Permeable Reactive Barriers for Preventing Water Bodies from a Phosphorus-Polluted Agricultural Runoff-Column Experiment

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Abstract: This paper aims to examine the potential of permeable reactive barriers (PRBs) as an in-situ removal approach for phosphate polluted agricultural runoff. Four different reactive materials (RMs) of: autoclaved aerated concrete (AAC), Polonite®, zeolite and limestone were tested. The study was conducted as a column experiment with a sandy loam soil type charging underlying RM layers with phosphorus (P) and a soil column without RM as a reference. The experiment was carried out over 90 days. During this time the $P-PO_4$ load from the reference column equaled 6.393 mg and corresponds to 3.87 kg/ha. Tested RMs are characterized by high $P-PO_4$ retention equaling 99, 98, 88 and 65% for Polonite®, AAC, zeolite and limestone, respectively. At common annual P loss rates of 1 kg/ha from intensively used agricultural soils, the PRB volume ranged from 48 to 67 m^3 would reduce the load between 65 and 99% for the RMs tested in this study.

Keywords: agricultural areas; diffuse pollution; phosphorus permeable reactive barrier; reactive material; surface and subsurface runoff

1. Introduction

Phosphorus (P) is regarded as a limiting factor of the eutrophication process that concerns water bodies worldwide. Increasing levels of P the in water from anthropogenic sources has been a huge environmental problem threatening the proper existence of ecosystems [1]. P enters to water from both point and nonpoint sources however, the pollution from point sources is easier to recognize and remove from the environment through the implementation of end of pipe solutions. Much more problematic are nonpoint sources, which come from diffuse and difficult to identify intermittent sources of pollutants such as urban and agricultural runoff [2]. In agricultural areas, P mainly comes from livestock, mineral and natural fertilizers, municipal sludge and wastewaters. The surplus of P results in a decrease in the soil capacity for P sorption and as a consequence, the soil can accelerate the loss of P into the watershed when there is heavy rainfall and runoff [3,4]. The main pathways through which mobilized P can reach bodies of water are surface and subsurface runoff, vertical flow [5] and tile drainage runoff [6] to the surface water interaction zone. Furthermore, the main sources of the anthropogenic loss of P to surface waters originate from agricultural areas [5,7].

Soil types are considered to be a sink for P, however dissolved and sediment-bound P will be lost to runoff [7]. The amount of P loss depends on many factors such as climate, soils, fertilization, landform, plant cover and others [5,7,8]. Szejba et al. [9] noted that the total annual phosphate load ranged from 0.1 to 2.0 $kgP-PO_4$/ha from loam and clay soils that drain flow from agricultural areas. Similar values of annual P load were reported by Pulikowski et al. [10] equalling 0.81 kgP/ha for

arable land located in a mountainous region. A lower value of leaching loss through tile drainage from clay soils (0.60 kgP-PO$_4$/ha/year) was reported Ulén et al. [11]. On the other hand, the annual load from an arable land of brown soils with a particle size of light and medium loam and clays and small amounts of well decomposed peat was found to equal 0.15 kgP/ha in a study by Pulikowski et al. [10]. It was estimated that during the period of 1985 to 2005 Europe discharged 0.2 to 0.3 Tg P/year to its coastal waters [12–17].

A new approach to water remediation in agricultural areas are permeable reactive barriers (PRBs). This technology is defined as an emplacement of reactive media in the subsurface designed to intercept a contaminated plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downstream of the barrier [18]. Permeable reactive barriers (PRBs) are also listed as an active barrier system [19], permeable reactive interceptors [20], a structure lime drainage system [8] or permeable drainage filters [21]. This method has been developed over the past decade and is used to treat groundwater and subsurface runoff from inorganic constituents such as P [22,23], ammonium [23], and heavy metals [24]. The main advantage of PRB is in situ treatment of contaminated groundwater which significantly reduces the treatment costs [25]. The efficiency of P removal mainly depends on the reactive media used to fill the PRB. Initially, P reactive materials (RMs) were successfully used as an additional filter at on-site sewage treatment plants [26,27]. Nowadays, the range of RM applications have been spreading not only to wastewater but also to surface water [28] and green roof leakage treatment [29].

The removal of pollutants at the PRB occurs in two ways, which are by introducing an adsorption medium for the contaminants and by introducing a medium which will alter the contaminants and reduce their bioavailability [18]. Some attempts have previously been made to apply RMs into PRBs as a method to increase P removal efficiency in agricultural areas. Some studies have been based on simple batch tests [22,23,30], laboratory scale experiments [20] and even full-scale working system applications [31–33].

This paper aims to examine the potential of PRBs filled with four different RMs (zeolite, Polonite®, AAC and limestone) as an in situ removal approach for phosphate polluted agricultural runoff. The sorption properties of RMs were tested in a column leaching experiment. Moreover, this study attempted to estimate the volume of PRBs based on the sorption properties of tested materials.

The novelty of this study is in assessing the sorption properties of RMs in a column experiment with strongly polluted soil leaching to imitate polluted subsurface runoff. Most of the studies which have estimated the sorption properties of RMs has been conducted with synthetic P solution. The results obtained in this way can inform whether such a material is even reactive or to what extent in terms of P sorption. Such theoretical values do not give a practical sorption capacity in the case of treated surface water, wastewater or agriculture leachates. On the other hand, the cost of a pilot scale system implemented in field conditions which may not give a satisfactory P sorption results should be considered. This study is an attempt to fill the gap between batch test studies with an artificial P solution and full scale implementations.

2. Materials and Methods

2.1. Soil

The soil used in the experiment was sampled from intensive use agricultural land (52°26′41.1″ N 22°15′49.6″ E) located at the Cetynia River catchment and is classified as a sandy loam (Table 1). The soil sample was taken from the top layer of 0.1 m depth. Organic matter content was determined by the loss of ignition at 550 °C. The hydraulic conductivity of the sample was obtained using the Witt filtration apparatus. Bulk density was determined in accordance with standard PN EN 1097-3:2000 [34]. P that is bound to both crystalline and/or less crystalline Fe, Al or Ca compounds as well as acid-hydrolysable organic P compounds was determined by extraction with 1N HCl [35] Triplicate samples of soil (5g)

were shaken at 135 rpm for 24 h with 10 mL 1N HCl at room temperature to obtain extracts. Extracts were filtered by syringe filter of 0.45 μm pore size, and analyzed with the ammonium-molybdate method in a FIAstar 5000 analyzer in two ranges of 0.005 to 1 mgP-PO_4/L and 0.1 to 5 mgP-PO_4/L depending on the phosphate concentration in the extract. Then, P-PO_4 concentrations in the extracts were converted into the loads to obtain P leaching (in mg) per kg of soil. The specification of soil properties is presented in Table 1.

Table 1. Characteristic of soil used in the experiment.

Granulometric Composition	[%]
Sand	77
Silt	13
Colloidal clay	7
Organic matter [%]	3
Hydraulic conductivity [m/d]	636
Bulk density [g/cm^3]	1.46
HCl extractable phosphorus [mg P/kg dry mass]	236.56

2.2. Reactive Materials

Four different P RMs (zeolite, Polonite®, autoclaved aerated concrete [AAC] and limestone) were used in the column experiment as a PRB.

Polonite® (Ecofiltration) is manufactured opoka rock which is a calcium silicate sedimentary rock, heated at temperature of 900 °C. Autoclaved aerated concrete (AAC) is a lightweight popular material used in civil engineering. Quartz sand, lime or cement and water are used as a binding agent. The structure of AAC is characterized by its high porosity and low density. Limestone is a sedimentary rock, composed mainly of the skeletal fragments of marine organisms. Its major materials are the minerals calcite and aragonite, which are different crystal forms of calcium carbonate [36]. Zeolite is a hydrated aluminosilicate mineral that contains alkali and alkaline-earth metals. The materials are noted for their lability toward ion-exchange and reversible dehydration. Due to their framework structure, they may be used as a RM [36].

The physical properties of RMs were determined in accordance with the following standards: particle size distribution PN EN 933-1:2012 [37] and PN-ISO 11277:2005 [38], bulk density PN EN 1097-3:2000 [34], porosity PN-EN 1936:2010 [39] and water absorption PN EN 1097-6:2013-11 [40]. The mineral composition of tested RMs, physical properties and SEM microphotographs are presented in Tables 2 and 3 and Figure 1, respectively.

Table 2. Main mineral compounds of tested reactive materials [%].

	Zeolite	Polonite®	AAC	Limestone
SiO_2	47.80	55.11	57.24	0.61
CaO	2.84	23.86	24.62	29.30
Al_2O_3	6.07	5.65	1.96	
K_2O	2.19	1.04	0.48	
P_2O_5	0.18			0.31
Fe	1.07			0.14
Fe_2O_3		2.10		0.14
MgO			0.52	6.79
SO_3			1.35	
Ti				0.14
Cl				0.10

Table 3. Physical properties of tested reactive materials.

	Zeolite	**Polonite®**	**AAC**	**Limestone**
Grain size [mm]	1-2	1-2	1-2	1-2
Porosity [%]	50.0	55.0	65.0	40.0
Bulk density [g/cm^3]	0.90	0.75	0.40	1.50
Water adsorption [%]	9.00	5.30	70.00	4.00
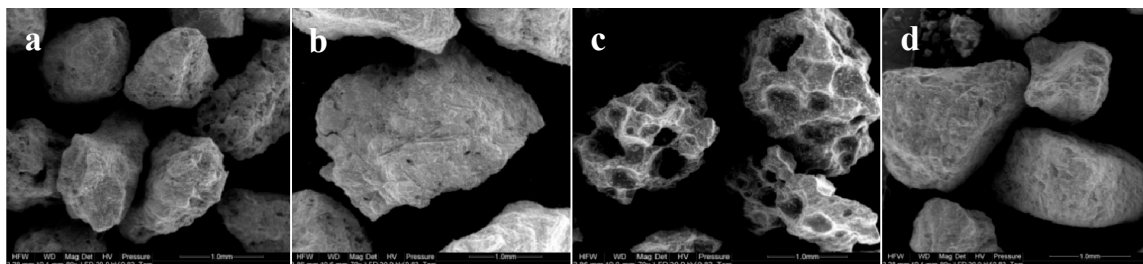
Figure 1. Scanning electron microscope (SEM) micrographs of (**a**) zeolite; (**b**) Polonite®, (**c**) AAC, (**d**) Limestone.

2.3. Leaching Experiment

The leaching experiment was performed to assess the P-removal efficiency of RMs. Five columns with a diameter of 14.5 cm were filled with 10 cm of soil. Four of them were underlined by 2 cm layer of RM as a PRB (Figure 2). The columns were filled by the disturbed top soil layer samples. The ratio between soil and RM layers was 5:1. The soil volume was 1650 cm^3 and the RM 330 cm^3. The RM layer was adjusted to the volume of PRB, not to the same mass of RMs. The experiment was performed at room temperature (≈20 °C).
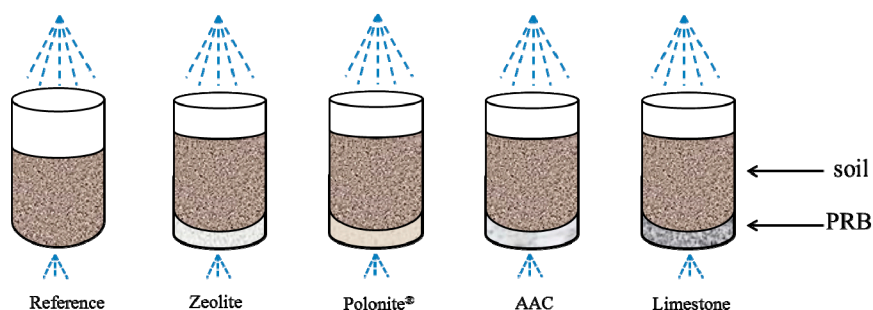
Figure 2. Setup of leaching experiment with examined soil (reference) and four different reactive materials as a phosphorus permeable reactive barriers (PRBs).

Columns were periodically irrigated with tap water to simulate rain events and create the leakage. The effluents from each column were sampled and analysed for electrical conductivity (EC) (Con110, Lovibond), pH (Volcraft PH-212 meter), suspended solids (SS) (DR2400, Hach) and turbidity (TurbiDirect). Also, the effluents after filtration by syringe filter of 0.45 μm pore size were analysed for P-PO$_4$ concentration on FIA Star 5000, FOSS analyser in two ranges 0.005–1 mgP-PO$_4$/L and 0.1–5 mgP-PO$_4$/L depending on phosphate concentration. Phosphate was determined with the ammonium-molybdate method. The experiment was carried out for 90 days. During this time, 37 precipitation events were simulated.

The sorption of each RM at the PRB was calculated by reducing the total P-PO$_4$ load from the reference column by load effluent from each PRB.

Based on the effluent P-PO$_4$ load from the reference column (mg P-PO$_4$) and column area (165 cm^2), the estimated out flowing load was calculated (kgP-PO$_4$/ha). Converting the retained by PRBs loads (mg P-PO$_4$) and barrier volume (330 cm^3), the P-PO$_4$ retention volume of 1 m^3 PRB was calculated

(kg/m^3). Then, the estimation of PRB retention volume (m^3/ha) was calculated by dividing the out flowing load by retention volume.

2.4. Statistical Analysis

The obtained data were evaluated using analysis of variance (ANOVA) with the Statistica 12 software by StatSoft. One-way ANOVA was used to test the differences between the columns, and when the differences were detected, Tukey post hoc tests were performed in order to determine the nature and magnitude of these differences. The significance level was set to 0.05. Also, the means and standard deviations (SD) were calculated using Statistica 12 software.

3. Results

3.1. Leakages Quantity

Over the entire duration of the experiment, 4320 mL of simulated precipitation was delivered. This value corresponds to 262 mm precipitation. The observed water retention equaled 64, 66, 63, 69 and 77% for reference, zeolite, Polonite®, AAC and limestone PRBs, respectively. The performed analysis showed that there is a significant ($p < 0.05$) difference between retention of columns.

3.2. Leakages Quality

In most cases, $P-PO_4$ concentration in tap water used for column irrigation was below the detection limit of 0.005 mg/L, with the exception of two events at 10th (0.02 mg/L) and 70th day (0.09 mg/L) of experiment. In contrast, leakages from the reference column were strongly polluted by phosphate. The average indicated value was 4.561 ± 0.682 mgP-PO$_4$/L. The highest noted values were 3.313 and 6.033 mgP-PO$_4$/L which correspond to the extractable P (Table 1) [29]. The results obtained for PRBs showed that tested RMs are efficient in phosphate reduction. The average phosphate concentration in leakages from Polonite® PRB was 0.044 mgP-PO$_4$/L which corresponds to 99% removal. An approximate three times higher concentration was noted with AAC PRB (0.081 mgP-PO$_4$/L) however, the reduction was at similar level (98%). The others tested RMs removed 86% of phosphate with an average phosphate concentration of 0.658 mg/L (zeolite PRB) and 47% with 2.409 mg/L (limestone PRB). The changes in $P-PO_4$ concentration during the experiment are presented in Figure 3a. The results from the column experiment show that the application of Polonite® and AAC PRBs secured soils from phosphate outflow (Figure 4a). The obtained results of the column experiment $P-PO_4$ concentration sequence were as follows: tap water = Polonite® PRB = AAC PRB < zeolite PRB < limestone PRB < reference column.

Water used for irrigation was characterized by a slightly alkaline and alkaline pH, which ranged from 7.10 to 8.70. Slightly lower values were observed for reference column leakages and ranged from 6.80 to 8.20. Similar ranges of pH were noted of PRB with zeolite (6.90 to 8.50) and limestone (7.30 to 8.60). The leakages from Polonite® PRB were characterized as being the most alkaline (7.10 to 10.80) of all tested RMs. In addition, for AAC the pH was alkaline (7.20 to 9.00) (Figure 3b). There were no significant differences between the pH values observed for tap water and both zeolite and limestone PRBs. On the other hand, the Polonite® and AAC PRBs, resulted in an increase in alkaline leakages (Figure 4b).

In the case of all columns, the electrical conductivity (EC) reached higher values at the beginning of the experiment and decreased over time (Figure 3c). The average values were 1.84, 2.09, 2.35, 3.40, 3.57 and 0.57 mS/cm for the reference column, Polonite®, zeolite, limestone, AAC PRBs and tap water, respectively. The higher values obtained for PRBs relative to the reference column are probably a result of the washing out of some components, for example Mg and Ca (see Table 2) from used RMs. There were no significant EC contamination differences ($p < 0.05$) in the case of leakages from the reference column and zeolite and Polonite® PRBs. Also, the average EC in the leakages of AAC and limestone PRBs were similar to each other (Figure 4c).
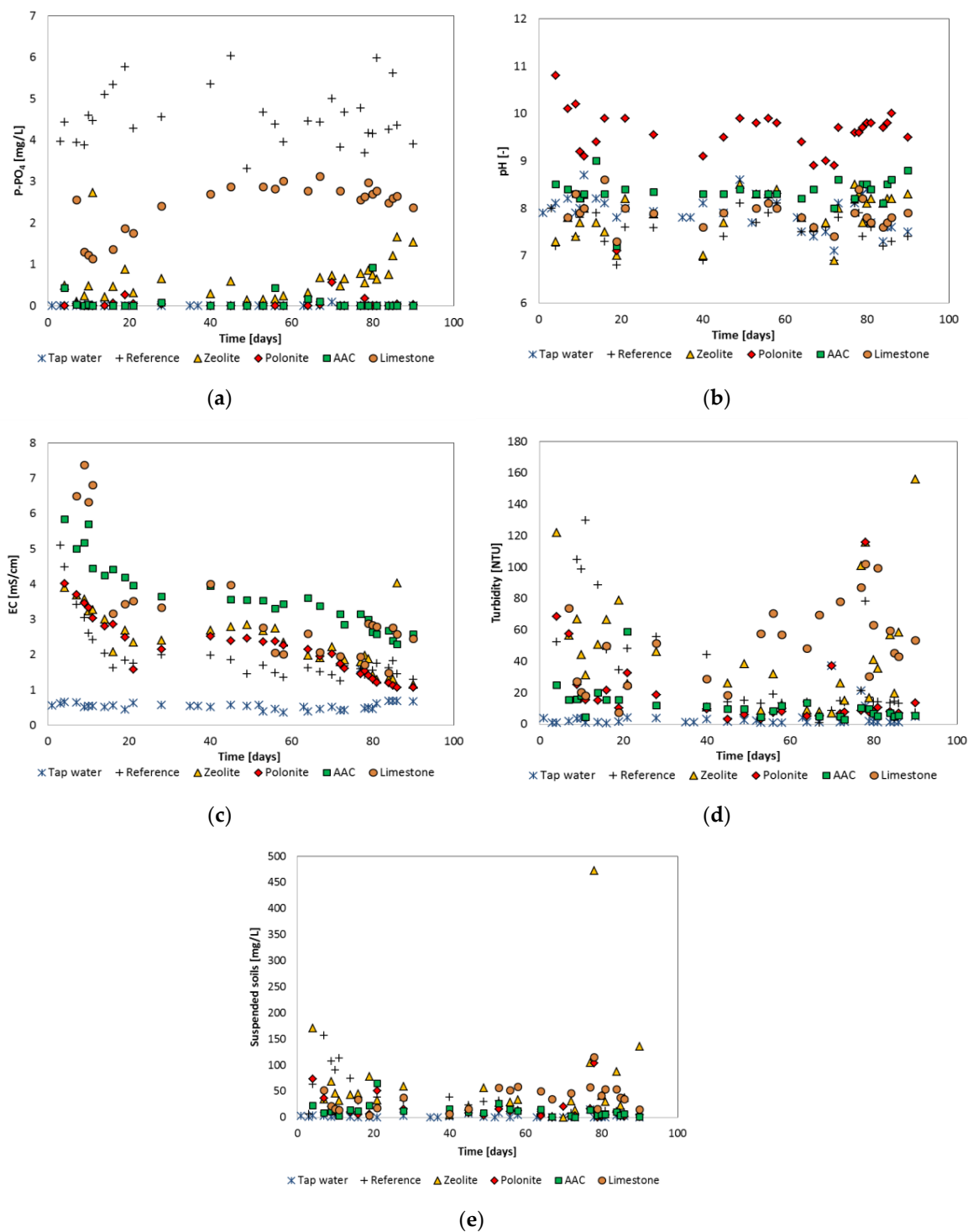
Figure 3. The P-PO$_4$ (**a**); pH (**b**); electrical conductivity (EC) (**c**); turbidity (**d**) and suspended solids (**e**) changes of simulated precipitation (tap water), leakages from the reference and PRBs columns over the duration of the experiment.
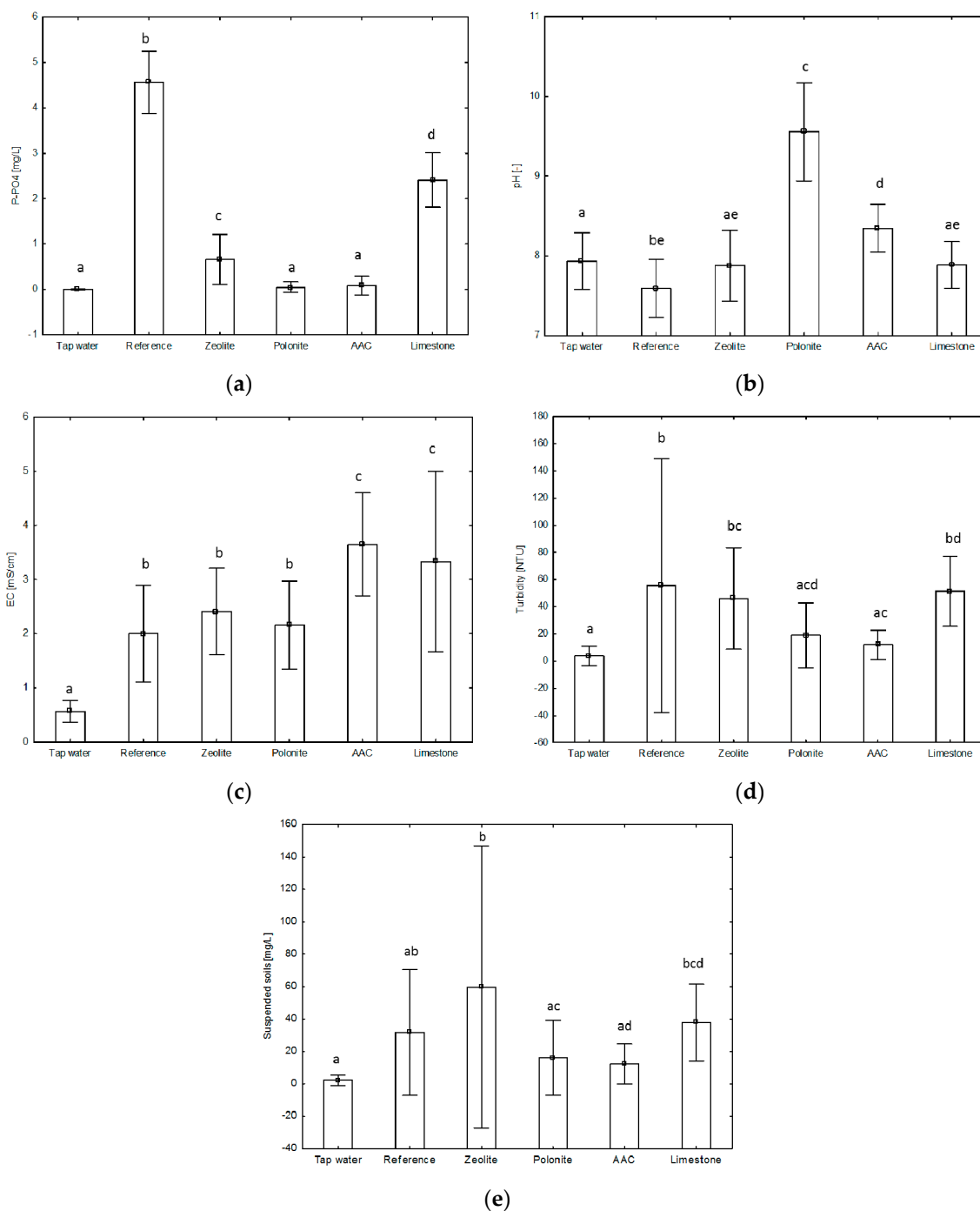
Figure 4. The P-PO$_4$ (**a**); pH (**b**); electrical conductivity (EC) (**c**); turbidity (**d**) and suspended solids (**e**) concentration in simulated precipitation and PRBs leakages. Columns with error bars indicate the average values with standard deviation. Bars marked with different letters differ significantly ($p < 0.05$) according to the Tukey test.

The turbidity of tap water used for irrigation was low (average 3.85 NTU) and stable over the duration of the experiment (Figure 3d). The highest average values were observed in the case of the reference column (soil) (55.63 NTU). The limestone and zeolite PRBs were characterized by slightly lower average values of 51.39 and 46.23 NTU. Further decreases of turbidity were observed for Polonite® (18.92 NTU) and AAC PRBs (12.09 NTU). All applied PRBs influenced turbidity reduction from used soil (reference column > limestone PRB > zeolite PRB > Polonite® PRB > AAC PRB).

In the case of suspended solids (SS), tap water had the lowest average value (2.30 mg/L). The highest average concentration of SS was observed for zeolite PRB (59.79 mg/L). The average limestone PRB SS concentration was lower and equaled 37.88 mg/L. SS concentration from the reference column was 31.80 mg/L. Values lower than that of the reference column were observed for both Polonite[®] (16.10 mg/L) and AAC PRBs (12.22 mg/L).

3.3. P Sorption

By converting the obtained $P-PO_4$ concentrations leakages and volumes into loads, the reference column was determined to be the source of 6.939 mg $P-PO_4$. Comparing different PRBs, the highest loads were retained by Polonite[®] (6.902 mg $P-PO_4$) and AAC (6.786 mg $P-PO_4$) PRBs. Lower retained loads were observed in the case of zeolite (6.081 mg $P-PO_4$) and limestone (4.967 mg $P-PO_4$) PRBs. The retained $P-PO_4$ loads correspond to a reduction of 99, 98, 88 and 65% for Polonite[®], AAC, zeolite and limestone, respectively. Based on the total retained $P-PO_4$ loads, the unit sorption followed the sequence: AAC (0.05 mg/g dry mass) > Polonite[®] (0.03 mg/g dry mass) > zeolite (0.02 mg/g dry mass) > limestone (0.01 mg/g dry mass). The highest unit sorption was observed in the case of AAC PRB (0.05 mg/g dry mass), which could be a result of low bulk density (Table 2).

Based on the effluent $P-PO_4$ load from the reference column and column area, the estimated out flowing load equalled 3.78 kg$P-PO_4$/ha. Converting the loads retained by PRBs and the barrier volume (330 cm^3), the $P-PO_4$ retention volumes of 1 m^3 PRB were calculated and found to be 0.018, 0.021, 0.020 and 0.015 kg $P-PO_4$ by zeolite, Polonite[®], AAC and limestone, respectively.

4. Discussion

4.1. Reactive Materials Sorption Limitations

Generally, the sorption capacity is obtained with synthetic solution contaminated only with phosphate ions which differs from real water, wastewater or soil leakages sorption. Usually such conditions promote better sorption properties [41]. However, there are many more other factors influencing the sorption properties of RMs. Cucarella and Renman [42] considered the most important factors to be the particle size of the RM, hydrological conditions, organic matter, ionic strength and salinity, redox potential, temperature and microbiological transformations. Such relationships have been well observed in synthetic solution and real surface water studies with box experiments using Polonite[®] [41]. Depending on the mass of the RM used in the experiment, the sorption obtained for synthetic solution is approximately 40% higher than for surface water. Also, the experiments conducted under laboratory conditions are characterized by better sorption results than field scale studies. The minimalization of full scale systems often does not bring satisfactory results such as higher sorption [43]. It also must be taken into account that the sorption for the column experiment was obtained over 90 days and the RMs such Polonite[®] and AAC were not saturated.

In addition, it has to be remembered that the sorption results obtained for the same RM during different studies may differ. The maximum sorption capacity (S_{max}) obtained for Polonite[®], AAC and limestone showed similar configurations [41]. The highest value was noted for Polonite[®] (94.32 mg/g) and was more than two times higher than that of AAC (43.17 mg/g) and eight times higher than that of limestone (11.12 mg/g). Likewise, even higher values for Polonite[®] were reported by Cucarella et al. [44] for fine fraction of material (181 mg/g). Published data regarding AAC sorption capacity range from 0.134 mg/g [45] to even 70.9 mg/g [46], both obtained during theoretical batch studies. Lower values of P sorption were noted for limestone. Johansson [47] reported the sorption of limestone ranged from 0.0003 to 0.02 mg/g with the higher sorption observed for a higher initial P concentration. A similar low value of maximum sorption capacity was calculated by Drizo et al. [48] and equalled 0.00068 mg/g. Zeolite also had close sorption properties which ranged from 0.30 mg/g [48] to 0.46 mg/g [49] obtained from the Langmuir isotherm model. In contrast, Ibrahim et al. [20] obtained a higher P maximum sorption capacity for zeolite that equalled 18.3 mg/g.

4.2. Permeable Reactive Barrier Efficiency and Dimensioning

Some of the authors examining PRBs have made mention of the calculation or estimation of barrier efficiency (Table 4). Miller et al. [22] estimated the PRB lifespan for two aluminum residuals from the drinking water purification process Punta Gorda Al-WTR and Manatee Al-WTR. The evaluation were made for saturated flow conditions and two different P-PO$_4$ concentrations of 1 and 10 mg/L. The calculations were based on the theoretical S$_{max}$ value obtained during batch test studies. Results obtained by Miller et al. [22] showed a very long lifespan efficiency for both tested materials.

Table 4. Comparison of PRBs based on literature review.

RM	PRB Dimensions (W × D × L)	C$_{in}$ [mg/L]	Removal [%]	"Lifetime" Efficiency [year]	Calculation Method	Reference
Punta Gorda Al-WTR		P-PO$_4$: 1.0	-	4789	Calculated based on S$_{max}$ according to Darcy flow	[22]
	1 m width	P-PO$_4$: 10.0	-	120		
Manatee Al-WTR		P-PO$_4$: 1.0	-	1367		
		P-PO$_4$: 10.0	-	34		
Limestone	1.5 × 1.5 × 10	P-PO$_4$: 0.02–7.71	58	-	Pilot scale experiment in Zarzącin, Poland	[33]
Fosfilt-s	5 × 1.5 × 15	P-PO$_4$: 0.666	45	-	Pilot scale experiment in River Pyhäjoki catchment, Finland	[32]
		TP: 0.698	37	-		
Lime and sand	0.5 × 1.0 × 30	Before renovation: P-PO$_4$: 2.642	62.6	-	Pilot scale experiments in River Yläneenjoki catchment, Finland	[31]
		TP : 3.055	60.0			
		After renovation: P-PO$_4$: 4.005	61.1	-		
		TP : 3.302	61.3			
Burnt lime and sand	10 × 0.9 × 50	P-PO$_4$: 0.011	52.0	-		
		TP: 0.090	67.0	-		
Burnt lime and spent lime	7.5 × 0.9 × 50	P-PO$_4$: 0.009	46.0	-		
		TP: 0.076	82.0	-		

The lifetime of PRBs depends not only on the sorption properties of RMs but also on such factors as bulk density and the total mass filling the barrier, hydraulic conductivity, chemical characteristics of the RM, rate of reaction within the barrier and the physical properties of RMs such as porosity and permeability [50]. It is well seen in the case of AAC in this study. The material is characterized by the highest sorption properties obtained during the column leaching experiment, whereas the material's P-PO$_4$ reduction is not the highest.

Furthermore, P RMs for PRBs should fulfil some basic criteria and requirements to enable their use in full scale systems; they should be available locally to avoid additional transport costs, characterized by high activity to retain the contaminants, physically and chemically stable to be not harmful and toxic for water environments, have sufficient hydraulic conductivity and should be a renewable and natural material [19,51]. Not all RMs are able to meet all of these criteria, but is important to fulfil as many of them as possible.

It has to be remembered that the sorption values obtained during pilot scale studies often differ from laboratory tests [42]. Izydorczyk et al. [33] and Kirrkala et al. [31,32], obtained similar results for P-PO$_4$ removal during field experiments when the removal efficiency ranged from 45 to 62%. In the case of total phosphorus (TP) the values are much more scattered (37 to 82%), which may be a result of different climate conditions at both locations.

In discussing how deep and wide a PRB should be Izydorczyk et al. [33] recommended the barrier of 1.5 m width and depth. A width of 1 m was proposed by Miller et al. [22]. In contrast, Jacobs and Förstner [19] proposed the installation of a reactive barrier made of zeolite of 0.2 m thickness. Based on the conducted research (the outflowing load and P-PO$_4$ retention volume of RMs) the estimated volumes of PRBs were calculated as 215, 184, 193 and 258 m^3 per 1 ha of catchment for zeolite, Polonite®, AAC and limestone, respectively. The highest value was obtained for limestone, which is used as a filling in pilots scale RPBs applications [31,33]. Recalculating obtained results of PRB volume at common annual P loss rates of 1 kg/ha from intensively used agricultural soils, the PRB volume equalled 56, 48, 50 and 67 m^3 and would reduce the P-PO$_4$ load of 88, 99, 98 and 65% for

zeolite, Polonite®, AAC and limestone, respectively. The estimated values have been obtained only for the considered case of the Cetynia River catchment. For other cases the estimation should be based on individually obtained data.

The estimated load outflowing through the column was estimated to be 3.78 kgP-PO$_4$/ha for the conditions of the experiment. Such a value seems to be high, however the Cetynia River located in this area is strongly polluted by phosphate [52]. The estimated outflow of phosphorus from agricultural areas to surface waters of 1 kgP/ha/year is common, higher outflow values (>2 kgP/ha/year) are observed in the case of exhaustion of the sorption capacity of the soil [53]. The outflow of phosphorus from agriculture to inland waters in many areas of Europe exceeded 0.1 kg/ha annually and in the most exposed areas reached 1.0 kg/ha/year [54]. The average amount of phosphorus washed out from arable land in Poland is estimated to be 0.4 kg/ha/year [55]. At the Vistula River catchment where the testing site is located, the area specific total phosphorus load varied from 0.084 to 1.38 kgTP/ha/year and corresponds to a mean TP water concentration of 0.262 mg/L [56].To protect water bodies, the PRB should be placed in the way of potential subsurface and surface runoff to protect fragile water ecosystems against degradation. For this reason the length of the barrier is different and difficult to unequivocally estimate and should be individually selected. The PRBs should be implemented at the most pollution emitting sub-basins to protect water bodies, such as the water supply reservoir [33]. However, it must be remembered that the catchment should be limited only to sub-basins directly at risk of pollution runoff into the water bodies. The PRB site selection should be preceded by P monitoring, identification of P sources, creation the risk maps and also preparation and prediction the most fragile ecosystems and places that should be protect. Additionally, the efficiency of PRBs may also be increased by the implementation of a buffer zone near the barrier location. Izydorczyk et al. [33] reported that a buffer zone located at Sulejów Reservoir, Poland consisted of *Phalaris arundinacea*, *Phragmites australis*, *Iris pseudacorus*, *Acorus calamus*, *Calla palustris*, *Caltha palustris*, *Mentha aquatic*, *Urtica dioica* and *Salix* sp., increased P-PO$_4$ removal efficiency by 12% and additionally protected the water bodies against diffuse pollutions.

5. Conclusions

Tested RMs were found to have good results with regard to P-PO$_4$ removal efficiency from polluted agricultural runoff. The removed loads of P-PO$_4$ ranged from 65% to as high as 99%. These results confirm the statement that RMs can also be used as a filling in PRBs. The highest removed loads were observed in the case of AAC and Polonite®. Based on the results obtained from the column experiment, the volume of PRBs were calculated and found to equal 184, 193, 215 and 258 m^3/ha of a sub-basin under the strong pressure from agricultural pollution, for Polonite®, AAC, zeolite and limestone, respectively. Recalculating obtained results of PRB volume at common annual P loss rates of 1 kg/ha from intensively used agricultural soils, the PRB volume ranged from 48 to 67 m^3 would reduce the load between 65 and 99% for the RMs tested in this study.

However, it must be remembered that even laboratory experiments based on real soil leakages do not give completely representative results. It should also be considered that ex-situ results widely vary from those obtained from in-situ PRB implementation. Such differences can be caused by climate conditions, discharged P-PO$_4$ load, contact time of RMs with treated liquids and hydraulic conditions.

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