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Article

A Field Study to Assess the Impacts of Biochar Amendment on Runoff Quality from Newly Established Green Roofs

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Abstract: Green roofs (GRs) are a widely recognized green infrastructure (GI) strategy that helps reduce runoff volume and runoff pollution caused by the significant increase in impervious urban areas. However, the leaching of several nutrients from GR substrates is a growing concern. Biochar, a carbon-rich material, possesses advantageous properties that can help address such environmental challenges associated with GRs. Therefore, this paper aimed to undertake a field study to investigate the impacts of various biochar application methods, particle sizes, and amendment rates on the quality of runoff from GRs. Observational data of runoff quality were collected over a two-month period from five newly established 1 m × 1 m biochar-amended GR test beds and a control test bed without biochar, with all test beds subjected to artificially simulated rainfall. The results indicated that the addition of biochar did not result in a significant improvement in runoff pH, whereas the electrical conductivity (EC) was higher in runoff from GRs with biochar-amended substrates. When comparing the total nitrogen (TN) concentration in runoff from the non-biochar GR (ranging from 3.7 to 31 mg/L), all biochar test beds exhibited higher TN release (4.8 to 58 mg/L), except for the bed where medium biochar particles were applied at the bottom of the substrate (ranging from 2.2 to 21 mg/L). Additionally, all biochar-amended GRs exhibited higher TP concentrations in runoff (0.81 to 2.41 mg/L) when compared to the control GR (0.35 to 0.67 mg/L). Among the different biochar setups, GR with fine biochar particles applied to the surface of the substrate had the poorest performance in improving runoff water quality. Despite these mixed results, biochar holds significant potential to improve runoff quality by significantly increasing water retention, thereby reducing pollutant loads.

Keywords: green roofs; biochar; green infrastructure; runoff quality; stormwater; runoff retention

1. Introduction

Due to rapid urbanization, the significant increase in impervious surfaces in urban areas not only exacerbates the volume of stormwater runoff but also negatively affects runoff quality [1]. Green roofs (GR) have been recently introduced as an innovative green infrastructure (GI) to reduce runoff volume and mitigate water pollution. However, the leaching of several nutrients from GR substrates is an increasing global concern. Though nutrients are essential for plant development, rainwater or irrigation activities can release them into GR runoff, thereby degrading the water environment. Nevertheless, an agreement regarding the environmental effects of GRs has not been reached, since they significantly vary according to the characteristics of GR substrates [2]. For example, while the GRs in [3] acted as a sink for all examined heavy metal ions in all artificial rainfall events, Beecham and Razzaghmanesh [4] found that a GR was the source of all pollutants. Loads of total phosphorus (TP) and total nitrogen (TN) were lessened by GRs in the study of [5]; however, GR modules in [6] failed to absorb TP, TN, and other pollutants. Runoff quality from GRs

is strongly influenced by substrate composition (organic content), substrate depth, GR age, maintenance frequency, and fertilizing methods [7,8]. Runoff from GRs with higher organic content is believed to have higher pollutant concentrations [4]. Zhang, et al. [9] concluded that a nitrogen-rich substrate could result in a high concentration of TN in GR discharge. On the contrary, Gregoire and Clausen [10] observed low concentrations of TP and TN due to the application of a slow-release fertilizer, expanded shale, and biosolids media that had a high sorption rate of pollutants. Additionally, loads of TP and TN from GR runoff were minimal in the study by Gong, Yin, Li, Zhang, Wang, Fang, Shi, and Wang [5] because of the used substrate not containing nitrogen and phosphorus fertilizers. The performance of GRs in terms of runoff quality can be more difficult to determine when the age of GRs, types of GRs, plant performance, temperature of substrates, and other factors are taken into consideration [4,11–14].

Biochar, a carbon-enriched material, is manufactured through "pyrolysis", which is the burning process of biomass in an oxygen-deficient environment [15]. The commonly used feedstocks for producing biochar are organic wastes including wood chips, wood pellets, tree bark, crop residues, and municipal solid wastes [16,17]. As previously discussed, GR substrates play a major role in their serviceability. Biochar, a substrate additive, has numerous advantageous properties to enhance different benefits of GRs, including runoff reduction and runoff quality improvement. The physiochemical characteristics of biochar, such as high porosity, large specific surface area, functional groups, and cation exchange capacity, significantly contribute to its benefits [17]. More particularly, the addition of biochar to GR substrates increases the cation and anion exchange capacities, thereby reducing the leaching of ionic nutrient compounds such as nitrogen due to functional groups on the biochar surface [18]. Biochar, which contains ash residue, is also favorable for use in acidic soils by altering soil pH [19]. An increase in soil pH alleviates the amount of soluble plant-essential nutrients and chemicals that are essential for the development of plants and microbial communities [20,21]. The enhanced runoff quality is also a result of the decrease in runoff volume. The highly porous structure of biochar holds a considerable amount of rainwater [22]. The high water retention capacity limits the availability of GR runoff for nutrient leaching [23]. Different approaches have been taken to investigate this capability of biochar, and positive results were reported in previous studies. For example, Kuoppamäki, et al. [24] found positive impacts of biochar on GR runoff volume when biochar was either applied at the substrate bottom or on the substrate surface. Runoff retention rates from field experiments were shown to increase by up to 10% due to the addition of biochar in the summer. Another finding from D'Ambrosio et al. [25] was observed by applying a hydrological simulation model called "CHEMFLO-2000", which also supported the benefits of biochar in GRs. GRs with biochar added to substrates of expanded clay and loam were compared with GRs without biochar. The modelling results indicated that 3 cm and 5 cm depths of biochar enhanced GR runoff retention from 55.05–65.29% to 66.9 and 69.15%, respectively. A soil test column was used in the study of Huang et al. [26]. Similarly, a considerable improvement in runoff retention in biochar-amended substrates from 45.5% to 69.3% was observed. Furthermore, biochar indirectly improves runoff quality by enhancing plant performance followed by increased plant uptake of water and nutrients [2,27].

The performance of GR in terms of runoff quality has been inconsistently reported in the literature [28]. Similarly, different concentrations and loads of pollutants were also observed in runoff from biochar-amended GRs. The characteristics of biochar, depending on feedstocks and pyrolysis conditions, affect the efficiency of biochar in capturing pollutants [29]. For example, GRs with biochar either as the top substrate layer or as the bottom substrate layer [24] had lower loads of TP and TN in GR discharge as compared to non-biochar GRs. A similar finding was found in studies by [30,31]. Loads of TP and heavy metals such as potassium (K^+), calcium (Ca^{2+}), iron (Fe), zinc (Zn), and Mg (Magnesium) were lessened after the application of biochar in the studies of [27,32]. Oppositely, loads of TP in runoff from biochar-amended GRs were higher than that from non-biochar GRs in

experiments carried out by [1,32,33]. In line with the loads of pollutants, concentrations of pollutants in runoff from GRs modified with biochar were mostly lower than those from conventional GRs. The biochar in [34] improved the retention of TP and TN, thereby reducing the concentrations of TP and TN in GR discharge. Wood biochar and olive husk biochar in [35] were both able to significantly adsorb different heavy metals, including Cd (Cadmium), Cu (Copper), Cr (Chromium), Ni (Nickel), Pb (Lead), and Zn. However, opposite findings were observed in some studies. Event mean concentrations (EMC) of TP were from 0.05 to 1.47 mg/L and from 0.18 to 2.09 mg/L in runoff from non-biochar and biochar-amended GRs, respectively. Additionally, concentrations of TN, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) were reported as increased after the application of biochar in the study of Petreje et al. [36].

The primary aim of this research was to investigate how runoff quality from a GR was impacted by (1) amending GR substrates with biochar, and (2) different biochar-GR setups (with varying biochar-related variables). The work presented in this study is a continuation of previous work by Nguyen et al. [37], wherein the water retention capacity and runoff outflow delay of biochar-amended GRs were studied. In this study undertaken at the same experimental site, the authors examined GR runoff quality to further understand the effectiveness of biochar in GRs. Most previous studies only focused on investigating the influence of biochar amendment rates and particle size [27,33,38–41]. Research investigating various biochar-GR setups has not been undertaken previously and hence this research aimed to study all existing biochar variables to find an optimal biochar–GR system in terms of improving runoff quality. To achieve this, the observational data of runoff quality from six 1 m^2 GR test beds were analyzed using a pressurized nozzle-based rainfall simulator. More specifically, there were five biochar-amended test beds that were different from each other in application methods, particle sizes, and amendment rates of biochar. One test bed without biochar was used as the control test bed. During the observational period, the differences in plant conditions of each test bed were minimal, thereby restricting the influence of vegetation on the research outcomes. While there are a significant number of important water quality indicators, the measured water quality parameters in this research were narrowed down to the following parameters: pH, EC, TP, and TN. TP and TN are important parameters to evaluate the quality of water bodies and they are used as primary criteria in urban stormwater guidelines and standards across Australia [42,43]. pH was also measured to understand the GR's benefit in neutralizing acid rain, whereas EC provides general information about the leaching of pollutants into runoff in the form of nutrient ions. In the present study, tap water was used in the rainfall simulator. Given that the chemical properties of tap water affect the results of GR runoff quality, this study attempted to evaluate the capabilities of different GR test beds in mitigating the release of nutrients from GR substrates. The performance of various GR test beds in retaining nutrients in the substrates was reasonably compared under the same experimental conditions, including the tap water source and atmospheric conditions. Nevertheless, factors such as the properties of tap water and weather conditions can significantly influence runoff characteristics and are recommended for examination in future studies. Consequently, the suitability of light expanded clay aggregate (LECA)-based GR substrates with biochar and the optimal biochar–GR systems in terms of runoff quality could be evaluated.

The following outlines the structure of this paper. The information about the research site; experimental design, including GR materials, the GR test beds, biochar types, rainfall simulation device; and methods of collecting and analyzing data is described in Section 2. The subsequent two sections present and discuss the results of the runoff quality performance of various biochar-amended green roof (GR) systems. The conclusions regarding the effectiveness of biochar in improving GR leachate are presented in Section 5.

2. Materials and Methods

2.1. Experimental Setup

Runoff samples were collected from six GR test beds on the roof of Building M at the Footscray Park campus of Victoria University (VU), Victoria, Australia. The six GR test beds were identically made from galvanized steel with dimensions of 1 m × 1 m (Figure 1). They were then elevated 0.3 m above the roof tiles by steel frames underneath, to conveniently collect GR runoff. An extensive GR (EGR) system was chosen with a 150 mm substrate depth. The substrate was dominated by light expanded clay aggregate (LECA)—80% *v/v*, whereas hardwood mulch and coir chips made up 15% *v/v* and 5% *v/v* of the substrate mix, respectively. Other components included a non-woven geo-textile membrane (which acts as the filter layer) and a drainage layer made up of trays of Atlantis 20 mm Flo-cell and VersiDrain® 30 manufactured by Atlantis Corporation, Chatwood, NSW 2067, Australia and Elmich, Newington, NSW 2127, Australia, respectively.


Figure 1. The six green roof test beds on Building M at Victoria University's Footscray Park Campus.

Biochar was added to five out of the six GR test beds using different application methods, particle sizes, and amendment rates. The configurations of the biochar-amended GRs are illustrated in Table 1. The two selected amendment rates were 7.5% *v/v* and 15% *v/v* in this study, and 1–3 mm and less than 1 mm particles were studied as medium and fine biochar particles, respectively. Biochar was thoroughly mixed with other substrate components in most test beds. Additionally, one test bed applied biochar as a bottom layer of the substrate and one test bed mixed biochar with water and then spread it on the substrate surface. The abovementioned biochar application methods, particle sizes, and amendment rates were found to affect the quality of GR runoff in previous studies [24,27,33,38].

Table 1. Characteristics of the six green roof test beds developed as part of this study.

GR Test Bed	Biochar Amendment Rate (% *v/v*)	Biochar Application Method	Biochar Particle Size
GR-0	0	NA	NA
GR-7.5M-M	7.5	Mixed	Medium
GR-7.5B-M	7.5	Bottom Layer	Medium
GR-15M-M	15	Mixed	Medium
GR-7.5M-F	7.5	Mixed	Fine
GR-7.5T-F	7.5	Top Dressing with Water	Fine

A rainfall simulation system (Figure 2) was utilized to uniformly produce rainfall events for each GR test bed. This nozzle-based rainfall simulator uses the pressure from tap water to create numerous droplet sizes [44]. By contrast, the application of an unpressurized system requires a 9.1 m fall height to obtain the actual kinetic energy of rainfall [45]. A pressurized simulator is more advantageous to apply and can better simulate rainfall compared to an unpressurized simulator [46]. The MPL 0.21M-B spray nozzle was supplied by Spray Nozzle Engineering Company–Melbourne. A pressure reducer was also used to maintain a pressure of 3 bars during the experiments. At that pressure, the nozzle produced 0.82 L/min of large droplets with a full-cone spray pattern to entirely cover the 1 m^2 area of the GR test beds. Additionally, it needed to be installed 600 mm above the top surface of the test beds. More information about the experimental setup was provided in the previous research of Nguyen, Chau, and Muttil [37].
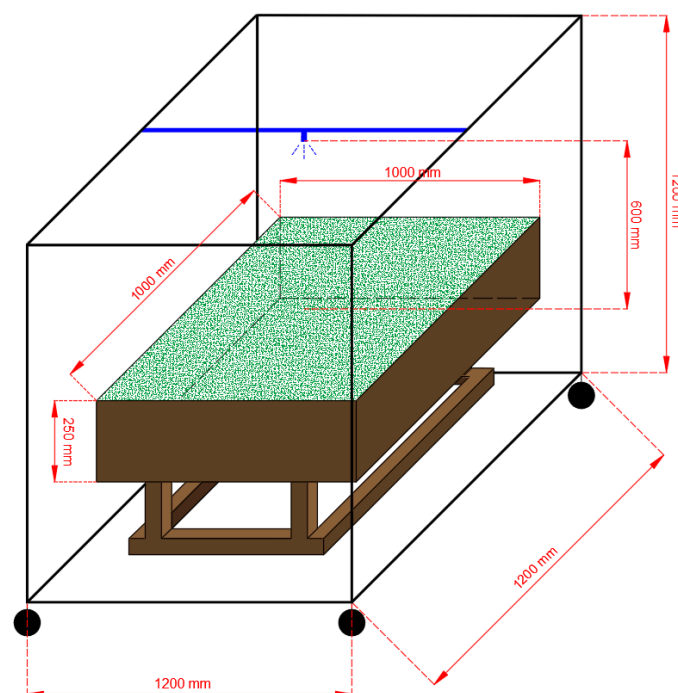
Figure 2. Design of the rainfall simulation device above a GR test bed.

2.2. Data Collection and Analysis

Water quality sampling commenced on 2 October 2023 and concluded on 8 December 2023. Five sets of runoff quality samples were collected on 2 October, 9 October, 23 October, 6 November, 20 November, and 8 December. There was a gap of 2 to 3 weeks between runoff sampling to allow noticeable changes in the amount of nutrients in the GR substrate/runoff. A smaller gap may not have led to any differences in the water quality of the collected runoff samples between experiments. Additionally, the selection of date/time of runoff sampling depended on favorable weather conditions. Experiments were carried out during

dry weather and there were no strong winds that could have potentially affected the GR runoff quality results. Other climatic factors such as antecedent dry weather periods could also have had an impact on the chemical properties of GR runoff. However, all test beds were subjected to the same atmospheric conditions, thus supporting a reliable basis for comparing their performance.

A 10 min artificial rainfall was identically simulated for each test bed to produce adequate runoff for the water quality analysis. The rainfall simulation device used the same source of tap water to prevent the chemical properties of the tap water from affecting the comparison of runoff quality between the test beds. The analyzed water quality parameters consisted of pH, EC, TP, and TN. Then, 5 L plastic containers were pre-cleaned and placed under the drainage outlet of each test bed to collect runoff. Immediately after the collection, pH and EC were measured using portable pH and TDS/EC meters. Successively, runoff samples were moved into pre-cleaned 500 mm plastic bottles and then transported to the laboratory and prepared for the measurements of TP and TN on the same day of collection. Concentrations of TP and TN were spectrophotometrically analyzed by using a HACH DR 5000™ instrument manufactured by Hach Pacific, Dandenong South, VIC 3175, Australia. While TN was measured in the range of 2 to 150 mg/L and/or 0.5 to 25 mg/L using the persulfate digestion method, TP was measured in the range of 0.06 to 3.50 mg/L using the acid persulfate digestion method. The selection of these two methods was in accordance with the concentration range of TP and TN that has been frequently reported by previous studies. The observation data were illustrated using bar graphs, not only to determine the differences in quality of runoff from non-biochar and biochar test beds in an event, but also to assess the influence of GR aging on runoff quality. Single factor ANOVA analysis was also utilized to examine the statistical significance of difference between specific groups of test beds. Accordingly, conclusions about the impacts of biochar on the GR runoff quality and the ideal biochar–GR design could be drawn.

3. Results

The materials used in the GR substrate mixture in this study only included LECA, mulch, and coir chips. Since nutrition from the substrate was sufficient for the chosen GR plants, no fertilizer was applied at the time of constructing the test beds. Therefore, the concentration of TN in all runoff samples was below the minimum detection range of the selected HACH methods in the first sampling on 2 October 2023. The two selected HACH methods for measuring TN concentration have a wide detection range from 0.5 to 150 mg/L. However, the amount of runoff TN from all test beds in the first sampling was nearly zero, which could not be used for data analysis. To achieve the research objective, an identical amount of nitrogen fertilizer (nitrogen as blood and feather meal 14% w/w) was added to each GR test bed through well top-dressing with water on 3 October 2023 prior to the second sampling on 9 October 2023. Consequently, the results of TP and TN concentrations were only available from the second sampling, whereas the measurements of runoff pH, TDS, and EC started recordings from the first sampling itself.

3.1. pH

Natural processes and anthropogenic activities have led to serious acid rain globally, causing numerous negative impacts on ecology and human health [47,48]. Therefore, the solution of constructing GRs on building rooftops has huge potential to mitigate acid rain in urban areas, since rainwater passing through GR substrates becomes more alkaline [33]. Modifying GR substrates with biochar is expected to further enhance this ecological service (of mitigating acid rain) provided by GRs. Figure 3 reveals pH values of runoff from six GR test beds, including one without biochar and five differently modified by biochar. The effectiveness of biochar on runoff pH was more pronounced in the first three rainfall events when all biochar-amended GRs had higher runoff pH than the conventional GR. After that, the runoff pH of the biochar test beds gradually decreased, whereas the non-biochar test bed remained stable. More particularly, the pH of runoff from GR-7.5M-M, GR-15M-M, and

GR-7.5M-F was lower than that from the zero-biochar test bed for the last three events. On the other hand, GR-7.5B-M and GR-7.5T-F had the highest runoff pH during the monitoring period. However, the differences in pH, ranging from 7 to 7.5, between all test beds were negligible (p-value = 0.1 > 0.05).
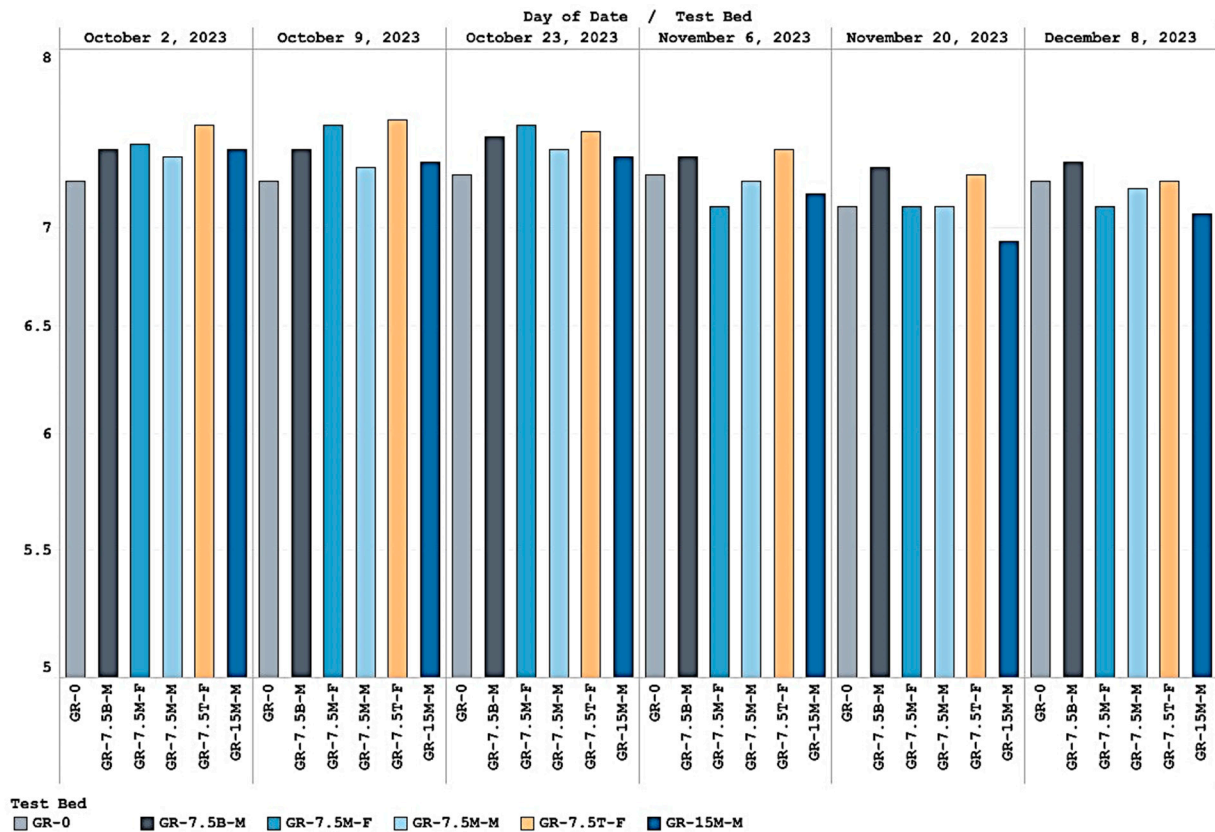

Figure 3. pH values of runoff from different biochar–green roof test beds.

3.2. Electrical Conductivity (EC)

Electrical conductivity (EC) is a useful representative of the amount of total dissolved solids (TDS) in water and is a good water quality indicator for estimating salinity level [49,50]. Runoff with a high EC value contains a high number of nutrient ions leached out from GR substrates. Observations from this study showed that biochar-amended GRs tended to increase EC in runoff as compared to the control GR (Figure 4). In addition, substrates amended with fine biochar particles (GR-7.5T-F and GR-7.5M-F) released more nutrient ions into the runoff than medium particles. However, no significant impact of biochar application method was found between these two GRs (p-value = 1 > 0.05). In addition, a negligible impact of biochar amendment rates on EC was detected when comparing GR-7.5M-M and GR-15M-M (p-value = 0.67 > 0.05). Among the biochar-amended test beds, the EC in runoff of GR-7.5B-M was the lowest. Moreover, this GR with medium biochar particles applied at the bottom of the substrate had a lower EC in runoff than the non-biochar GR for the last sampling (8 December 2023). An increasing pattern of EC for all test beds over the study period was identified, which has a strong relationship with the increasing trend of TN concentration that will be discussed in the Discussion section.
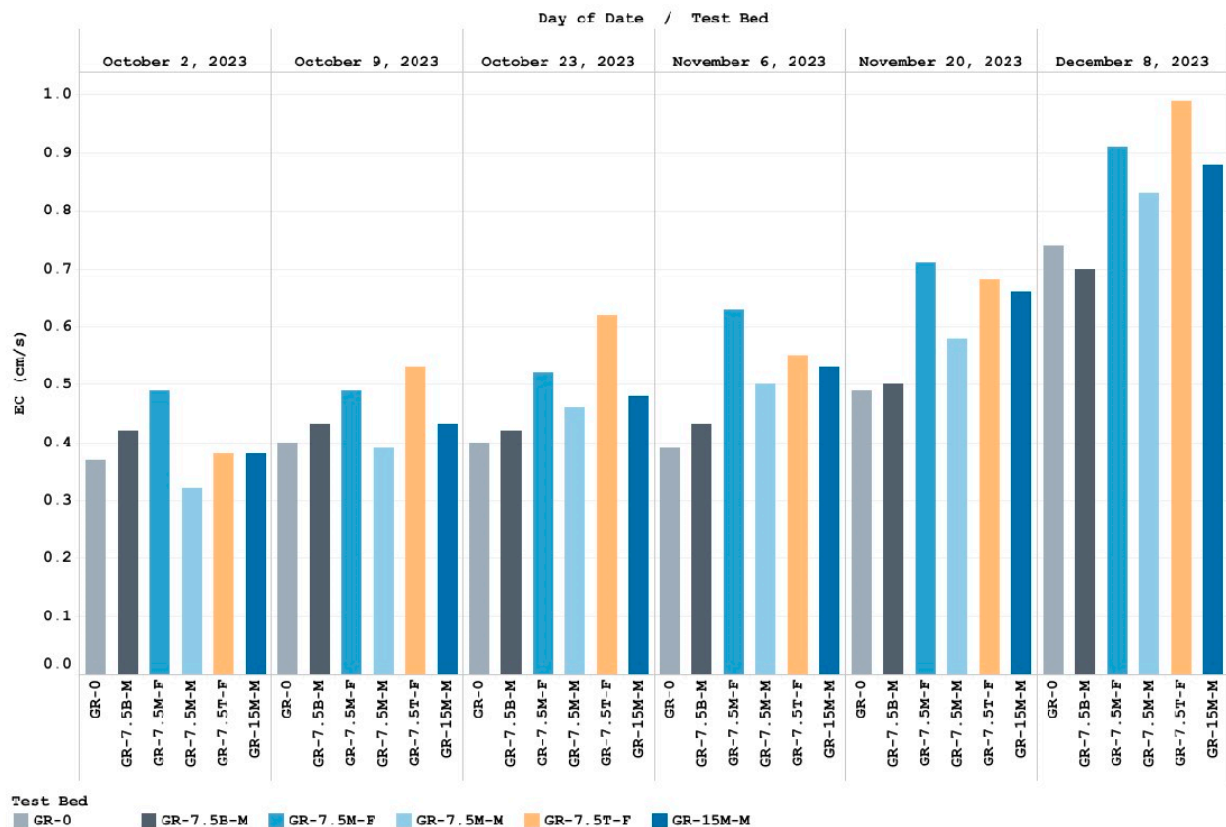
Figure 4. Electrical conductivity (EC) values of runoff from different biochar–green roof test beds.

3.3. Concentration of Total Nitrogen (TN)

Figure 5 illustrates that the TN concentrations in runoff of most biochar test beds were higher than that of the test bed containing no biochar. The only exception was the test bed with medium biochar particles placed at the bottom of the substrate (GR-7.5B-M). For 5 out of 6 rainfall events, GR-7.5B-M released less TN in runoff than the control test bed (GR-0). TN concentrations in runoff of GR-7.5B-M and GR-0 were twice as low as those of the other test beds. More specifically, the TN concentration of runoff from GR-7.5B-M was 2.2 to 21 mg/L, whereas the other biochar test beds (4.8 to 58 mg/L) released a higher amount of TN in runoff when compared to the non-biochar test bed (3.7 to 31 mg/L). An increasing trend in TN concentration in GR runoff was observed, from 2.2–9.5 mg/L in the first sampling to 21–58 mg/L in the last sampling. Fine biochar particles on the top surface of GR-7.5T-F tended to have the weakest impact on mitigating TN release in runoff. Runoff from GR-7.5T-F had the highest TN concentration under all simulated rainfall events. With the same fine particle size, the application method of thoroughly mixing in GR-7.5M-F performed slightly better than the top-dressing application method in GR-7.5T-F (p-value = 0.62 > 0.05). Medium biochar particles in GR-7.5M-M and GR-15M-M tended to have a higher TN retention when compared to fine particles. However, there was no significant difference between these two test beds when increasing the amendment rates from 7.5% to 15% (p-value = 0.87 > 0.05).
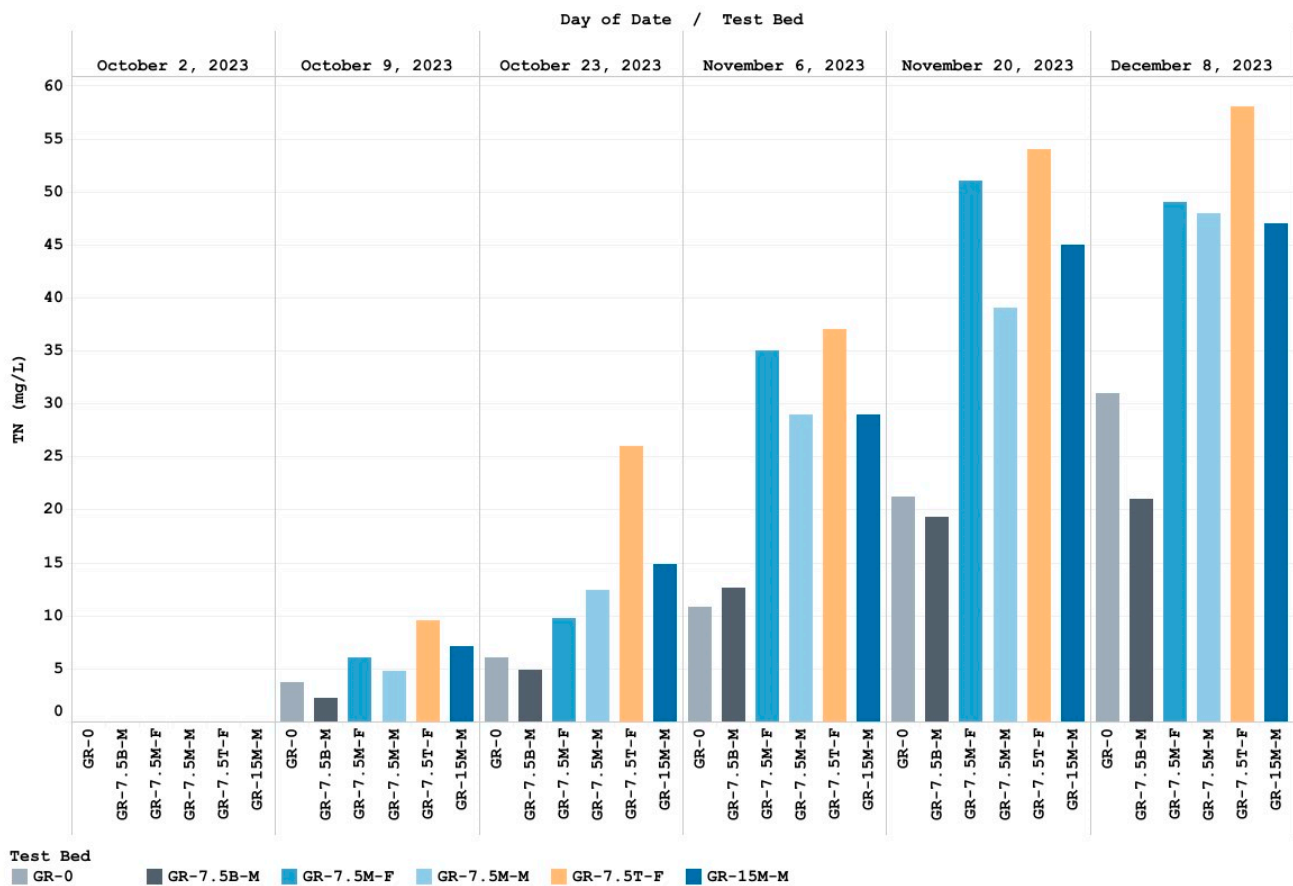
Figure 5. Total nitrogen (TN) concentration of runoff from different biochar–green roof test beds.

3.4. Concentration of Total Phosphorus (TP)

The addition of biochar to GR substrates did not have a reducing impact on TP concentration as compared to GR without biochar (Figure 6). All biochar-amended GRs (0.81 to 2.41 mg/L) had higher TP concentration in runoff than the control GR (0.35 to 0.67 mg/L). GR-7.5T-F with fine biochar particles on the top of the substrate continued to have the poorest performance in retaining TP (0.98–2.41 mg/L). Furthermore, the top-dressing method of biochar in GR-7.5T-F significantly increased the runoff TP concentration as compared to the mixing method in GR-7.5M-F (p-value = 0.048 < 0.05). The fine biochar particles in GR-7.5M-F were also found to be significantly more effective in retaining TP than the medium biochar particles in GR-7.5M-M (p-value = 0.05). With the same mixing biochar method and particle size, the lower amount of biochar (7.5% v/v) performed significantly better than 15% v/v biochar in the first two experiments. However, a similar trend was not observed in the other experiments. Similarly, an inconsistent trend was observed when comparing the impact of biochar application methods (mixing and bottomed layer) on TP retention between GR-7.5B-M and GR-7.5M-M. A decreasing pattern of runoff TP concentration was observed. Runoff TP concentrations decreased quickly in a short monitoring period of about 2 months.
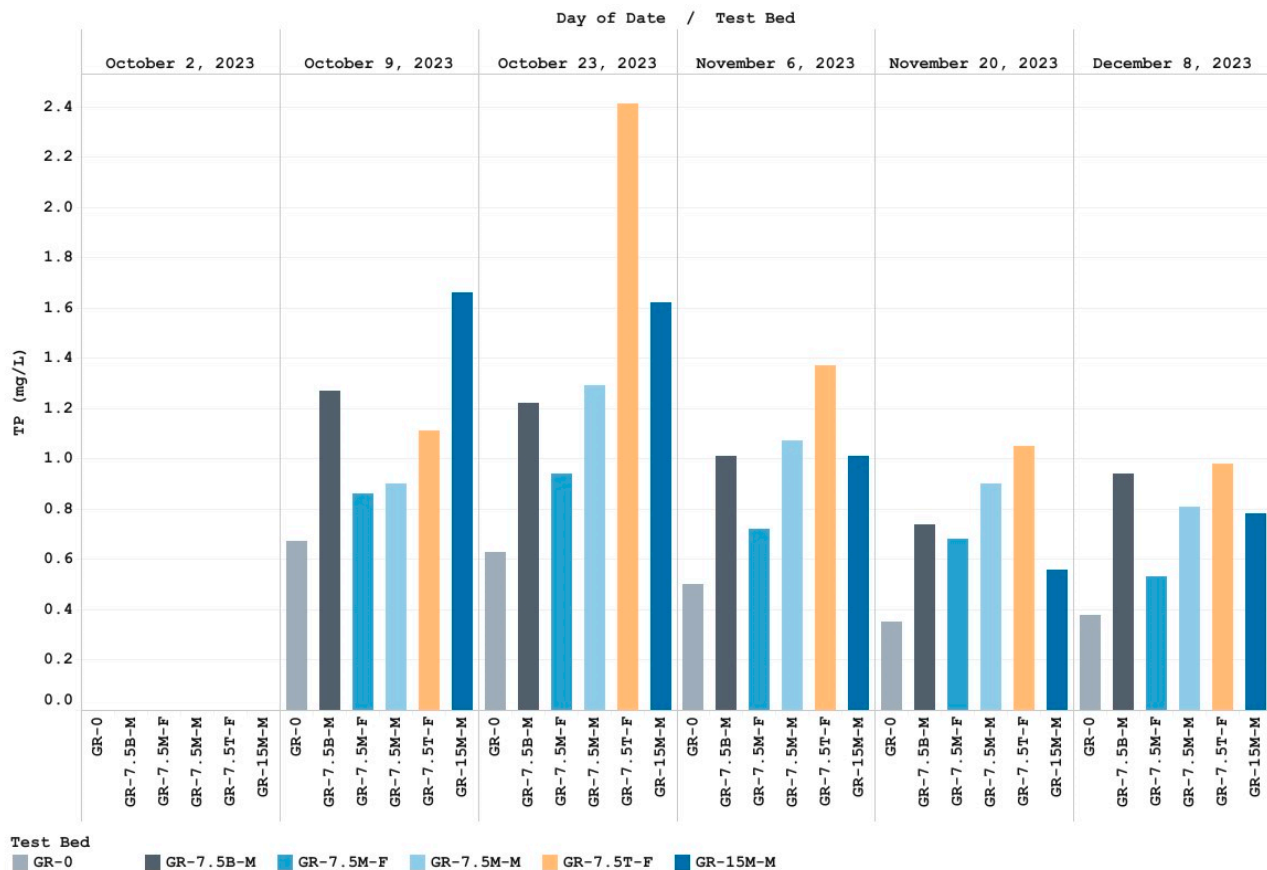
Figure 6. Total phosphorus (TP) concentration of runoff from different biochar–green roof test beds.

4. Discussion

4.1. pH

Though GR-7.5B-M and GR-7.5T-F had the highest runoff pH during the monitoring period, the benefit of biochar in increasing GR runoff pH could not be confidently concluded. Moreover, the differences between the test beds and the influences of biochar particle sizes, amendment rates, and application methods on runoff pH were negligible. The results obtained from this study are comparable with those from the study of Xiong, Li, Wang, Wu, Li, and Xue [33]. The runoff pH of the GR treatment without biochar was lower than that of the GR treatments with different biochar types and biochar addition rates in the first month of monitoring. In the next 2 months, the runoff pH slightly decreased and became constant, and no significant difference was found between the biochar and non-biochar GRs. Similar observations were reported by Liao, Drake, and Thomas [27] when analyzing runoff quality of pilot-scale GRs (71 cm^2) amended with different types and particle sizes of biochar. In the first flush at the beginning of the experiment, the runoff pH of non-biochar GR was lower than that of biochar GRs. In the second flush (115 days after the 1st flush), the effect of biochar decreased, and no significant difference was found between non-biochar and biochar GRs. Opposite findings were reported in the study of Qianqian, Liping, Huiwei, and Long [1]. The authors also measured the pH of runoff from modular GRs (50 × 33 cm) using artificial rainfall. Under different rainfall depths over 6 months, the substrates modified with biochar produced higher runoff pHs. No impacts of biochar on runoff pH were observed when Kuoppamäki, Hagner, Lehvävirta, and Setälä [24] investigated three GR treatments, including one without biochar and two with two different biochar types using plastic boxes (18 × 18 cm) in a 6-week laboratory experiment. Additionally, Meng, Zhang, Li, and Wang [32] recorded the runoff pH of 18 extensive GR test beds (1 × 1 m) for 25 runoff samples from 93 actual rainfall events. The mean pH values from a 1.5-year monitoring period indicated that the addition of

biochar resulted in a slight increase in runoff pH as compared to non-biochar GRs and rainwater. It is worth noting that the influence of different biochar amendment rates (5, 10, 15, and 20%) on runoff pH was inconsiderable. Similarly, Goldschmidt [38] reported a higher runoff from biochar GR substrates in a full-scale experiment over two growing seasons. The increase in biochar amendment rate from 2.5% to 10% also did not lead to a remarkable difference. Runoff pH values from three simulated rainfalls reported by Novotný et al. [51] were also slightly higher due to the addition of three types of biochar. Wood biochar, food waste biochar, and sewage sludge biochar retained positive effects on runoff pH after 10 months. In general, biochar substrates tend to neutralize pH and produce runoff that is more alkaline than non-biochar substrates, due to the presence of alkaline metals in biochar [7]. Similar results were found in numerous papers using either tap water (artificial rainfall) or actual acidic rainwater. However, the addition of biochar does not result in a significant improvement and the impact decreases over time.

4.2. Electrical Conductivity (EC)

The effects of biochar on the EC of biochar-GR runoff have been inconsistently reported. Similarly to the findings of the present study, Kuoppamäki, Hagner, Lehvävirta, and Setälä [24] concluded that biochar tended to increase EC when they measured EC in runoff from pilot-scale GRs amended with two different biochar types in the 6th week of a lab experiment. Goldschmidt [38] conducted a full-scale experiment including various GRs in plastic trays (60 × 20 cm). They found that the average EC during two growing seasons was also higher in runoff from biochar substrates than that from non-biochar substrates. However, the differences were not significant and higher biochar amendment rates (2.5, 5, and 10%) slightly increased the EC in runoff, which is consistent with the present study. In the study of Liao, Drake, and Thomas [27], all particle sizes of processed biochar had positive impacts on EC in runoff, especially in the second flush (115 days after the 1st flush), whereas the runoff EC was higher with all particle sizes of unprocessed biochar in both flushes, except for 2.8–4 mm biochar particles. Moreover, particle sizes for both processed and unprocessed biochar had a negative relationship with runoff EC. Those findings were also observed in the present study. Runoff EC was much lower in the second flush than in the first flush, which was different from the increase in EC over time in the present study. This could be explained by the low amount of nutrients in GR substrates 115 days after the substrate preparation as compared to nutrient-rich substrates, due to the shorter monitoring period of only about 60 days in the present study. On the other hand, biochar was also found to have positive effects on runoff EC. For example, Qianqian, Liping, Huiwei, and Long [1] measured the EC of runoff from commercial substrates and biochar substrates. Under all simulated rainfalls with different rainfall depths, the runoff EC of biochar substrates was slightly lower. Another similar result was recorded by Meng, Zhang, Li, and Wang [32]. The average runoff EC from 1 m² extensive GRs by analyzing 25 runoff samples over more than one year indicated that biochar succeeded in reducing runoff EC. However, the effect of biochar did not become significantly greater by adding more biochar (5, 10, 15, and 20%). Biochar type affected the runoff EC in the study by [51]. While GRs added with biochar from food waste and wood increased the runoff EC, GRs with sewage sludge released significantly lower levels of ions in runoff. To conclude, biochar performs inconsistently in terms of runoff EC according to the time of sampling, substrate type, and biochar type. Biochar particle sizes have a more pronounced influence on runoff EC, which is reported in the present study and others.

4.3. Concentration of Total Nitrogen (TN)

Biochar failed to alleviate the TN concentration in this study, except for the GR-7.5B-M test bed. Therefore, medium biochar particles are recommended to be amended at the bottom of LECA-based GR substrates to reduce TN concentrations. The application methods of mixing and top-dressing with medium and fine biochar at two amendment rates (7.5 and 15%) in the other biochar test beds did not effectively improve the TN

retention. However, some consistent trends were found. As compared to the top-dressing method, thoroughly mixing fine biochar particles was a more effective solution to decrease TN concentration in runoff. Medium biochar particles tended to perform better than fine particles in TN retention. Nevertheless, the differences between those test beds were inconsiderable. An increasing trend in TN concentration in GR runoff was observed, which could be explained by more and more dissolved nutrients being released over time from the nitrogen-rich fertilizer added to the GR substrates before the second sampling (9 October 2023) through rainfall and irrigation. Accordingly, the release of increased fertilizer salt ions was the reason for the increasing trend in EC in runoff.

Negative impacts of biochar on TN concentration in GR runoff were also observed by Liao, Drake, and Thomas [27]. Two biochar types (unprocessed and processed) with four different particle sizes thoroughly mixed into substrates of GRs in growth containers (71 cm^2) also released higher levels of TN in runoff. Only 2.8–4 mm unprocessed biochar was lower in concentration of TN than non-biochar GRs in both samplings. There was a considerable decrease in runoff TN in the second sampling (115 days after the 1st sampling), and non-biochar and biochar GRs were not significantly different from each other in runoff TN concentration. Furthermore, Novotný, Šipka, Miino, Raček, Chorazy, Petreje, Tošić, Hlavínek, and Marković [51] could not find a TN-reducing effect of biochar by testing three different types of biochar. Those GR test beds (0.5 × 1.0 m) only produced runoff that was close to the no-biochar test bed in TN concentration for the last simulated rainfall (10 months after GR installation). On the other hand, the TN concentrations in runoff from biochar GRs reported in the present study are inconsistent with most previous studies. For example, the mean TN concentration of runoff from the biochar substrate in the study of Qianqian, Liping, Huiwei, and Long [1] was significantly lower than that from commercial substrate (9.85 and 16.14 mg/L, respectively). Those results were collected from 50 × 33 cm modular GRs under eight simulated rainfalls with different rainfall depths. Xiong, Li, Wang, Wu, Li, and Xue [33] investigated two types of biochar, including rice husk (RH) biochar and maize straw (MS) biochar. They found that both biochars successfully reduced TN leaching in runoff in all six studied rainfall events in three months. The TN-reducing effects of these two types of biochar were significantly different at the same amendment rates. Moreover, neither biochar type had a better performance at higher amendment rates. Runoff TN concentration also quickly decreased in roughly two months. Biochar added to stabilized sludge-based pilot-scale GRs effectively improved runoff quality by reducing the runoff TN concentration from 3.27 to 2.16 mg/L [52]. A longer observation of 18 extensive 1 m^2 GR test beds in 1.5 years under real rainfall also indicated that coconut shell biochar mixed with peat, vermiculite, sawdust, and perlite as GR substrates succeeded in decreasing TN concentrations [32]. Average TN concentrations in runoff from non-biochar GRs were twice as high as those from biochar GRs. The increase in biochar addition rates also did not significantly affect the concentration of TN in the runoff in this study. In another study by Beck, Johnson, and Spolek [30], the performance of two GR metal trays (61 × 61 cm) planted with two different plants, sedum and ryegrass, under artificial rainfall was positive in terms of TN concentration. TN concentrations of the ryegrass trays were 10.1 mg/L, compared to 79.2 mg/L for the control trays. It is noted that only two rainfall simulations were run, and the second simulation started 2 h after starting the first simulation. The performance of biochar in TN retention depends on many factors, such as the suitability of biochar within the GR system. While amendment rates tend to have less effect, biochar types, application methods, and particle sizes were found to influence the release of TN in runoff in this study and others. Therefore, further research on biochar variables should be conducted, and biochar–GR systems need to be tested before large-scale applications.

4.4. Concentration of Total Phosphorus (TP)

The addition of biochar to GRs in the present study did not positively affect the concentration of TP in runoff. Biochar substrates act as a potential source of TP, since they might release part of the P into the runoff [1]. A review by Li et al. [53] found that

the addition of biochar to soil could result in either an increase or decrease in runoff P concentrations. Soil P availability was increased by adding biochar, and P in soil became available P, leading to higher P levels in runoff [33,54]. Fine biochar particles evenly spread on the GR surface released the most TP into runoff. Oppositely, the mixing application method of fine biochar particles released significantly less TN into runoff. In contrast to TN retention, higher TP retention was recorded with fine biochar particles. These findings are consistent with previously conducted studies. For instance, a long-term observation of several 1 m^2 GR test beds found that all biochar substrates did not reduce the TP concentration in runoff [32]. Various biochar addition rates (5, 10, 15, and 20%) also did not result in a significant difference. Additionally, the use of two types of biochar by Xiong, Li, Wang, Wu, Li, and Xue [33] did not lead to lower TP concentrations in runoff. However, the performance of rice husk biochar substrates was closer to that of non-biochar substrates. The impacts of biochar amendment rates on runoff TP concentration were significant in this study. A higher amount of biochar released more TP, especially for maize straw biochar, into runoff and the trends were consistent during the study period. Biochar produced from three different feedstocks, including wood, sewage sludge, and food waster, in the study of Novotný, Šipka, Miino, Raček, Chorazy, Petreje, Tošić, Hlavínek, and Marković [51] could also not alleviate TP levels in runoff during the experimental period of 10 months. Biochar type also significantly affected the TP release, with the best performance by food waste biochar. One possible explanation for the low effects of biochar was the low initial concentration of TP in GR substrates, limiting the TP adsorption ability of biochar. The GR substrates used in the present study were also low in TP. Moreover, the studies of both Qianqian, Liping, Huiwei, and Long [1] and Meng, Zhang, Li, and Wang [32] used the same substrate with a low initial TN concentration. Under both artificial rainfall and natural rainfall, their biochar-amended GRs did not succeed in reducing TP release in runoff. Opposite findings were found in the study of Beck, Johnson, and Spolek [30] when their initial GR substrates were higher in TP concentration. There were still positive results. For instance, the TP concentration in runoff was lower with biochar substrates (8.3–8.4 mg/L) than with non-biochar substrates (10.3–17.4 mg/L) [30]. However, only two rainfall events were simulated. The decreasing trend in TP in the present study was also observed in the studies by [29,33]. Observation data illustrated that phosphorus was significantly washed out from GR substrates at the initial stage and then gradually decreased over time [29]. Xiong, Li, Wang, Wu, Li, and Xue [33] stated that biochar made from different feedstocks could possibly be responsible for the different results regarding runoff quality. Therefore, the compatibility of biochar with a GR system needs to be evaluated before a field-scale implementation. The use of a batch or column test is suggested [29].

4.5. Long-Term Impacts of Biochar on Green Roof Runoff Quality

Most studies reported a decreasing trend in nutrient concentrations in runoff, which could be explained by newly established GR substrates containing several nutrients that are gradually released into runoff over time. This indicates that GR acts as a source of pollutants, especially at the early stage [33,55]. The results of runoff EC, nutrients, and heavy metal concentrations in the study by Novotný, Šipka, Miino, Raček, Chorazy, Petreje, Tošić, Hlavínek, and Marković [51] also supported this conclusion. The pollution of runoff was more severe one month after installation, which gradually decreased over time. Conversely, the TN concentration and EC in runoff were not observed to decrease in the present study. One possible reason for this was the high application of nitrogen fertilizer in the substrates. The number of dissolved fertilizer nutrients kept increasing, so decreasing trends in TN concentration and EC could not be detected in the short monitoring period of about two months. Therefore, results of GR runoff quality strongly depend on sampling time, and future studies are recommended to investigate runoff quality at different stages of a GR's lifetime. Since the availability of nutrients in GR substrates changes and tends to decrease over time, long-term observations are necessary to understand the performance of biochar as the age of the GR increases.

Despite mixed findings regarding nutrient concentrations, biochar still has huge potential to improve runoff quality due to its significant water retention capacity, leading to lower pollutant loads in runoff. Numerous papers have highlighted the effects of biochar in reducing TP loadings in runoff, regardless of higher TP concentrations. For example, Kuoppamäki, Hagner, Lehvävirta, and Setälä [24] found higher TP and TN concentrations in runoff from biochar GRs than those from non-biochar GRs. By contrast, loadings of TP and TN were reported as lower with both application methods of biochar, due to a higher water retention. The results of Cheng, Vaccari, Johannesson, and Fassman-Beck [29] extracted from observations and modelling also supported the long-term positive impacts of biochar on GR runoff quality. The reduction in annual cumulative TP loading when compared to an un-greened reference roof could have been largely due to the reduction in runoff volume. Similarly, the LECA-based substrates amended with biochar in the present study did not effectively reduce nutrient concentrations in GR runoff during the short study period. However, the benefits of these GR systems regarding runoff quality could not be concluded early and require a long-term monitoring period. The potential for improving the GR runoff quality by increasing runoff retention and decreasing pollutant loads from the test beds could be supported by the runoff volume data reported in the previous study of Nguyen, Chau, and Muttil [37]. At the same experimental site with the same GR test beds, the runoff retention capacities of the biochar-amended GRs were apparently higher than those of non-biochar GRs under different rainfall scenarios. With a total rainfall of 110.7 L, the maximum volume of rainfall retained by biochar-amended GRs was 58.9 L, while the non-biochar GRs retained 37.9 L of rainfall. Nevertheless, selection of correct biochar types for GR substrates is still necessary. The suitability of biochar with GR substrates plays a major role in determining the efficiency of biochar in improving GR runoff quality [33].

5. Conclusions

Green roofs (GRs) provide a wide range of ecological services, consisting of runoff retention, urban thermal reduction, energy saving, and air purification. However, GRs tend to act as a potential source of pollutants, especially immediately after the establishment of GRs. Nutrient loss to runoff causes water pollution, while insufficient nutrients in GR substrates can hinder the growth of plants and subsequently diminish the effectiveness of GR services. The addition of biochar to GR substrates has huge potential to reduce the release of nutrients into GR runoff. Therefore, this paper aimed to investigate the effects of biochar on GR runoff quality by measuring pH, electrical conductivity (EC), and TN and TP concentrations in newly established GR test beds. Furthermore, the influence of biochar amendment rates, application methods, and particle sizes on GR runoff quality was also evaluated. The quality of runoff from six 1 m^2 GR test beds, which included five biochar-amended test beds and one control test bed (without biochar), was analyzed using six artificial rainfall events within a two-month period.

The following is a summary of the key conclusions and recommendations based on this study:

(a) GRs tended to neutralize rainwater by producing alkaline runoff (pH ranging from 6.93 to 7.59). The impacts of biochar on runoff pH were insignificant and more pronounced at the beginning of the experiment.

(b) All GR substrates were a source of EC, and runoff EC was higher with biochar-amended substrates. Small biochar particles tended to produce runoff with higher EC. Among the biochar-amended test beds, the EC in runoff from the test bed with medium biochar particles applied at the bottom of the substrate was the lowest.

(c) TN concentrations of runoff from most biochar GRs were significantly higher than from non-biochar GR. The only exception was the test bed with medium biochar particles applied at the bottom of the substrate. Compared to medium biochar particles, fine particles exhibited a slightly weaker capacity to reduce TN in GR runoff.

(d)   The addition of biochar resulted in an increase in TP concentration in GR runoff due to a higher P content in substrates, which is also consistent with previous findings. In contrast to TN retention, fine biochar particles were observed to be more effective for TP retention than medium biochar particles.

(e)   When compared to the other biochar test beds, the test bed with biochar applied to the surface of the substrate (GR-7.5T-F) exhibited the poorest performance in terms of runoff quality.

(f)   Despite mixed findings regarding nutrient concentrations, biochar still holds huge potential to enhance runoff quality, due to the considerable reduction in runoff volume that it can achieve.

(g)   A pronounced relationship between runoff quality and GR aging was also recognized. The availability of nutrients in GR substrates tends to decrease over time and long-term observations are necessary to understand the performance of biochar as GRs age.

(h)   The compatibility of biochar with a GR system significantly influences the effectiveness of biochar in improving GR runoff quality.

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