparent P sorption capacity is high. This observation suggests that the SRF curtain system, when spaced periodically along ditches or streams draining from agricultural areas, can be used for a long time, because the variability of the flow will regulate the periodicity of the SRF activity. In the case of streams that permanently carry water, the use of this measure would be recommended from time to time at ‘hot moments’ connected with high P runoff. The easy installation and removal of SRFs favours such a solution.

Different RMs may be used to fill the SRFs, depending on price and local availability. Well-known RMs, such as different slags, lightweight aggregates, Polonite®, Filtralite-P®, shell sands, crushed concrete, iron reach sands, etc., in grains over 2 mm in size, can be used. They have different P sorption capacities as proven under laboratory conditions;
however, some are not active at low P concentrations, or they can even release amounts of P into the water. For example, Pollytag® is an effective RM for wastewater, but fails in low P concentrations (Karczmarczyk et al. 2014). In previous studies (Karczmarczyk et al. 2016), we tested Polonite® for use in SRFs with water containing different initial P concentrations (1.439–3.012 mg P-PO4·dm−3). In that range, the initial P concentration did not influence the rates of P removal.

Other applications of SRFs

The concentration of phosphates in water is a significant factor for controlling the growth of algae. The nutrient enrichment of aquatic ecosystems can also cause an increase in aquatic plants, the loss of its component species and a decline in ecosystem function (Aslan & Kapdan 2006). From a human perspective, it is desirable to prevent or minimize the eutrophication of receiving waters. However, it is not clear what concentration of phosphorus is acceptable, as P is a dynamic and biologically active element and its behaviour in water will differ in different bodies of water (Correll 1998).

Figure 4  Possible applications of P RMs in SRFs.

In this paper, we discussed use of AAC in SRFs to control P in bodies of water receiving agricultural runoff; however, the universality of the method gives many other options for its application (Figure 4). It can support free water surface CWs treating river water, stormwater or effluent from fishponds or municipal wastewater treatment plants. The use of SRFs can minimize the wetland area necessary to remove an excess of P (Bus & Karczmarczyk 2017). Another option is to use SRFs in backyard ponds or urban stormwater retention ponds to keep the P concentration at levels that limit algae growth. It can also be effective in ponds that retain green roof runoff, which is now a popular solution for retaining rainwater in urban residential areas. SRFs can also be used periodically in swimming ponds (natural swimming pools), when standard purification methods fail to maintain the concentration of P below 0.01 mg·dm−3. In the case of backyard ponds, urban stormwater retention ponds and swimming ponds, the main goal of limiting the concentration of P is aesthetic (i.e., controlling algae growth). Green roof runoff may be contaminated with phosphorus, and therefore it is necessary to treat it as a potential source of water pollution in urbanized areas (Karczmarczyk et al. 2014). On-site wastewater
treatment is also an option for applying SRFs, e.g., by hanging the filters in effluent collection wells. An increased interest in reducing P non-point and diffuse pollution sources will help European rivers to reach a good ecological status (Orderud & Vogt 2015).

CONCLUSIONS

In this study, we proposed the innovative method of ‘harvesting’ of P from polluted bodies of water, which can be used alone or together with other P control measures, e.g. surface flow CWs. The method is named the SRFs, and it is an option for easy application of P RMs in streams receiving diffuse pollution. In this study, AAC as P reactive material was tested in the form of bags suspended in water. The observed behaviour of AAC SRFs suggests that they may be the optimal solution for removing P from ditches and channels that periodically carry water contaminated with P.

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REFERENCES


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