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Design and Development of Low P-Emission Substrate for the Protection of Urban Water Bodies Collecting Green Roof Runoff

Agnieszka Karczmarczyk [1,*], Anna Baryła [1] and Paweł Kożuchowski [2]

[1] Faculty of Civil and Environmental Engineering, Department of Environmental Improvement, Warsaw University of Life Sciences (SGGW), Nowoursynowska 159, 02-776 Warsaw, Poland; anna_baryla@sggw.pl

[2] Paweł Kożuchowski, Green Roofs Laboratory, Ceglana 2B, 05-250 Słupno, Poland; pawel@dachyzielone.pl

* Correspondence: agnieszka_karczmarczyk@sggw.pl; Tel.: +48-22-5935382

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Abstract: Urbanization leads to higher phosphorus (P) concentration in urban catchments. Among different stormwater retention measures, green roofs are the least efficient in phosphorus retention. Moreover, much research has shown that green roofs act as sources of phosphorus, and they can emit P in significant loads. In this study low P emission green roof substrate was developed based on the proposed step by step procedure for the selection of materials including laboratory tests, column experiments, and the monitoring of the open air green roof model. Developed substrate is the mixture of crushed red brick (35% of volume), crushed limestone (20% of volume), and sand (45% of volume), and is characterized by a bulk density of 1.52 g/cm^3, water permeability of 9 mm/min, water capacity of 24.6% of volume, and granulometric composition that meets the Landscaping and Landscape Development Research Society (FLL) guidelines. Limestone was added to limit the potential P leaching from crushed red brick and vegetated mate consisted of *Sedum album*, *Sedum acre*, *Sedum kamtschaticum*, *Sedum spurium*, *Sedum reflexum*, *Sedum sexangulare*, *Dianthus deltoides*, *Dianthus carthusianorum*, and *Thymus vulgaris*. The open air model experiment was run for 319 days, from March 2015 to February 2016. The total water runoff from the green roof model amounted to 43.3% of runoff from the reference roof. The only one runoff event polluted with phosphorus was connected with the outflow of melted snow from an unfreezing green roof model.

Keywords: extensive green roof; phosphorus; substrate composition; runoff quality

1. Introduction

Urban waters are known to be phosphorus (P) rich environments [1]. In urban areas, sources of phosphorus (P) in stormwater runoff originate from lawn fertilizers, atmospheric deposition, soil erosion, animal wastes, grass litter, soil microbial communities, vegetative detritus, and detergents [1–3]. Urbanization generally leads to higher phosphorus concentration in urban catchments, what is seen in both total phosphorus and dissolved phosphorus concentrations [2,4,5].

Among different stormwater measures e.g., retention soil filters, sedimentation basins, trench infiltration, or swale infiltration; green roofs are the least efficient in phosphorus retention [6]. Moreover, much research has shown that green roofs act as sources of phosphorus, and they can emit P in significant loads. In different studies, observed phosphates concentration in leachate amounted: 0.27–0.40 mg/L for Rooflite® drain extensive growth media [7], 2.7 mg/L for extensive mix with 20% of compost and woodchips [8], 1.8 mg/L for GaiaSoil [8], 19.8 mg/Lfor Pro-Gro extensive mix, and 11.2 mg/L for Pro-Gro extensive mix amended with biochar [9], 1.0–3.4 mg/L for Tremco's aggregate-base extensive substrate [10], 0.4–1.9 mg/L for commercial soil substrate type STT [11], 0.003–0.079 mg/L for GreenGrid® substrate with lightweight expanded shale, composted biosolids and perlite [12], 5.64 mg/L for 6 cm substrate made of pouzzolane, bark and peat [13], 0.23 and 0.18 mg/L for LWA-based green roofs, and sod roofs, respectively [14], 0.16–0.36 mg/L for substrate made of volcanic rock, compost, blonde peat, cooked clay, and washed sand [15], 2.35–3.58 mg/L for extensive green roof models [16], 19.8–40.0 mg/L for substrate made of white peat, black peat, and clay, and 20 mg/L for substrate from volcanic material and compost mixed with mineral and organic fertilizers [17].

Factors affecting green roofs runoff quality are: substrate composition; volume, dynamic and pH of precipitation; season; type of growth media; plant species; and, management of fertilization and irrigation [10,18–20]. Green roofs usually work as a part of stormwater management in urban areas, with the main function focused on rainwater retention. Modelling studies have shown green roofs water retention in the range from 22.9 to 77.8 mm, and the retention rates ranged from 67 to 98% of precipitation [21].

Although with reduced volume, green roof runoff is discharged to receivers. As P is typically the limiting nutrient in freshwater ecosystems and its enrichment can lead to eutrophication, P contaminated runoff from green roofs may pose a threat to aquatic ecosystems [4,22]. In areas where nutrient loads are particularly problematic, an alternative medias without leachable nutrients but with sufficient water holding capacity may be able to provide much of the same engineering benefits without the risk of low quality runoff [19].

Some countries in Europe, Asia, and North America have regulations and guidelines that apply to green roofs. The list of green roof guidelines, manuals, codes, and standards in Australia, Canada, Germany, Hong Kong, Japan, Singapore, United Arab Emirates, and United Kingdom have been presented in [23]. The supplement to this list including China and USA can be found in [24]. Other countries with green roof regulations are Costa Rica, Egypt, France, Greece, Iceland, Switzerland, and Sweden. In Poland, the green roof manual DAFA [25] is patterned on German standard released by the Landscaping and Landscape Development Research Society e.V. [26]. The guideline contains the types of greening and forms of vegetation, functions, and effects of green roofs, requirements related to construction and materials and procedures for maintenance and servicing. The guideline [26] also gives requirements for green roof substrates. Among them, the most important are: granulometric distribution, frost resistance, structural and bedding stability of aggregate materials, behavior of substrate under compression, water permeability, water storage ability, air content, pH value, organic content, salt content, and nutrient content. Guidelines mentioned above does not give any list of materials to be used in substrate composition, apart from some comments on pH range, which can be exceeded by addition of e.g. dolomite or travertine gravel.

The literature review shows, that from the total of 54 analyzed substrates, the most popular mineral components are: clay [9,11,17,27–30], sand [9,15,17,27,28,31–34], volcanic materials [11,28,35,36], crushed brick [17,29,30,37–40], and expanded lightweight materials [15,29,32,41,42]. The most popular organic components are compost [13,36] and peat [11,13,15,17,28,32,43,44].

The ultimate goal of manufacturing substrate is to maintain a proper balance between weight, water retention, nutrients for plants, thickness, and durability [45]. Composition of different manufactured substrates is usually determined by local availability, cost, and weight of materials, not by materials contamination. The quality of green roof runoff, however, strongly depends on the materials used in the substrate mix [17]. Substrate compounds and amendments have been implicated as one of the most important determinants of P in green roof runoff [10]. If P levels exceed the binding and uptake capacities of the substrate and biota, then P will be leached from the system [10]. P contamination of green roof runoff is the result of substrate organic content, carbon content, and microorganisms activity [18]. However, what is often forgotten is that the mineral particles used in substrate composition can also be a significant source of P in runoff.

Due to the overloading of public storm water sewage networks in cities, newly constructed residential areas have to manage collected rainwater on site. Systems consisted of green roofs, retention ponds, and infiltration systems are the most popular solution. To keep the water in urban ponds in high quality and aesthetic value, P in green roof runoff has to be limited.

The aim of the study was to develop and test low P emission substrate to be implemented in green roofs connected via discharge with sensitive water bodies e.g., residential or urban water reservoirs.

2. Materials and Methods

This study selected popular materials, often found in commercial green roof substrates, which were firstly tested in the laboratory batch test for P releasing as a base for primary selection. Secondly, the substrate mix was prepared. Thirdly, the physical parameters of developed substrate were tested according to FLL [26] and P releasing from substrate mix was assessed in the batch test. Fourthly, short-term small column experiment was performed for an assessment of P leaching under artificial irrigation. As the last step, 1 m width and 2 m long open air green roof model filled with developed substrate covered with vegetation mate was constructed to monitor P release from green roof in natural conditions. The adopted "step by step" procedure for development of low P emission green roof substrate is presented in Figure 1. The time scale of these tests varies. The most time consuming in this study was Step 5. The testing time of the open air green roof and reference models covered 319 days. The preceding column experiment was run for 20 days only, as no $P\text{-}PO_4$ was detected in subsequent leachate events. Steps 2–3 can also consume significant amount of time. The total time to complete the procedure can be estimated at about 1 year.

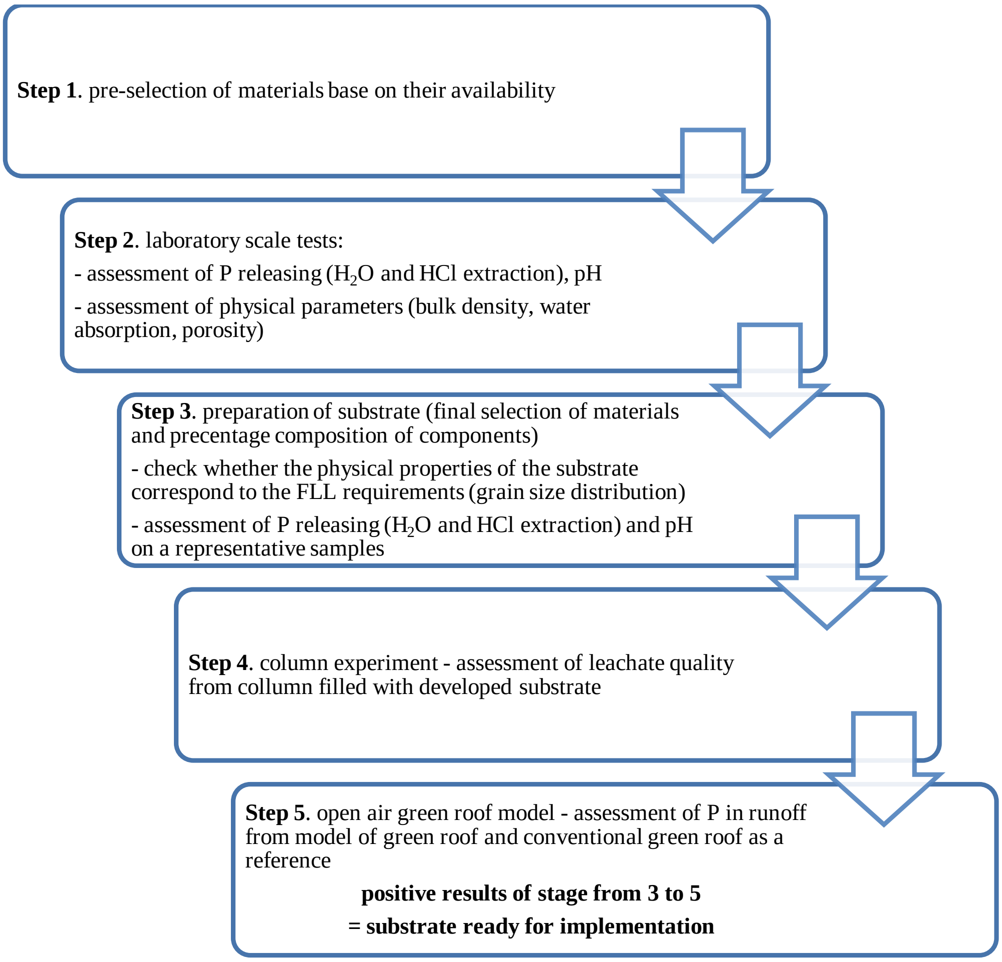

Figure 1. Step by step selection of materials for being use as components in green roof substrate preparation and testing of substrate mix. The procedure was proposed by authors and used in presented study.

2.1. Materials

For the preliminary tests, seven materials were selected: crushed red brick, gravel, sand, crushed limestone, crushed volcanic rock, expanded clay, and lightweight aggregate (pollytag). Materials were classified based on origin, availability, price, and weight, as those characteristics are important in the commercial production of green roof substrates (Table 1). Crushed brick, gravel, sand, and limestone, as well as expanded clay aggregates are common materials. Crushed red brick is debris from demolition. Its use as the recycled material is beneficial, both due to the non-deposition (dumping it as a waste) and conservation of natural stone aggregates [46]. Expanded clay aggregates in some countries are used as P reactive materials [47], but it cannot be treated as a rule, because their properties depend on the origin material. Volcanic rock is also available on market, however due to the high cost of purchase in this study we decided to reuse material from nine years old green roof that was demolished due to leakage. Pollytag is a manufactured product in the form of rounded pellets made from fly ash from thermal-electric power station [48]. Aggregates made from wastes, similarly to clay aggregates, are resistant to extreme temperatures and insulate heat, quickly absorb water, and are resistant to fungi and bacteria.

Table 1. Origin, availability, approximate weight of 10 cm thickness on 1 m^2, cost of purchase and main advantage of preliminary selected materials.

Material	Origin	Availability	Weight [kg/m^2]	Cost [Euro/Mg] * [Euro/m^3] **	Main Advantage
crushed red brick	recycled waste	common	92	5.4–5.8 *	price/availability
gravel	natural	common	150	8.4–19.1 *	price/availability
sand	natural	common	150	4.0–8.4 *	price/availability
crushed limestone	natural	common	115	9.8–25.6 *	P-sorption capacity/availability
volcanic rock	natural/recycled waste	limited	75	232.6–418.6 **	free in this study
expanded clay	product	common	60	48.8–81.4 *	weight/availability
pollytag	product/recycled waste	common	670	46.5 *	weight/availability

Note: * cost in Euro per Mg; ** cost in Euro per m^3.

2.2. Laboratory Tests of Selected Materials

2.2.1. Physical Properties

The physical properties of selected materials were determined in accordance with the following standards: particle size distribution PN EN 933-1:2012 [49] and PN-ISO 11277:2005 [50], water capacity [25], bulk density PN EN 1097-3:2000 [51], bulk density at max water holding capacity (WHC), and porosity PN-EN 1936:2010 [52]. For pH, PN-ISO 10390:1997 standard [53] was used, which specifies an instrumental method for the routine determination of pH using a glass electrode in a 1:5 (*v/v*) suspension of soil in water. The pH was measured by Volcraft PH-212 meter.

2.2.2. Potential P Leaching

For the estimation of potential P leaching from selected mineral materials, the procedure developed by [54] was adopted. Triplicate samples of materials of different weights depending on the material grain size were shaken for 16 h with distilled water or 1n HCl to obtain extracts for the assessment of the P content. Extracts (triplicate from both extractions) were decanted for 15 min, filtered, and analyzed on FIAstar 5000 analyzer in two ranges 0.005–1 mgP-PO_4/L and 0.1–5 mgP-PO_4/L depend on phosphate concentration in extract. Then, P-PO_4 concentrations in extracts were converted into the loads to obtain P leaching (in mg) per kg of tested material. The estimation of potential P leaching from mixed substrates was performed with the same procedure on triplicate samples. To be representative the mass of sample amounted from 100 to 200 g in different tests.

2.2.3. P Sorption Capacity of the Limestone

For the estimation of P sorption capacity of the limestone, the artificial P solution prepared from KH_2PO_4 was used in concentrations varying from 1 to 1200 mgP-PO_4/L. The triplicate samples of material were shaken in Erlenmeyer glass flasks, each contained 5 g of reactive material and 100 mL of the various phosphorus solution for 30 min, 60 min (initial P-PO_4 concentrations between 1 and 100 mg/L) and 24 h (full concentrations range). Samples were decanted for 15 min, filtered, and analyzed by ammonium molybdate method on FIAstar 5000 analyzer in the range of 0.1–5 mgP-PO_4/L. The P-PO_4 sorption was calculated based on the difference of load of P added and obtained in a filtered sample. Data obtained for the contact time of 24 h were fitted to Langmuir isotherm [55] in Statgraphics Centurion XVI v.16.0.007 for the estimation of apparent P sorption capacity.

2.3. Column Experiment

The short column experiment was performed for the preliminary assessment of P occurrence in the leachate from developed substrate. Three columns with the diameter of 11 cm were filled with the substrate of 1.1 kg d.m. each. The initial moisture of the substrate amounted 17%. Columns were irrigated with constant amount of 0.2 L (21 mm) of tap water eight times within 20 days of observation. The days of irrigation were selected randomly. All of the samples of a tap water were analyzed for P-PO_4, as in some supply networks phosphorus is added as corrosion inhibitor and its concentration is not limited in drinking water [56,57]. Measurement of leachate volume and sampling were made manually. The P-PO_4 concentrations in tap water and leachate samples were analyzed by ammonium molybdate method on FIAstar 5000 analyzer in the range of 0.005–1 mgP-PO_4/L. Electric conductivity (EC) was controlled by SENSoDirect Con110. pH was measured by Volcraft PH-212 meter (range 0–14). In the column experiment, P-PO_4 leaching from bare substrate was tested, without using vegetation mate and plants.

2.4. Open Air Model Experiment

The green roof model (2 m $\times$ 1 m) with a prepared substrate has been constructed to estimate P runoff in natural conditions. The model consists of seven layers, from the bottom to the top (Figure 2): wooden base, roots resistant hydroisolation, protection membrane (DuPont Typar SF 32, GRK 2, 110 g/m^2), drainage mate (Terrafond Garden 20, 2 cm), filtration layer (Polyfelt TS 20, GRK 2, 125 g/m^2), 15 cm of mineral substrate, and a prefabricated vegetation layer grown in 2.5 cm of soil substrate (moss-sedum-herbs XF317). According to the manufacturer, the seed mixture of vegetated mat consists of: *Sedum album, Sedum acre*, *Sedum kamtschaticum*, *Sedum spurium*, *Sedum reflexum*, *Sedum sexangulare*, *Dianthus deltoides*, *Dianthus carthusianorum*, and *Thymus vulgaris* (Xero Flor 2016 personal communication [58]).

As a reference, the conventional roof model consists of wooden base and hydroisolation with the same dimensions has been constructed. Both of the models are equipped with a runoff collection system. The measurement of runoff volume and sampling were made manually from March 2015 to February 2016 to monitor P-PO_4 concentration, pH, and EC in rainfall and runoff from green roof and reference model. The methods of the analyses were the same like in the column experiment. Data of precipitation were obtained from the Institute of Meteorology and Water Management-National Research Institute (IMGW-PIB) for nearby meteorological station.

Figure 2. The view of the open air experiment: green roof model, reference model, construction layers of green roof model, and photo of vegetation mate and substrate.

3. Results

3.1. Laboratory Tests of Selected Materials

3.1.1. Physical Properties

Roof substrates should, on the one hand, have the maximum capacity for retaining rainwater in the vegetation layer and, on the other hand, ensuring the drainage of its excess to the drainage layer. That is why one of common components of the roof substrates is crushed red brick. The high porosity of 60% and the shape of the material play an important role in increasing the water permeability of the substrate. The physical properties of all of the tested materials are suitable to consider them as components for substrate preparation (Table 2).

Table 2. Physical properties of tested mineral materials.

Material	Grain Size [mm]	Porosity [%]	Bulk Density [g/cm^3]	Bulk Density at max WHC [g/cm^3]
crushed red brick	1–10	60	0.95	1.30
gravel	4–25	39	1.50	1.57
sand	0.02–2	32	1.50	1.71
crushed limestone	5–10	55	1.20	1.27
volcanic rock	4–16	53	0.75	9.25
expanded clay	6–18	50	0.67	0.69
pollytag	6–14	54	0.77	0.81

3.1.2. Potential P Leaching

Only in the case of one of tested material—crushed limestone—P was not detected in water and hydrochloric acid extracts. The pH of material is high, what is typical for materials containing Ca, but it also creates a potential for being reactive for P leaching from other substrate components [59–61]. Gravel, sand, volcanic rock, and expanded clay were not the source of easily dissolved P, however they contain P than can contaminate the runoff in specific conditions (Table 3). It is always recommended to test P leaching from sand, especially if it is excavated from the rivers. From our previous experience (data not published) river sand can be extremely rich in phosphorus due to water pollution. Crushed volcanic rock has appropriate properties for being a component of green roof substrate due to bulk density, low P content, and pH. However, the price of the material is too high to be competitive on the local market. Pollytag contains the highest amount of P (130 mg/kg), twice higher than red brick (65 mg/kg) tested in the study. That is the reason, why pollytag, even if it has positive desired properties e.g., low bulk density and high water adsorption (Table 2), was not considered as a green roof substrate component. Expanded clay aggregates and gravel are comparable materials in case of P content. Expanded clay has half of the gravel bulk density, but a much higher price. The price will play a key role in the desire to use low-P-emission substrates, until there will be suitable legal regulations limiting runoff of phosphorus into water from green roofs.

Table 3. Phosphate concentrations in water and hydrochloric acid extracts and pH measured in water extract (mean ± SD—standard deviation; n.d.—not detected).

Material	$P\text{-}PO_4$ in H_2O Extract [mg/kg]	$P\text{-}PO_4$ in HCl Extract [mg/kg]	pH
crushed red brick	8.8 ± 0.5	65.0 ± 1.0	9.27
gravel	n.d.	45.2 ± 11.3	7.44
sand	n.d.	18.8 ± 6.0	7.84
crushed limestone	n.d.	n.d.	9.68
volcanic rock	n.d.	5.3 ± 2.8	6.08
expanded clay	n.d.	38.4 ± 1.8	8.10
pollytag	2.9 ± 0.5	130.0 ± 1.2	8.59

Apart from the mineral materials, prefabricated vegetation layer moss-sedum-herbs (2.5 cm of soil substrate) can be a potential source of P in runoff from the green roof model tested in open air conditions. Soil substrate from the vegetated mate was extracted according to the procedure described in Section 2.2.2. In water extract, the mean value of $P\text{-}PO_4$ amounted 2.9 mg/kg and in 1n HCl extracts 27.7 mg/kg, which confirms that the prefabricated vegetation layer can be a significant source of phosphorus. P releasing from prefabricated vegetation layer can be extended in time due to mineralization of organic material.

3.1.3. P Sorption Capacity of the Limestone

Crushed limestone used in this study was the only one material with no P content (Table 3), and as a Ca reach material, is potentially active for P sorption. The assumption has been confirmed in a batch sorption test experiment. Limestone was P reactive in long and short contact times (Figure 3). The time of water retention in green roof structure depends on rain characteristics and climatic conditions. High P removal activity in short contact times makes the material useful for application in green roof substrate composition. The sorption capacity obtained for 24 h contact time was estimated on 4.66 mgP-PO_4 per 1 gram of the tested limestone. When comparing this value with the classification of the filter materials given by [62], it can be classified as material with a high P sorption capacity.

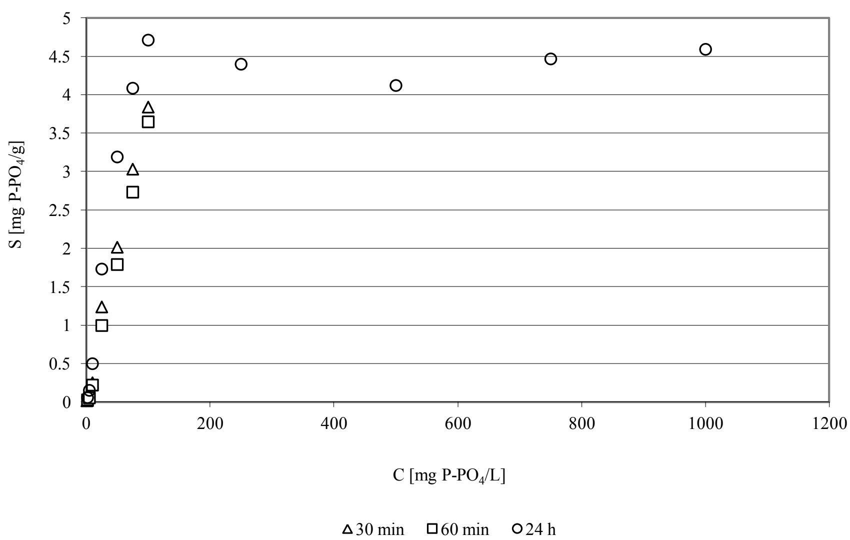

Figure 3. Sorption of Phosphorus (P) by the limestone in different contact times.

3.2. Preparation of the Substrate Mix

In the decision-making process of materials selection for the preparation of the substrate, a number of factors were taken into account. The most important, from the point of view of this study, was the amount of phosphorus in the leachate. The others were: the cost, the availability (including time and ease of delivery), and the physical properties (Table 2) of individual components. An important element of the evaluation in favor of the material was the origin from the recycling. Since in the future the substrate will be produced on an industrial scale, quite different from the laboratory conditions (e.g., mixing of materials at the construction site), it should consist of a limited number of components. From preliminarily tested seven materials, pollytag and volcanic rock were rejected for the reasons discussed above (see Section 3.1.2). Expanded clay was the second most expensive material, and despite the proper physical parameters, and the less gravel content of phosphorus was also rejected. Finally, three materials were selected: two low cost materials (sand and crushed red brick, Table 1) and the crushed limestone, which in price is comparable to gravel, but due to its high P sorption capacity can buffer the negative effect of the crushed red brick if used in the appropriate amount. In favor of the brick also speaks that most typical configuration for extensive green roofs, i.e., *Sedum* vegetation of a brick base substrate, offer the best all-round performance in terms of both retention and detention [29]. The high porosity of 60% (Table 2) and the shape of the material play an important role in increasing the water permeability of the substrate. This material perfectly loosens the substrate, increasing its water capacity. Both crushed brick and limestone are characterized by the preservation of shape, decomposition, and erosion caused by wind and water. Crushed red brick is a waste material that was considered as an additional benefit. Three selected materials were mixed in a laboratory scale in different volume rates. Each variant of the mixed substrate was extracted with H_2O and HCl and analysed for P content. Finally, developed substrate is the mixture of crushed red brick (35% of volume), crushed limestone (20% of volume), and sand (45% of volume). There was no P-PO_4 detected in both water and chloric acid extracts. The substrate is characterized by bulk density of 1.52 g/cm^3, bulk density at maximum water holding capacity 1.90 g/cm^3, water permeability 9 mm/min, and water capacity of 24.6% of volume. Grain size distribution of developed substrate fits to FLL [26] requirements (Figure 4). Those parameters make mixed substrate suitable for further test.

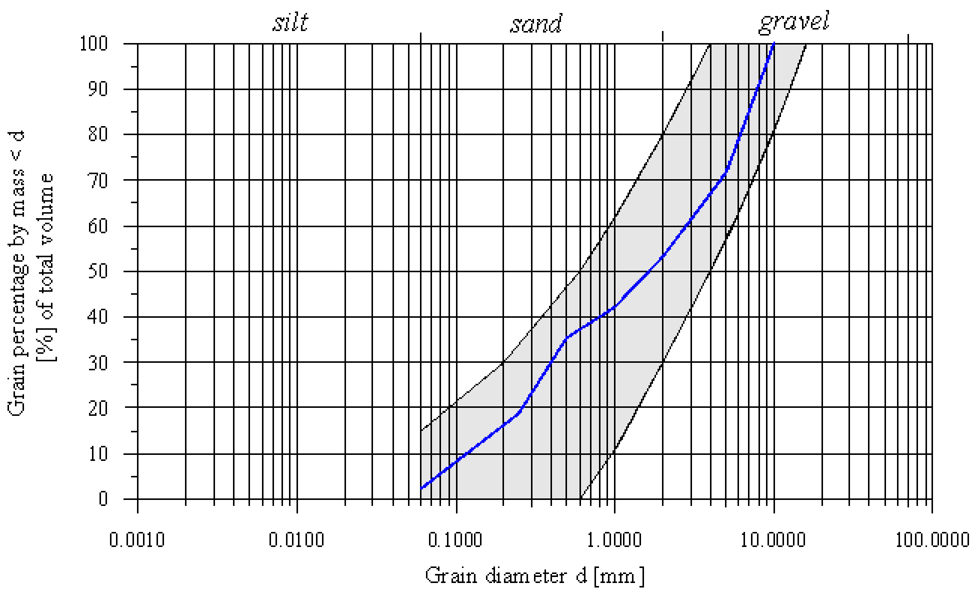

Figure 4. Grain size distribution of developed substrate on the background of limits for extensive substrate [26].

3.3. Column Experiment

A column experiment was conducted indoors in February 2015. Low temperature, low insulation, and low evaporation resulted in a water retention of only 25%. Moreover, potting substrate with fixed volumes of water does not reflect natural conditions, thus the estimation of water retention was not the aim of this experiment. Of the main importance was to monitor the quality of the leaching water base on P-PO_4 concentration, pH, and electric conductivity (EC). For the simulation of precipitation, tap water was used with a concentration of P-PO_4 = 0 mg/L, pH = 7.8 and EC = 48 mS/m.

The pH of collected leachate ranged between 7.6–7.9, with the higher values at the beginning of experiment, which demonstrate no negative impact of limestone on effluent pH. Ionic content of leachate is higher than the tap water, with higher EC values at the beginning, which shows the leaching of salts from mineral compounds. The load of P-PO4 in a small amount (0.006–0.012 mg/kg) was observed only in first effluent, which confirmed the proper pre-selection of materials for substrate composition. Since there was no change in the quality of the effluent, the experiment was ended after 20 days (Figure 5).

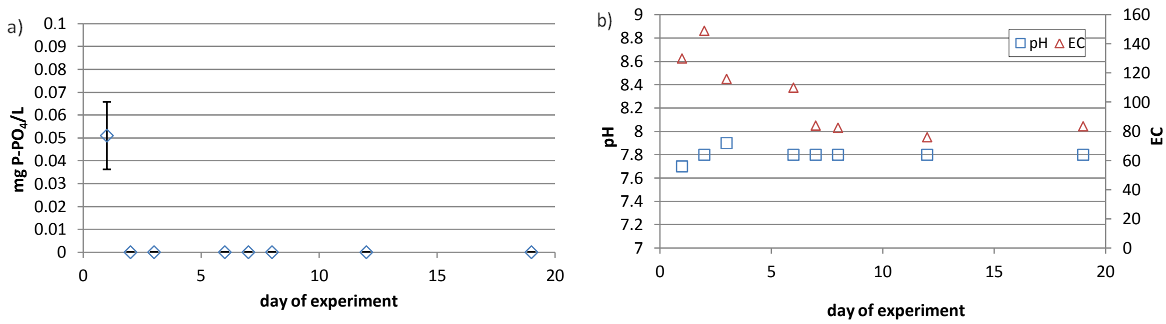

Figure 5. The P-PO_4 concentration (**a**), Electric conductivity (EC) and pH (**b**) in leachate from small column experiment.

3.4. Open Air Model Experiment

The monitoring period covered 319 days from March 2015 to February 2016. In this period the total precipitation amounted 312 mm, with a max depth of 21 mm (noted 17 October 2015). The rainiest months were: July (48.9 mm), October (43.7 mm), and November (48.8 mm). The driest was August, with the monthly rainfall of 4.6 mm and the average air temperature of 22.3 °C.

The total runoff from the green roof model amounted to 132.5 mm, equivalent to 43.3% of runoff from the reference roof (Figure 6a). The highest number of runoff events from the green roof model was observed in October–December and March–May periods, while 54% of runoff volume occurred in the October–December period (Figure 6b,c). In summer time green roof runoff was limited. In most events, the runoff volume from green roof was lower than from conventional roof, but in few cases higher volumes were observed, which is the result of the slow leaching of water retained in green roof construction layers. Such a situation was observed in early spring (February 2016) due to the slow melting of snow.

The pH of rain water ranged from 7.8 to 8.2 (Figure 7a), which is a high value when comparing the country average (pH 5.43) [63]. High pH values can be a result of dusts from the surrounding industrial area. In runoff from the reference roof model, an even higher pH was observed (7.8–9.1). In most green roof model runoff samples the pH values were between 7.5 and 8.7.

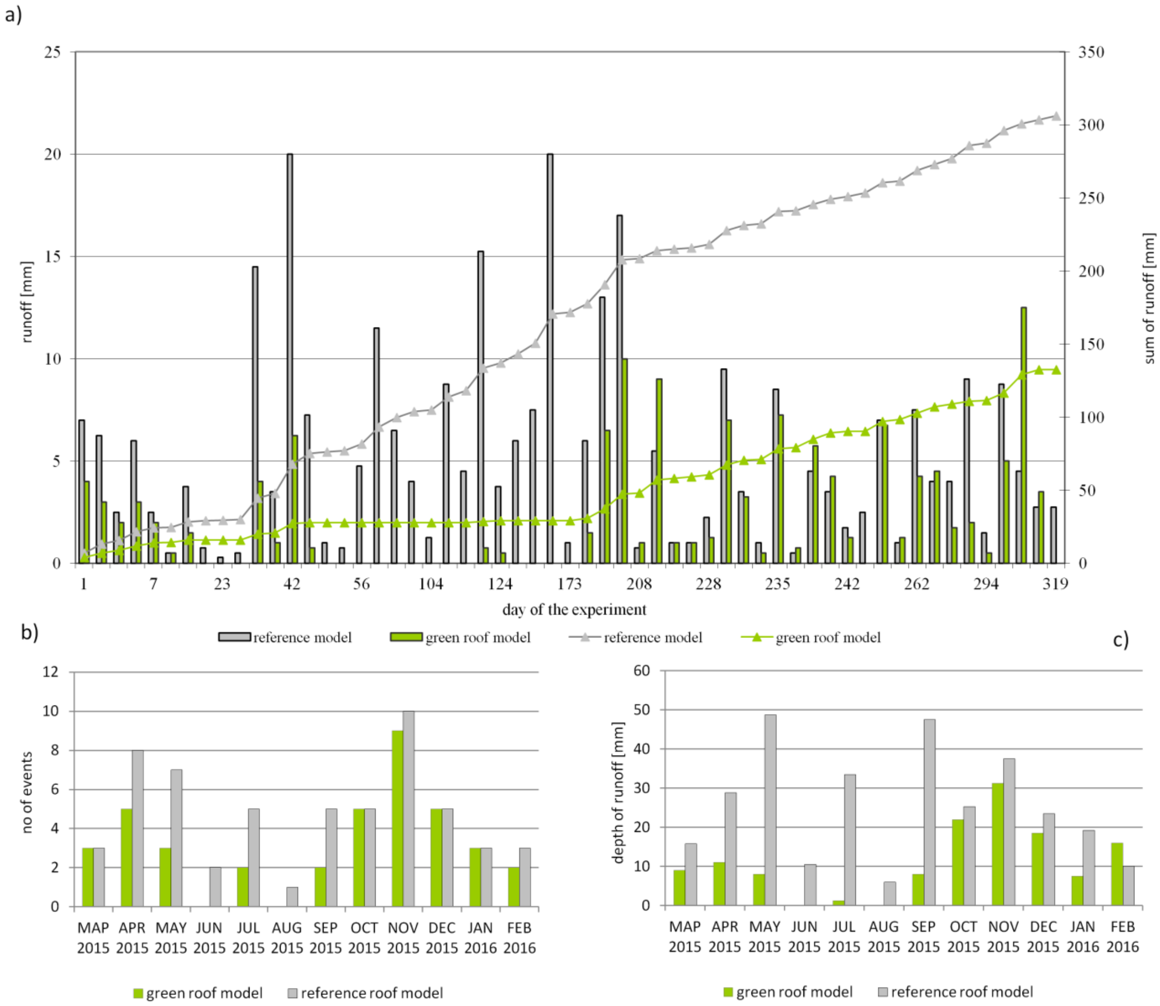

Figure 6. Cumulative runoff (**a**), the number of runoff events (**b**) and depth of runoff (**c**) from green roof and reference roof models from March 2015 to February 2016.

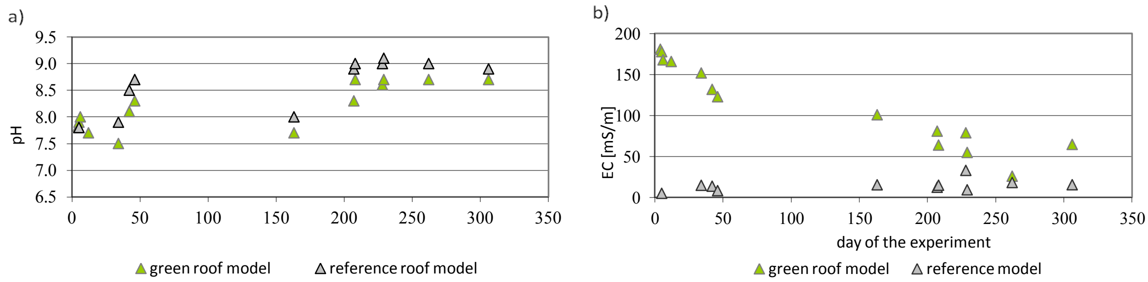

Figure 7. The pH (**a**) and EC (**b**) of runoff from green roof model and reference model.

Electric conductivity of collected rain water samples varied from 0 to 21.7 mS/m, but in most of the events, the EC of rain was close to 5.0 mS/m. The average EC of precipitation in Poland varied between 0.6 and 15.3 mS/m [63]. EC of runoff from reference model amounted to 14.7 $\pm$ 7.2 mS/cm and did not vary significantly from precipitation. In the case of the green roof model, initially high EC values showed a tendency to decrease due to the diminishing of ionic content in runoff by salts leaching (Figure 7b).

The P-PO_4 in runoff from the reference roof was detected twice in low concentrations of 0.027 mg/L (7 May 2015, day 42) and 0.036 mg/L (26 January 2016, day 331), and can be explained by atmospheric deposition. On 26 January, peak phosphorus was also observed in green roof runoff. It was the only event during whole experiment period, and the concentration of P-PO_4 was as high as 0.596 mg/L (Figure 8). An explanation of this finding may be the air temperature. The part of the temperature profile during this period is pasted to Figure 8. On 25 January 2016, the first excess above 0 °C occurred, which probably caused the melting of snow accumulated over the winter period. That day runoff from the reference model amounted to 8.75 mm, while from the green roof model it was only 5.00 mm. With this runoff, 2.98 mg P-PO_4/m^2 was discharged from the green roof model what is imperceptible load in the 319 days observation period.

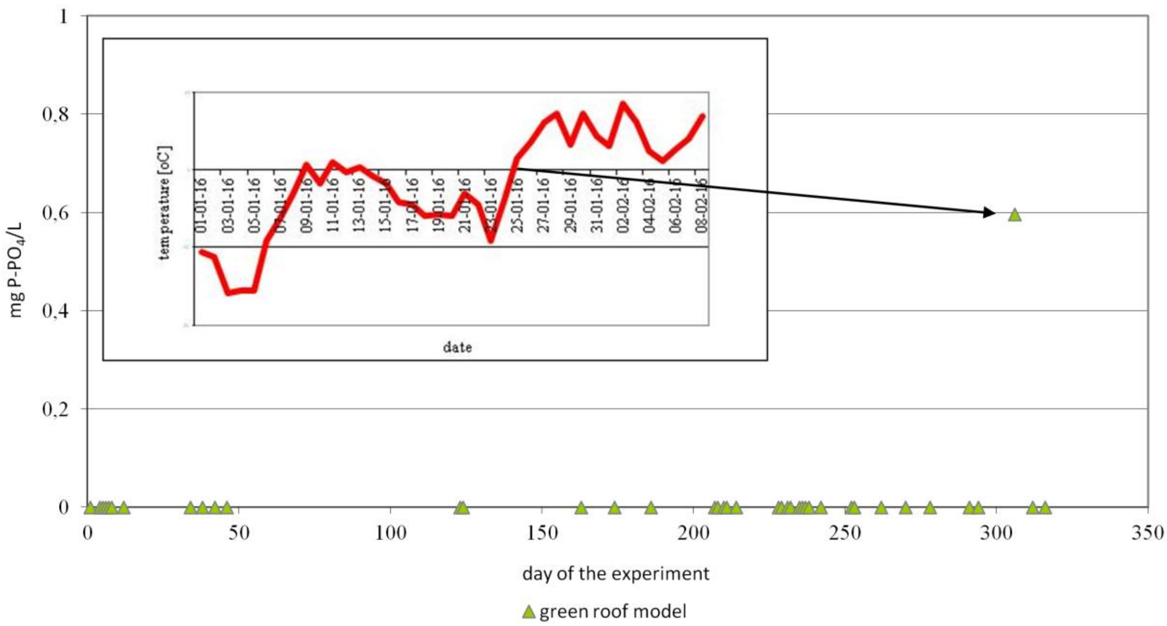

Figure 8. P-PO_4 concentration in runoff from green roof model. Pasted graph shows the moment when temperature exceeds 0 °C, what is connected with the occurrence of phosphorus in green roof runoff.

4. Discussion

As was stated by [18] in their review, research gaps still exists for factors affecting green roof runoff quality. Studies on the chemical properties of growth media and amendments are limited, as most of the research is focused on the observation of hydrological and chemical performance of green roof, not on the creation of the "perfect" green roof.

Most of the previous studies concentrate on the monitoring of green roof runoff quality [7,9–11,14], not on substrate chemical composition. In some exceptions, e.g., [64], substrate mix components are analyzed for chemical composition but phosphorus, which excess loads have the potential to increase eutrophication risk for lakes and rivers, is not included. For the sustainable use of green roofs it is therefore suggested to test the substrate and its components as a potential source of P in runoff. It was a research topic of e.g., [19]. They found a P content of 60 mg/kg and 219 mg/kg in two commercial green roof media: Arkalyte and GAF's Gardenscapes™ (GAF, Wayne, NJ, USA), respectively. Both media were tested under the cover of different sedum plants and results showed that substrate composition had a large effect on phosphorus in runoff. Cumulative P loads of 1200 mg/m^2 and 3700 mg/m^2 were noted during the nine-month evaluation period [19]. From the other side, [15] observed a phosphate load in runoff of 207.2 mg/m^2 from wildflower green roof made of volcanic rock, compost, blonde peat, cooked clay, and washed sand in two monitoring seasons. In the same time, bitumen roof was the source of 26.1 mg of phosphates per m^2. Authors also tested 11 green roof substrates manufactured in Canada for chemical and physical parameters and a leachate test [15]. They stated that physical properties had little apparent effect on the levels of nutrients in the leachate samples, and the chemical composition of bulk media was not correlated with the quality of leachate from the same media.

Most of the mineral materials tested in this study contain phosphorus in different amounts that ranged between 5.3–130 mg P-PO_4/kg in hydrochloric acid extracts. This fraction represents apatite and calcium associated P [64] and is not available for plants, however it can be released from substrate at low pH. The phosphorus found in water extracts was detected for crushed red brick and pollytag, and is available for easily leaching by rain percolation through green roof substrate. As the crushed red brick, which is a cheap and widely available recycled material, represents 35% of developed substrate mix, crushed limestone in volume of 20% of substrate was added as P-reactive material. Further tests: batch test, column experiment, and open air model experiment confirmed the reality of this assumption. The monitoring of runoff volumes and quality from the green roof model constructed base on developed substrate showed that for most of the observation period there was no phosphorus discharged to stormwater receivers. Cumulative water retention of 42.4% of rainfall was similar to results noted in other studies. For example, [65] observed water retention of 44% in sedum decks with media made with course crushed brick, course crushed tile, pelletized power station fly ash (Lytag®), and compost. Observed cumulative water retention leads to the conclusion that the basic function of constructed green roof model has been filled. What is more, only 1 of 39 runoff events contained phosphorus, which was connected with snow melting due to a rise of temperature. The concentration and the load of P-PO_4 amounted 0.596 mg/L and 2.98 mg/m^2, respectively. It can be taken into consideration if runoff from green roof is discharged to small water reservoirs, as it is often done in modern residential areas. One of the options is to discharge this specific spring runoff outside the rainwater retention system to avoid accumulation of P in ponds, as it can be a cause of unwanted algae growth in late spring or summer.

In the most of green roof model runoff samples, pH values varied between 7.5 and 8.7, which fits to results of other research performed in Europe. The following pH ranges for runoff water were reported: 6.0–8.2 [66], 7.6–8.8 [67], 5.8–8.4 [68], or 5.6–10.4 [69]. The green roof runoff pH values obtained in this study were lower than in the case of the reference model, which can be an effect of filtration and phytoremediation. The effect of lowering pH and EC due to plants presence was reported in [70]. As the pH values of runoff from the reference model are higher than from the green roof model, it is not possible to discuss the potential influence of substrate components (e.g., crushed limestone) on runoff pH.

The role of plants was not discussed in this study, as its importance is low in case of *Sedums*. Aloisio et al. [8] stated that plant presence has an effect on runoff volume and nutrient concentrations from extensive substrate composed of 80% of mineral components. Dissolved phosphorus concentrations in runoff from substrate planted with three types of *Amaranthus* were lower than from unplanted substrate [8]. In our study, we used a mix of succulents, the most widely used group of plants used on green roofs, which due to mentioned research are less effective in runoff as well as in phosphate concentration reduction despite similar dry biomass production. Dunnett et al. [71] also stated that *Sedums* were the least effective in the reduction of water runoff when comparing to grass and forbs species.

5. Conclusions

Proposed and applied step by step procedure of materials selection for the development of low P emission green roof substrate includes laboratory batch tests, column experiment, and open air model testing. It is time consuming (full year) but comprehensive, and evaluates the substrate prior to application on a full scale. Mineral materials commonly used in green roof substrates can be a significant source of P in green roof runoff. For sustainable use of green roofs, it is suggested to test all of the applied compounds before use, however, it does not exclude the material from being a substrate component. The addition of P-reactive materials (crushed limestone in this study) can efficiently stops P in green roof construction. Substrate developed from widely available and cheap materials not only reduces the outflow of P, but also allows for the proper development of *Sedum* plants and can be successfully implemented in extensive green roofs. The developed substrate can be composed for less than six Euros per ton. The cost of 100 m^2 of 15 cm depth substrate would amount about 120 Euro.

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Author Contributions: Agnieszka Karczmarczyk designed the concept of the work; Paweł Kożuchowski provided materials for laboratory tests, constructed culumns and green roofs models and collected samples of rainwater and leachates, Anna Baryła performed the tests of physical characteristics and created Table 2 and Figure 4; Agnieszka Karczmarczyk analyzed leachates quality from cullumn and model experiment, performed the tests of leaching potential and sorption capacity, analyzed the data, created a figures and wrote the manuscript; Agnieszka Karczmarczyk is also the author of the proposed procedure for the selection of green roof substrate components.

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