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Quality of Harvested Rainwater from a Green and a Bitumen Roof in an Air Polluted Region

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Abstract

A one-year study was conducted to evaluate the impact of air pollution and roof coating on runoff quality. An existing 440 sq meter bitumen roof of a single-story building was coated with an extensive green roof layer on one half. Rainfall and runoff samples from both roofs were collected during 11 rainfall events after the separation of the first flush. The study monitored several key parameters, including pH, electrical conductivity (EC), turbidity, chemical oxygen demand (COD), ammonium nitrogen, nitrate nitrogen, and phosphates. The study revealed that both types of roofs altered the rainfall quality, but the changes caused by the green roof were more substantial. Although the retention of runoff from green roofs has a widely acknowledged positive impact on collecting systems, our study shows that green roofs also result in a 7.5-fold increase in COD concentrations, a 5.4-fold increase in the sum of ammonium and nitrate nitrogen, and a 2.3-fold increase in phosphates compared to bitumen roofs. A clear link between the quality of rainwater/runoff and air pollution was not established. The study's findings will aid in the development and management of local rainwater harvesting systems and enhance global understanding of the primary quality parameters of various roof types, particularly in regions with air pollution.

Keywords: Runoff Quality; Rainwater Harvesting; Green Roof; Bitumen Roof; Air Pollution; Rainfall.

1. Introduction

Climate change has progressively imposed major water-related challenges in recent years. Some of the main issues are related to the increased number of consecutive dry days and extreme precipitation events that result in prolonged drought periods or intense flooding occurrences [1, 2]. Also, seasonal variations in rain events become significantly more pronounced. This accounts for the formation of regions with considerable water shortages for the residents of the settlements during the dry parts of the year, followed by downpours with sewerage system overload when the months with increased precipitation occur [3, 4]. According to the World Bank, such regions are also currently present in parts of the Bulgarian territory [5]. These abnormalities require the adoption of sustainable engineering solutions to mitigate the negative influences and safeguard the natural world [1].

To mitigate water scarcity and enhance the resilience of the water supply systems, the European Commission (EC) communicated a requirement to establish water reuse standards back in 2012 [6]. The consistent efforts in the same regard finally led to the issuing of Regulation (EU) 2020/741 on minimum requirements for water reuse, which became the norm across most of the European Union in June 2023 [7]. However, this regulation is an initial step in the direction of water recovery since it only focuses on treated wastewater. Every specific case study requires a more general approach

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to achieve optimal water management for the region with minimum natural source water allocation. The establishment of a comprehensive database related to both the alternative water source and its particular use would enhance the understanding of factors influencing the source's quality parameters and the imperative to treat collected water to an appropriate level if required.

One of the most widely discussed alternative water sources is harvested rainwater [8–10]. It is considered a promising local solution to water scarcity that can provide sufficient potable or non-potable water in homes [11–13]. However, the quality of the harvested rainwater is still a subject of conflicting results since the runoff is influenced by multiple factors [14], including the duration of consecutive dry days before the examined rain event [15, 16], the climatic zone of the study, the air pollution in the region [16, 17], and the roof type [12, 18, 19]. According to Mao et al. (2021), the decisive role in the harvested rainwater quality is played by the roof coating materials and the weather patterns [20].

Various roof coating materials have been developed through the years. In terms of the effect on the most commonly analyzed quality parameters of the harvested rainwater, they can be divided into two main groups: green roofs (either intensive or extensive; with different types of vegetation; varying thickness of the soil layer and installation specifics; etc.) and conventional roofs (asphalt shingles; bitumen coatings; different metal, concrete, wood, and clay tiles; and composite material coverings) [21]. Even though numerous studies investigated the harvested rainwater quality from different types of roof coatings, there are still contradictory reports in the literature, and no specific, unambiguous range for the parameters with relation to the roof coating is reached.

For conventional roofs, for instance, a paper by Farreny et al. (2011) analyzes multiple full-scale case studies with flat roofs with different coatings (concrete, metal sheet, plastic sheet, and flat gravel) and reports a range in the literature for total suspended solids (TSS) of 13 to 120 mg/L. However, their experiments showed even lower TSS concentrations, reaching up to 0 mg/L [18]. In another study conducted by Ubuoh et al. (2021), examining rainwater from asbestos, aluminum, corrugated iron, and harvey-tile roofs, the parameter analysis showed that apart from pH, other physiochemical properties and metals (Cu^{2+}, Pb^{2+}, and Fe^{2+}) were even below the World Health Organization's limiting values for drinking water [17]. On the other hand, the results of the analyzed parameters in Jamal et al. (2023) indicate that at minimum, a harvesting system for the first flush (initial rainwater) in combination with a three-stage purification system (UV-light exposure, sedimentation, and activated carbon filtration) is needed to provide safe water that can be used for almost all purposes (including potable needs) [13].

Green roofs, on the other hand, demonstrate diverse impacts on pollutant concentrations [14]. While some studies have reported a decrease in contamination levels, others have found that green roofs can result in increased runoff pollutant concentrations. Todorov et al. (2018) demonstrated that a green roof in Syracuse, New York, had no change in rain runoff parameters during a four-year monitoring period [22]. In Missouri, Harper et al. (2015) observed high initial concentrations of nitrogen and phosphorus, which had significantly decreased by the end of their nine-month study [23]. Santana et al. (2022) concluded in their study that the infiltration of rainwater through the green roof led to a reduction in the natural acidity of the water [24]. However, there was an increase in the concentration of color and turbidity caused by the presence of total solids, which acted as a source of electrical conductivity [24]. Nevertheless, Santana et al. (2022) concluded that according to Brazilian national standards, the harvested rainwater from the full-scale green roof can be used for non-potable purposes such as cleaning sidewalks, garden irrigation, and toilet flushing, hence reducing the consumption of water from the public supply system [24]. Also, if the green roof rainwater is not locally collected and used, its impact on the runoff quality of the urban sewerage system is uncertain, as it may lead to either absorption or increased discharge of pollutants into the sewer [14, 23, 25].

In conclusion, the literature review indicates that further research is required to harmonize the findings on harvested rainwater quality and to gain a more comprehensive understanding of the influencing factors.

In this article, we present findings from a year-long investigation into the water quality of directly collected rainwater, runoff from bitumen roofs, and runoff from extensive green roofs in the Sofia City area, Bulgaria. The purpose of the study is to analyze water quality variations between the two types of full-scale roofs and to compare these variations with the rainfall collected adjacent to the rooftops that had no contact with any roof coating. The results will help establish more precise ranges for the main quality parameters for the different roof types that 1) can help with the selection of the optimal water management options when a system is designed, and 2) can be used when the impact on existing infrastructure is assessed. Moreover, the study explores another aspect that potentially influences the rainwater quality: the correlation between the runoff quality and the seasonal air pollution in the investigated region. The findings will facilitate future research in this field and will contribute to a better understanding of rainwater harvesting systems, helping to address the research gaps discussed above.

2. Material and Methods

The research consists of three main phases, as presented in Figure 1.

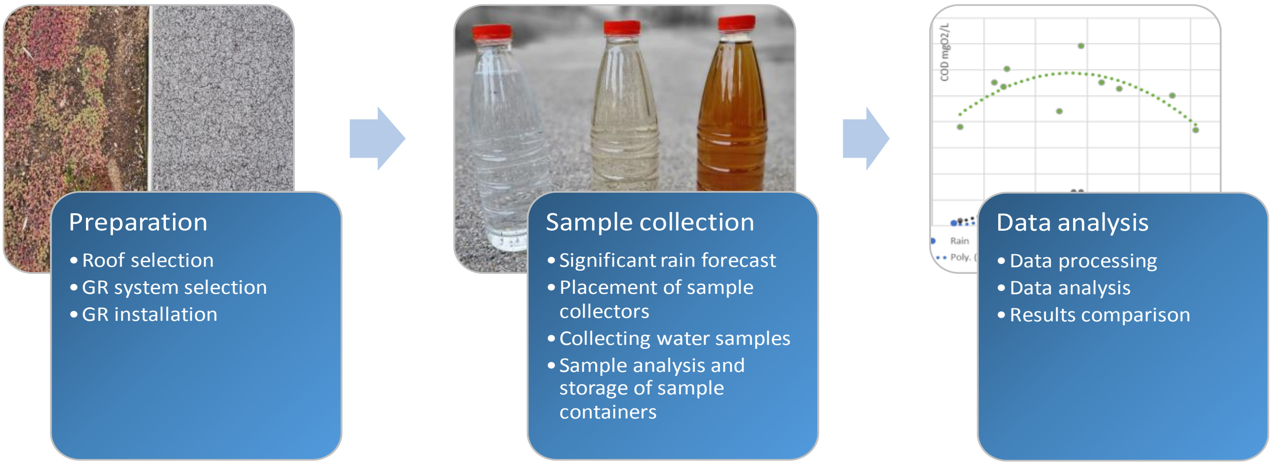


Figure 1. Research flow chart

2.1. Location, Climate, and Study Site

The research was conducted in the Sofia field, located in Bulgaria. The total area of the Sofia field is 1,311 km², comprising an urbanized area of 245.5 km², an agricultural area of 509 km², and a forested area of 466.5 km². The average altitude is 550 m. The field is situated amidst several mountains, as depicted in Figure 2. The study area is prone to temperature inversion, which exacerbates air pollution concentration levels, particularly during the colder parts of the year. Sofia, the capital of Bulgaria, is situated in the Sofia Field. The city is characterized by intensive social and economic development [26, 27].

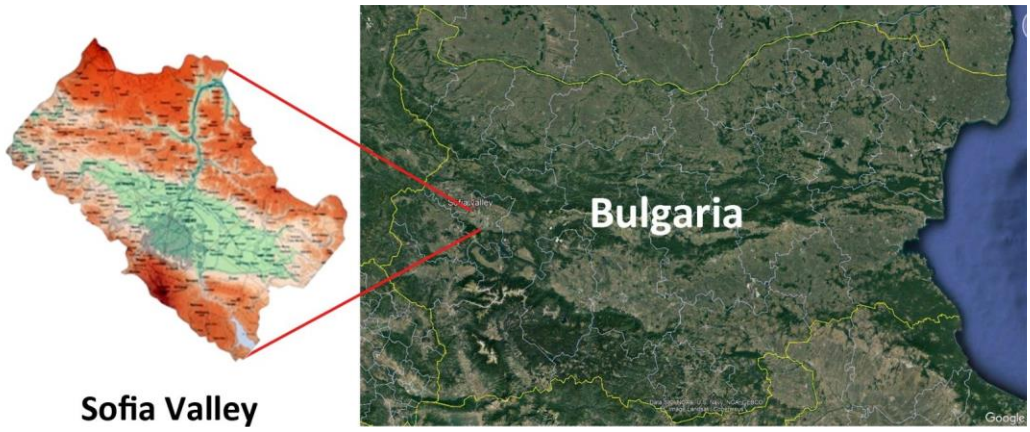
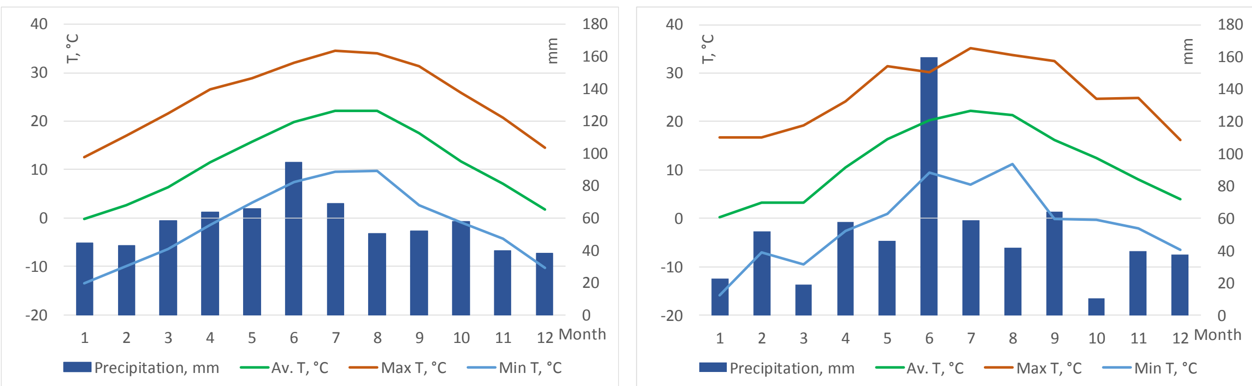


Figure 2. Study region [26, 27]

The climate in Sofia is classified as moderate continental, with distinct fluctuations in both temperature and precipitation throughout the year [28]. Monthly climate data for the period 2012–2022 and the year 2022 can be found in Figure 3.

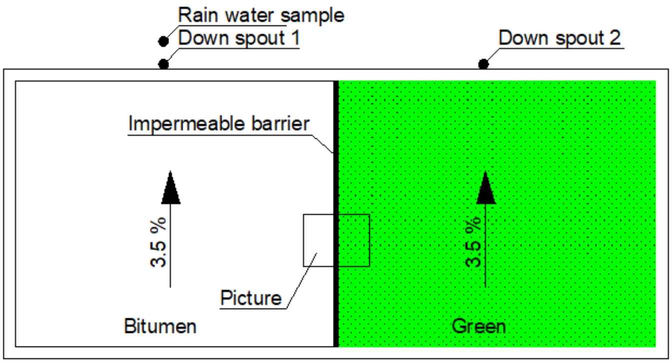


a) For 2012–2022 b) For 2022

Figure 3. Climate data [29]

The average annual precipitation from 2012 to 2022 was 676 mm, and it remained comparable in 2022 with 611 mm. Although in 2022 the total precipitation is near average, the monthly precipitation distribution shows higher variability. In June, the precipitation typically accounts for approximately 13% of the yearly total. However, in 2022, this amount increased to over 26%. Conversely, in March and September, the precipitation decreased from roughly 8% to less than 3%. The temperatures are within the expected range, and no correlation is evident between temperature and precipitation.

The site under investigation comprises a single-story building with a flat roof featuring a 3.5% slope and coated with bitumen. Enclosing the roof are surrounding boards with two drainage pipes. The total area of the roof is 440 m^2. For this study, a watertight barrier separated the roof into two halves, as shown in Figures 4 and 5. Of these, one-half had a green roof coating. The experimental site is devoid of tall vegetation or neighboring buildings that might shade it.



a) Layout

b) Picture

Figure 4. Layout and picture (top view) of the roof

15.11.2021

07.06.2022

21.09.2022

09.12.2022

Figure 5. The green roof condition throughout the study

The green roof type was selected for its low maintenance and ability to be installed on existing buildings due to its lightweight properties. The system comprises four layers: a Vegetation Mat, Peat Substrate, Drainage and Water Storage Element, as well as the Protection and Storage Fleece, which can be seen in Figure 6. The Vegetation Mat consists of approximately eight types of pre-cultivated sedum species and moss and has a depth of 5-7 cm (main species Sedum album L. and Sedum hispanicum). The substrate used in the green roof consists of a blend of mineral and organic components with a pH range between 5 and 7.9, and the water retention capacity is greater than 45%. The Drainage and Water Storage Component is constructed from recycled HDPE with a holding capacity of 77.5 l/m^2. The drainage capacity of this component is 1.41 l/s at a 2% slope and 2.20 l/s at a 5% slope. The Protection and Storage Fleece is utilized to separate the green roof from the waterproofing membrane and can hold up to 2 l/m^2. The green roof was constructed in October 2021, and data collection began in the initial spring season. Throughout the study, the roof underwent regular inspection, but there was no maintenance, i.e., the watering of the roof was only due to the rainfall. “No maintenance” of the roof was an explicit condition of the study.

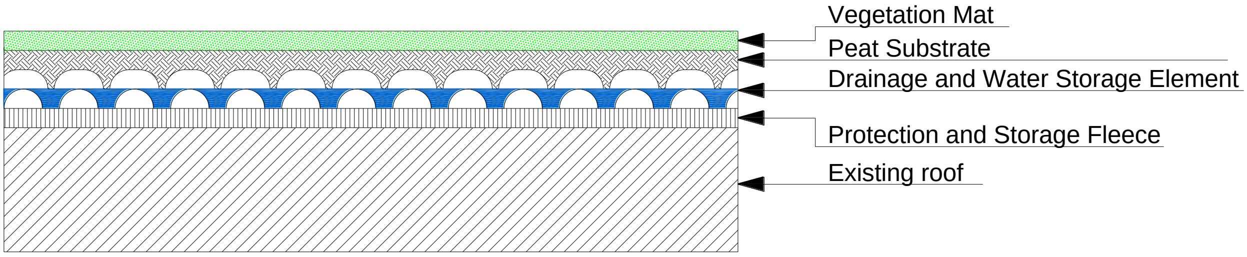


Figure 6. Green roof system layers

2.2. Sampling and Water Quality Analyses

The vertical section of the existing downspouts has been interrupted and left open for outflow, with sampling taking place at their outlet using vertically fixed plastic bottles. This method collects water during significant storm runoff and removes the first flush. In instances of low rainfall, no sampling occurs, as there is no runoff from the green roof. Additionally, a third sample is directly taken from the precipitation that falls. The collection method involves using a plastic container with an attached funnel to increase surface area. This container is positioned 1.5 meters above ground level, directly adjacent to the outlet of the drainage system, as indicated in Figure 4, for purposes of comparison. Before anticipated rainfall, all sampling containers are placed and subsequently sealed the following day to prevent contaminant buildup during dry periods.

After collection, the samples are transported to the university laboratory and stored under refrigeration until the analysis takes place. The monitored parameters were selected based on 1) the most commonly used indicators among the reviewed literature for the current study, and 2) the parameters used in the Bulgarian regulation norms for irrigation. The measured parameters during the experiment and the methods by which they were analyzed are provided in Table 1.

Table 1. Monitored parameters

Analysis	Method/laboratory device	Detection range	Uncertainty
pH	BDS 17.1.4.27-80/Sension+ MM374 Multi Meter pH and EC	0-14	± 0.010
Electrical conductivity (EC)	Sension+ MM374 Multi Meter pH and EC	147-1410 µS/sm	±2%
Turbidity	Laser turbidimeter Hach Lange TU5200	0-700 NTU	±2% (0 – 40) ± 10% (40 – 700)
COD	Spectrophotometrically with Hach Lange DR3900 and COD cuvette test O_2, LCK314	15-150 mg/L	±12%
Ammonium nitrogen (NH_4-N)	Spectrophotometrically with Hach Lange DR3900 and Ammonium cuvette test NH_4-N, LCK304	0.015-2.0 mg/L	-
Nitrate nitrogen (NO_3-N)	Spectrophotometrically with Hach Lange DR3900 and Nitrate cuvette test NO_3-N, LCK339	0,23-13,5 mg/L	±6%
Phosphorus (PO_4^{3-}–P)	Spectrophotometrically with Hach Lange DR3900 and Phosphate (ortho/total) cuvette test PO_4-P, LCK350	2-20 mg/L	±15%

3. Results and Discussion

3.1. Rainfall Events During the Monitored Year

Table 2 presents the sampled rainfall events, the antecedent dry weather days, and the respective total monthly rainfall height.

Table 2. General characteristics of the monitored rainfall events

Date	Antecedent dry period, days	Monitored rainfall events, mm	Total monthly rainfall, mm
20.4.2022	0	11	58
30.4.2022	8	1.2	58
07.6.2022	0	7.4	160
10.6.2022	0	2.4	160
31.7.2022	1	19.2	59
14.8.2022	11	2.1	42
21.8.2022	7	5.6	42
10.9.2022	5	7.8	64
27.9.2022	10	16.65	64
17.11.2022	11	10.2	40
10.12.2022	11	3.8	37.5

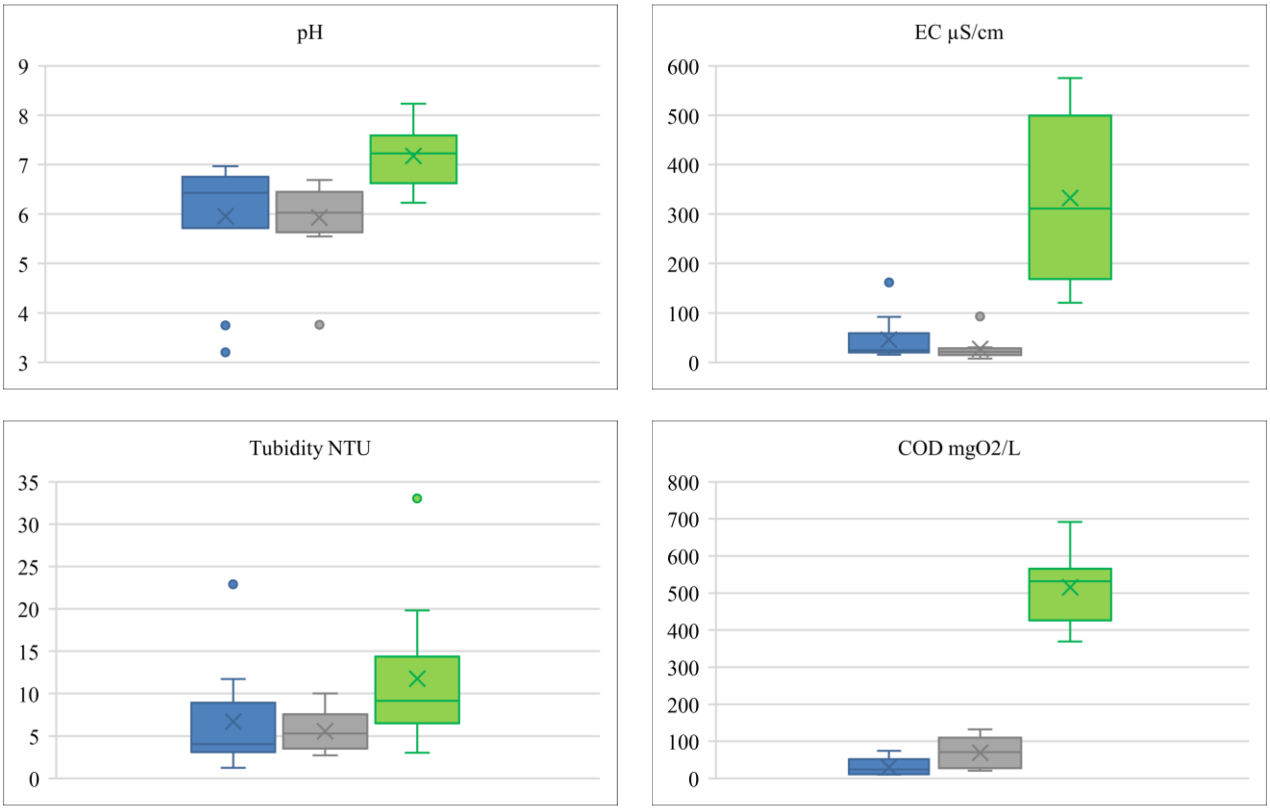
In total, 11 rainfall events were monitored between April and December. The monitored events were selected occasionally, following the weather forecast. They present between 1.5% to over 32% of the respective monthly total rainfall height. The rain sample taken on 30.04.2022 was contaminated and discarded from further analyses.

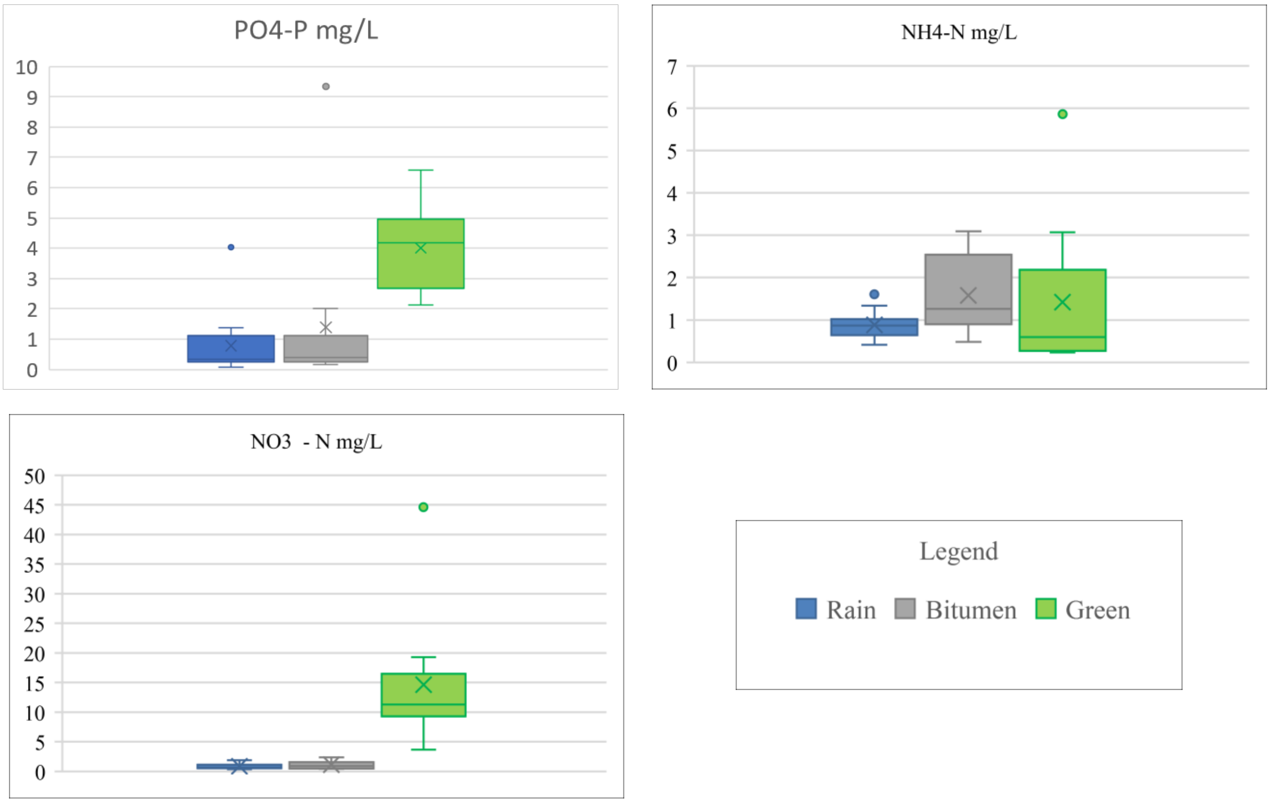
On the 14th of August, due to the small rainfall height, no runoff was registered from the green roof.

3.2. Physicochemical and Chemical Parameters

3.2.1. Comparison of the Quality of The Rainfall and The Runoff from the Two Types of Roofs

Figure 7 presents a summary of the results concerning key water quality characteristics of the rainfall (R), the runoff from the bitumen roof (B), and from the green roof (G) by using box & whisker type diagrams. The lower and upper lines of the boxes show the range of values falling between the 1st quartile (25% percentile) and the 3rd quartile (75% percentile), i.e., the so-called interquartile range (IQR). The end of the "whiskers" shows the minimum and maximum values of the set. The line inside the box gives the median value, and "x" presents the average value of the data set. Extreme values that are too low or too high are presented as dots outside the boxes.





Note: On 20.04.2022, 10.6.2022, and 27.9.2022 the results for PO_4^{3-}-P for R and B are < 0.5 mg/L (below LOQ) and they were taken into account for the calculation of the average value according to Directive 2009/90/EC [30]

Figure 7. Concentration of the studied physicochemical parameters for the rainfall, bitumen and green roofs

pH value

The rainfall is slightly acidic to neutral, with IQR values between 5.7 and 6.8, except for two extreme events with pH values of 3.2 (on 10.06.2022) and 3.75 (on 31.07.2022). The IQR of the bitumen roof runoff has slightly lower values, 5.6 to 6.5, while for the green roof runoff, the range is broader, 6.6 to 7.6. At the rainfall event on 31.07.2022, the pH of the bitumen runoff value dropped down to 3.76, and the green roof runoff also reached the minimum value of the data set, 6.23. In all the monitored cases, the green roof had a higher pH than the pH of the rainfall, while the pH of the bitumen roof was in general lower or equal to the pH of the rainfall (Figure 8). During the two extreme events with acid rain, both roof surfaces seemed to neutralize the acidic precipitation.

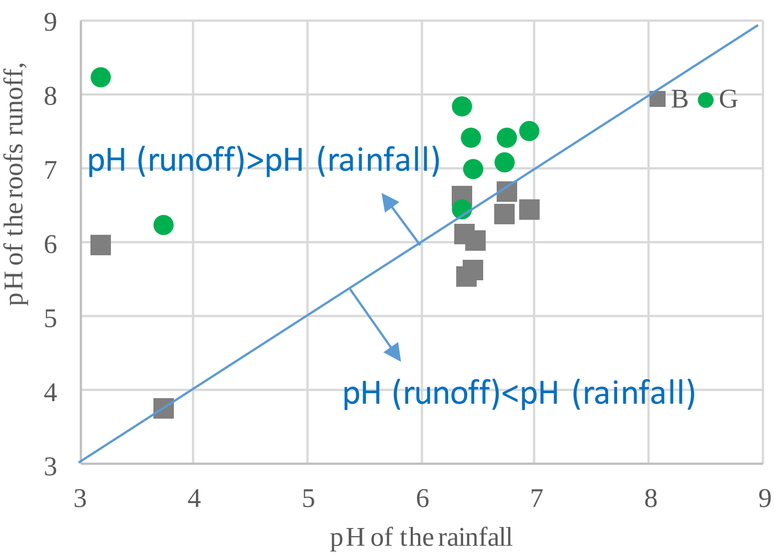


Figure 8. Relation between the pH of the rainfall and the runoff from the two roofs

Electrical conductivity (EC)

This is an indirect parameter of the salinity (total ion concentration) of water and can be strongly influenced by the region [12]. The IQR values of the rainfall were in the range of 20 to 59 µS/cm, except for one extreme event on the 27th of September with an EC value of 161 µS/cm. This event was characterized by relatively intensive rainfall (about 26% of the monthly rainfall height) followed by a 10-day antecedent dry period. The maximum value of the data set, 92.13 µS/cm, was observed on 10th June in a relatively small rainfall event (2.4 mm) with no antecedent dry period and during the wettest month (Figure 3-b). The runoff from the bitumen roof shows quite narrow IQR values between 14.6 and 28 µS/cm. In general, the bitumen roof runoff tends to have EC values closer to or lower than the corresponding values of the rainfall (Figure 9). In contrast, the electrical conductivity (EC) of the runoff from the green roof consistently exceeded that of the rainfall, with a range of 168 to approximately 500 µS/cm (Figure 9). The highest EC concentrations (465 to 575 µS/cm) were observed on the 30th of April, the 21st of August, and the 27th of September. These events are characterized by different rainfall heights but with relatively longer antecedent dry periods (see Table 2). The quite different characteristics of the green roof runoff, for sure, are influenced not only by the climate conditions but also by the specificity of the soil cover and the seasonal characteristics of the vegetation. The longer antecedent dry days seem to result in higher EC values in the runoff from the green roof.

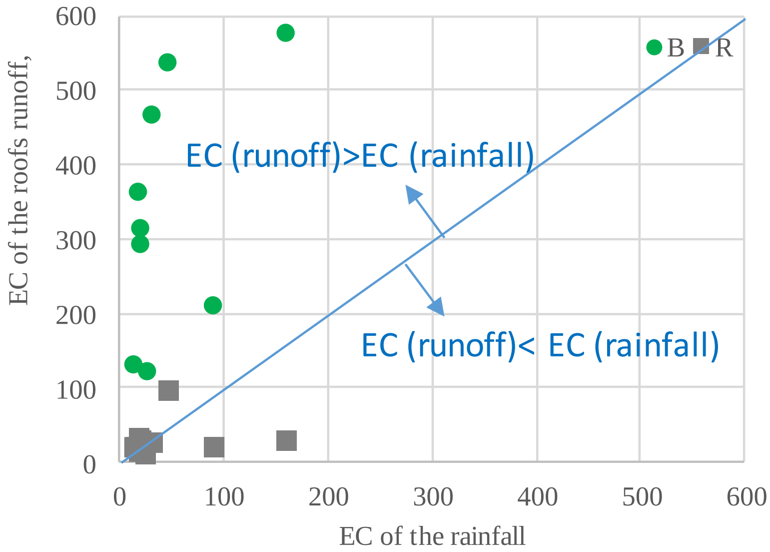


Figure 9. Relation between the EC of the rainfall and the runoff from the two roofs

Chemical Oxygen Demand (COD)

The IQR of the COD concentrations is between 10.40 and 51.6 mg/l. Both bitumen and green roof runoff have higher values and variations of the COD concentrations than the rainfall. As for the bitumen runoff, the IQR boundary values are about double higher (27.9 to 110 mg/l), and for the green roof runoff, several orders higher (IQR between 425.75 and 565.25 mg/l). Concentrations above 500 mg/l are observed almost throughout the year; slightly lower concentrations, i.e., below 400 mg/l, are observed only in two samples: on the 20th of April and the 10th of December. There is no evidently significant effect on the water quality resulting from the antecedent dry period or rainfall height.

While the COD concentrations of the bitumen run-off are close to the limiting value of 125 mgO2/L for a treated wastewater effluent according to Directive 91/271/EEC, the green roof runoff quality for COD is even higher than the typical values for urban raw wastewater, which are in the range of 300 to 500 mg/l [31]. This means that depending on the green roof runoff share of the combined sewer flow, the organic load in the sewer system may be increased, subsequently resulting in higher COD loads at the inlet of the WWTP and thus affecting the treatment process. The green roof runoff should also be taken into account when designing a separate sewerage system and discharging rainwater runoff directly to a surface water body, especially for smaller areas where the green roof runoff may have a higher share and for receiving water bodies in sensitive areas as defined in EU Directive 2000/60 (the Urban Wastewater Directive).

Turbidity

The IQR of rainfall turbidity values falls between 3.1 and 9 NTU, with one exceptional case on the 27th of September reaching 22.89 NTU. The bitumen roof runoff turbidity had a similar IQR of 3.5 to 7.6 NTU, while for the green roof, the corresponding range is broader: 6.5 to 14.4 NTU, with one exceptional case of 33.04 NTU on 30th April. Both exceptional cases (i.e., the rainfall and the green roof runoff) are characterized by long antecedent dry periods (Table 2) but with quite different rainfall heights. For rainfall turbidity up to 5 NTU, both bitumen and green roof runoffs have higher turbidity concentrations, with significantly higher values in the green roof runoff (Figure 10). Although, as mentioned above, extreme turbidity levels were observed at longer antecedent dry periods, there is no clear relation between this factor and the turbidity.

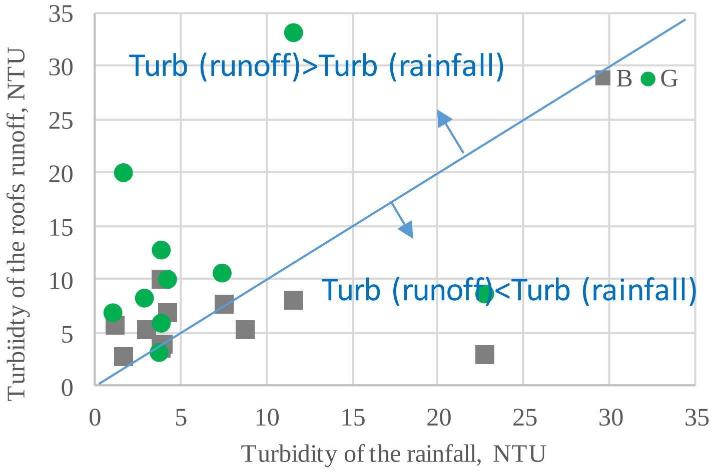


Figure 10. Relation between the turbidity of the rainfall and the runoff from the two roofs

Phosphates as PO4-P

The PO4-P concentrations of the rainwater fall in 0.25-1.11 IQR; the concentrations of the bitumen roof runoff are in the same range. The green roof runoff has a much higher variation of the concentrations, with an IQR between 2.67 and 4.95 mg/l.

During the investigated period, there were 3 rainfall events with PO4-P concentrations below the limit of quantification of the analytical method, which is 0.5 mg/l. The bitumen roof runoff concentrations were also below the limit of quantification. For data processing, these values have been taken as 0.25 mg/l according to Directive 2009/90/EC [30].

Two extreme values were observed during the monitoring period, i.e., on 30.4.2022, the PO4-P concentration in the bitumen runoff reached 9.34 mg/l (8 days antecedent period, 1.2 mm rainfall), and on 7.06.2022, it was measured at 4.03 mg/l PO4-P in the rainfall runoff (0 days antecedent period, 7.4 mm rainfall). There is no evident effect on the influence of the antecedent dry period and the rainfall height.

Both the bitumen roof and green roof have higher concentrations than rainfall (Figure 11). However, the bitumen roof only slightly increases it, while the green roof shows a significant increase. This rule was not valid for only three samples. Similar to the COD values, the green roof may increase the P load at the inlet of the urban WWTPs if it has a significant share of the sewer flows. Depending on the local conditions, the green roof runoff may also deteriorate the quality of the receiving water body.

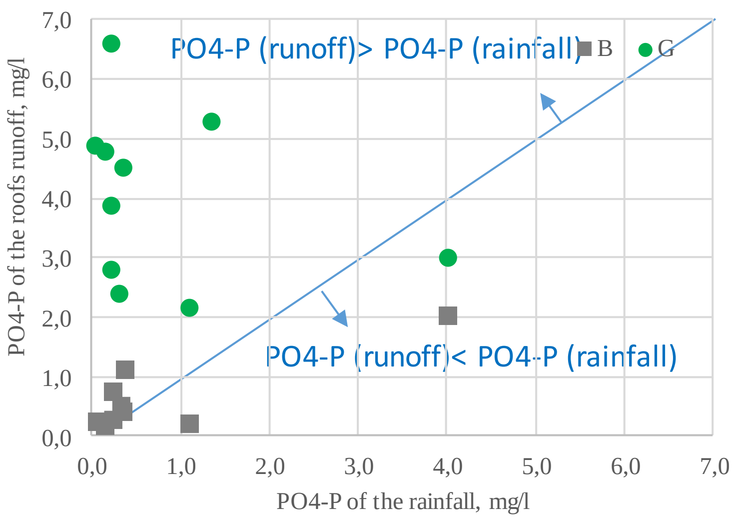


Figure 11. Relation between the PO4--P of the rainfall and the runoff from the two roofs

NH_4-N and NO_3-N

The range of change of NH_4-N in the rainfall water is narrower than the range of change in the bitumen and green roof runoffs. The IQR is as follows: 0.64 to 1.02 mg/l in the rainfall, 0.9 to 2.54 mg/l for the bitumen roof runoff, and 0.27 to 2.18 mg/l for the green roof runoff. Higher values are observed at lower rainfall events, below 10 mm, including two extreme values: 1.61 mg/l in the rainfall (at 2.4 mm rain) and 5.86 mg/l in the green roof runoff (at 1.2 mm rain).

The IQR for NO_3-N is as follows: 0.54–1.1 mg/l in the rainfall, 0.48–1.57 mg/l in the bitumen runoff, and much broader for the green runoff - 9.3 to 16.5 mg/l. The green roof runoff has one extreme value of 44.6 mg/l registered on the 6th of June during a continuous wet period.

There is no clear correlation between the NH_4-N concentrations in the rainfall and the runoff from the roofs. The majority of the values are close to the middle line, indicating that the two roofs do not significantly alter the concentration of NH_4-N (Figure 12). The NO_3 - N concentration from the green roof is higher than in the rain and from the bitumen roof in all samples, with a magnitude of up to 30 times (Figures 7 and 13).

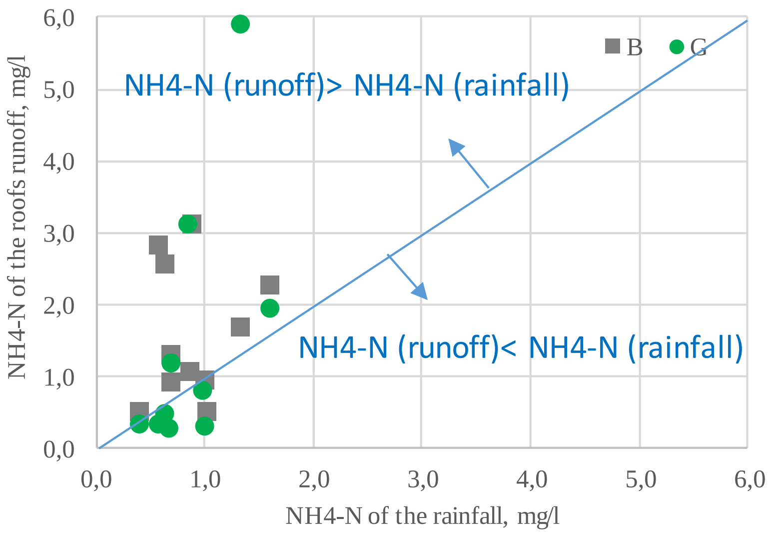


Figure 12. Relation between the NH_4-N of the rainfall and the runoff from the two roofs

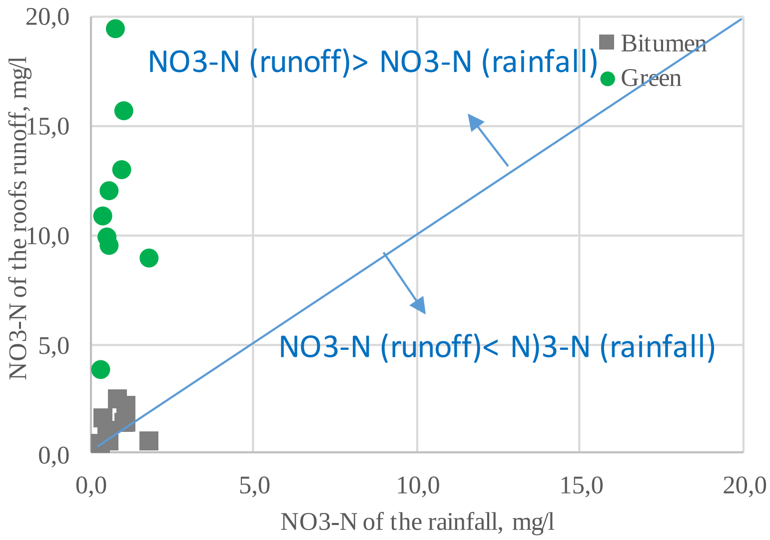


Figure 13. Relation between the NO_3-N of the rainfall and the runoff from the two roofs

The nitrogen concentration (expressed as the sum of NO_3-N and NH_4-N) of the green roof is higher than that of the rain and the bitumen roof in all samples by a factor of 2 to 30.

3.2.2. Comparison of the Experimental Results with Other Studies

The results obtained during the study and compared to other studies and legislation are shown in Table 3.

Table 3. Concentration of the measured physicochemical parameters, ions, along with their descriptive statistics, guideline values, and literature data

	Item	pH	EC µS/cm	Turbidity NTU	COD mgO_2/L	PO_4^{3-}-P mg/L	NH_4^+-N mg/L	NO_3^--N mg/L
R	Average	5.95±1.26	46.06±44.28	6.69±5.94	30.17±20.76	0.78±1.10	0.89±0.33	0.84±0.41
	Median	6.43	24.70	4.05	24.00	0.33	0.87	0.64
	Range	3.2–6.97	15.11–**161.9**	1.24–**22.89**	10.4–**74.2**	0.067–**4.03**	0.415–1.61	0.373–**1.87**
	Literature data	3.7 to > 8	0.02–82.4	below 3–7	2.5–24	0–0.4	0.07 to >1.52	0.07–1.4
	References	[15, 22, 24, 25, 32–34]	[24, 25, 33–35]	[12, 15]	[15, 32]	[22, 25, 33, 34, 36]	[15, 22, 25, 34, 35]	[22, 25, 33–35]
B	Average	5.93±0.77	26.83±23.05	5.57±2.21	68.96±42.21	1.38±2.57	1.58±0.9	1.14±0.64
	Median	6.03	21.02	5.28	70.70	0.40	1.26	0.93
	Range	3.76–6.69	7.67–92.8	2.7–10.01	20.3–**132**	0.151–**9.34**	0.479–3.09	0.408–2.37
	Literature data for non-green types	3.6–11.4	8.3–615	0–40	4–35	0–6.60	0.04–4.00	0.01 to>11.5
	References	[12, 13, 18, 20, 37, 15–17, 22, 23, 25, 38–42]	[13, 17, 18, 20, 37–39, 40, 43–47]	[12, 18, 37, 38, 46, 47]	[48]	[12, 18, 25, 44]	[12, 18, 41]	[12, 13, 18, 25, 39, 48]
G	Average	7.17±0.59	332.6±157.04	11.76±8.29	515.5±93.78	4.01±1.36	1.42±1.72	14.65±10.73
	Median	7.23	311.00	9.15	531.50	4.18	0.60	11.30
	Range	6.23–8.23	120.6–575	3.01–33.04	369–692	2.12–6.58	0.233–5.86	3.66–44.6
	Literature data	below 4.8–8.46	below 88–above 3500	-	2.5–above 700	0.00–13.5	0.0–above 85.6	0.00–above129
	References	[19, 22, 25, 32, 33–35, 49–51]	[19, 22, 25, 33, 34, 49–51]	-	[32, 50]	[22, 25, 28, 33–36, 49, 51, 52, 53]	[19, 22, 25, 35, 50, 38, 52, 53]	[19, 22, 25, 33–35, 50, 52, 53]
Bulgarian norms - water used for irrigation		6–9	<2000	-	<100		<5	<20

Notes:

1) On 20.04.2022, 10.6.2022, and 27.9.2022 the results for PO_4^{3-}-P for R and B are < 0.5 mg/L (below LOQ) and they were taken into account for the calculation of the average value according to Directive 2009/90/EC [30].

2) Values in Bold are those that are outside the literature range.

3) The range of the literature data is taken based on the reported min – max single monitoring values in the refereed studies.

Rainfall quality

The rainfall water quality for pH, EC, and NH_4^+-N falls within the range of reported values from other studies, although the results were obtained in different climate zones and at specific local conditions. Extreme values for EC, turbidity, and PO4-P, several times higher than the maximum values reported in other studies, have been measured in this study. The extreme values of 161.9 µS/cm and 22.89 NTU were registered during one rain event (27.09.2022), which was the one with the highest rainfall height. These values are far away from the range of other measured values (Figure 10). The obtained average value for EC is higher than the median values reported by Zdeb et al. (1 to 4 µS/cm for 2015 and 2016) for a zone with a low level of industrialization [12]. It has to be noted that Sofia, where the current study was carried out, is a highly industrialized zone, which may be the reason for these higher average EC values in the rainfall. Similar comments can be made concerning the PO4-P values. The extreme value of 4.03 mg/l was registered on 7.06.2022, during a wet period. The value is too far away from the range of change of other data, as shown in Figure 11. In general, the PO4-P concentrations in the rainfall seem to be higher than the values reported by other studies, although there were 3 samples (out of 11) with concentrations below the limit of quantification of the analytical method.

Bitumen roof runoff

The values of pH, EC, turbidity, NH_4^-N, and NO_3^-N are within the reported range by other studies. The average results are similar to those observed for other roof surfaces, such as asphalt, ceramic tiles, and asphalt shingles, and slightly lower than those for concrete, asbestos, aluminum, and corrugated iron roofs [17, 20, 25]. The measured COD values are higher than the reported range from other investigators, which also results in an average value (68.96 mg/l) beyond the reported literature data range. Concerning the PO4-P concentration, except for one extreme value of 9.34 mg/l, the other values are in the lower range of reported literature data, i.e., below 1.5 mg/l. The concentration of NO_3-N is comparable to that of concrete and ceramic roofs reported by Zdeb et al., 2020. However, their study includes a single extreme value of more than 10 mg/L from the concrete roof and an even larger one from the rain (more than 20 mg/L) [2].

Green roof runoff

The green roof runoff quality is characterized by the broadest range of values for almost all the parameters, which is also a conclusion reached by other studies. Many complex factors influence the quality of green roof runoff. Therefore, the quality parameters of the green roof runoff will be discussed in more detail.

The pH values are consistent with those reported in other studies, indicating that the various substrate layers used in these studies behave similarly. The results are also comparable to those obtained from a green roof with a substrate of treated sewage sludge [34]. The maximum measured pH value in the green roof runoff is similar to the results of Liu et al. (2021), who reported an average pH of 8.26 obtained by using simulated rainfall (with pH 8.45) and different combinations of vegetation, substrate, load, and slope variations [19].

The average EC values are right in the middle of the reported values from other studies [22–25, 33–35]. Except for Buffam et. al., where the difference in min and max concentrations is several folds [25], the other studies have a range of no more than 3 times the min value [19, 33–34, 50]. In the current study, the range is a bit wider, slightly above 5 times. Although some studies reported changes in time, like Baryla et al.'s higher concentration in the beginning [49] and Buffam et al.'s detection of the lowest concentration in the winter [25], the concentration doesn't seem to vary heavily. So, the average values likely depend heavily on the green system used in the studies and not so much on other factors.

Concerning PO_4^{3-}P there are some variations in the range of values reported by different authors. Some studies report maximum values below 1 mg/L [22, 34, 35, 49, 51, 52], and others report maximum values slightly above 3 mg/L [25, 36, 53]. The current study has measured a maximum value of 6.58 mg/l, which is similar to the reported values by Vijayaraghavan et al. ranging from 6.46 to 13.05 mg/L from a roof with universal garden soil covered with plants [33]. The great variability in the concentrations of the published studies suggests that the leaching of nutrients, particularly PO_4^3, from green roofs can be a concern, especially in the first few years after construction [25].

Buffam et al. (2016) found a significant difference between the median of P from the green roof and the asphalt shingle roof, with the former being 20 times higher [25]. In the current study, this difference is approximately 9 times. The similarity in values between the bitumen and green roofs in some of the measurements may be due to their proximity and potential material transfer between the two sections.

Similar to orthophosphates, the different studies report a significant range of changes in the concentrations of nitrogen compounds. Lim et al. reported high average concentrations of NH_4^+-N and NO_3^--N, respectively, of 53.1+31.5 mg/L and 75.6+53.9 mg/L for commercial substrate covered with vegetation and slightly lower values without plants [34]. Buffam et al., Liu et al., Berndtsson et al., and Todorov et al. report average concentrations below 1 mg/L [19, 22, 25, 52], while other studies, i.e., Cristano et al. and Lim et al., detected maximum values of NO_3^--N at 3 mg/L [50, 53], while Aitkenhead-Peterson et al. reported a maximum value of 6.6 mg/L [35]. The measured values for NH_4^+-N and NO_3^--N in the current study are in the lower boundary of the reported range in the literature.

In general, the monitored chemical parameters from the green roof runoff are significantly higher than those from the bitumen roof. The average concentrations from the green roof exceed the requirements for treated urban wastewater for COD 515 mg/L O_2 (125 mg/L O_2), total phosphorus 4 (1 to 2 mg/L P), and total nitrogen 14.6 NH_4-N +NO_3-N mg/L (10–15 mg/L N) (Directive 91/271/EEC). On average, the green roof has 7.5 times the concentration for COD, 2.3 times for P, and 5.4 times for N (ammonium plus nitrate nitrogen). This shows that in this particular study, the green roof contributes to nutrient pollution compared to the traditional roof material.

3.3. Air Pollution

The pilot area has seasonal air pollution with fine particulate matter 10 (FPM 10) due to its valley topology and the surrounding mountains (Figures 14 and 15). Figure 14 shows that although there is an excess of FPM 10 per year only in 2017 and 2018, all years have a significant number of days exceeding the daily allowable concentration. In 2022, there will be a total of 58 days, and the maximum concentration will reach more than three times the limit values (Figure 16). The majority of the days with high concentration values are in the cold period of the year (Figure 15).

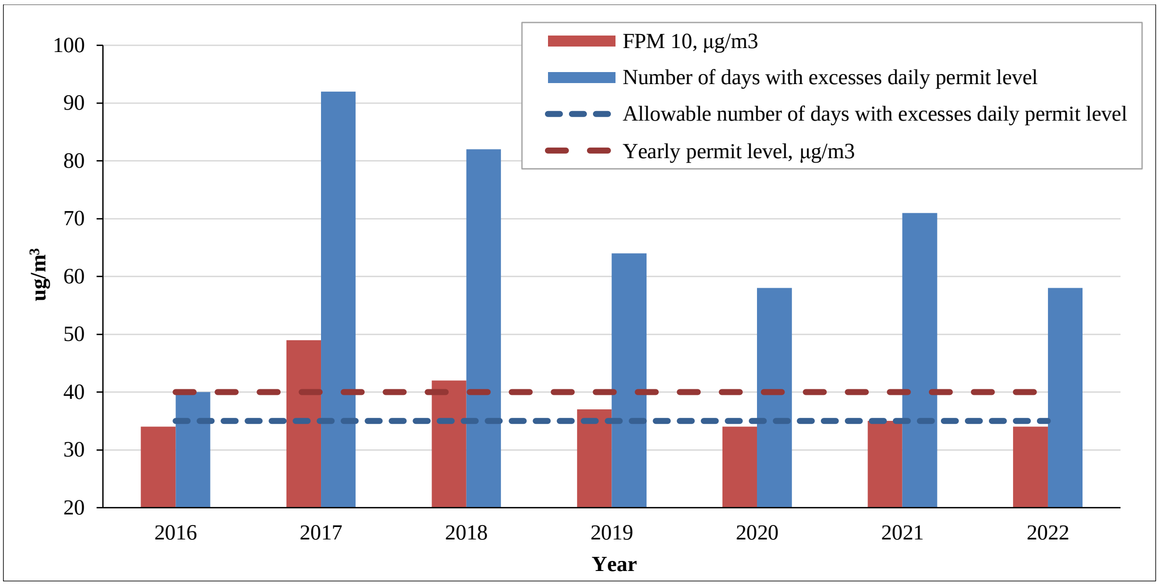


Figure 14. Fine particle matter (FMP) for 2016 to 2022 (processed data from ExEA [54])

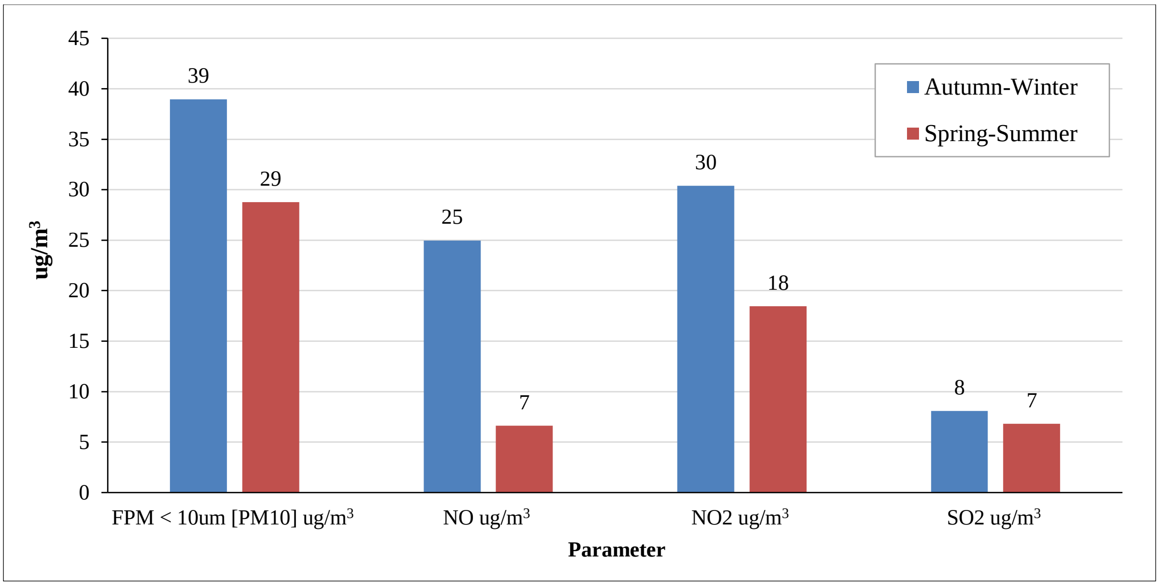


Figure 15. Average seasonal values of air quality parameters in 2022 (processed data from ExEA [54])

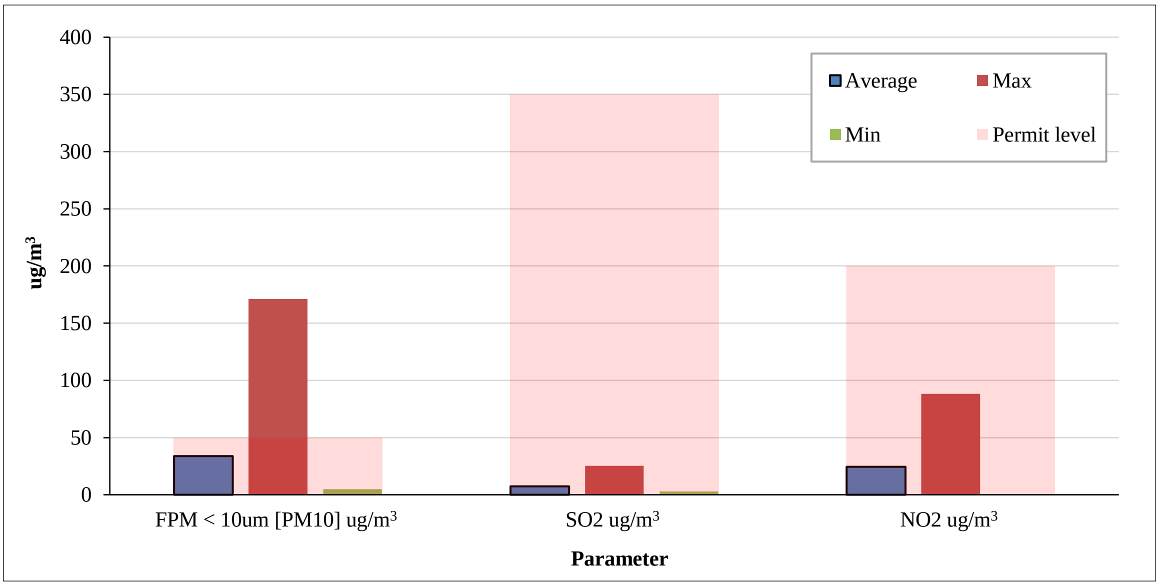
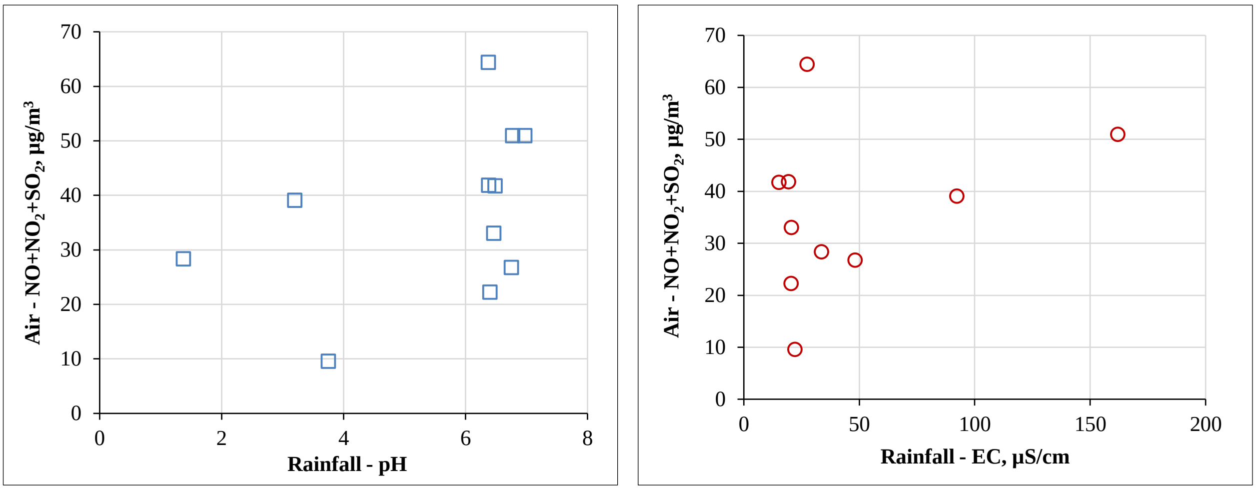


Figure 16. Air quality in 2022 – daily values (processed data from ExEA [54])

The increased air pollution is expected to worsen the rainfall quality due to the accumulation of nitric and sulphuric acids in raindroplets from nitrogen and sulphur dioxide in the air, leading to a change in pH [55]. An accumulation of fine particles in the rain could also lead to an increase in turbidity and EC [56], and in this case study, the obtained data for turbidity in the precipitation is in the upper range of those reported in other studies. On the other hand, accumulated air pollution can be washed out with the first rain event after a longer dry period. That is why the removal of the first flush before sampling and taking samples after a recent rain event can actually negate the effect of the air pollution on the rainfall quality [15, 57]. Even though the first flush was removed in our experiment, rain quality was tested against air quality since Sofia is considered a region with major air pollution in Bulgaria. The relationship between the two parameters is presented in Figure 17. The analysis of the figure is based on the measured values of rainfall quality for pH and EC and the official data reported to the Bulgarian Ministry of Environment and Water on air pollution from the nearest monitoring station.



a) Air $NO+NO_2+SO_2$ to Rainfall pH b) Air $NO+NO_2+SO_2$ to Rainfall EC

Figure 17. Relationship between rain and air quality

Figure 17 does not show a clear relationship between the pH and EC of the rainfall and the sum concentration of air polluting gases $NO+NO_2+SO_2$. A more detailed analysis of this issue necessitates a larger air quality database. The reuse of harvested water requires stable runoff quality. To avoid quality variations due to external factors such as air pollution or consecutive dry days, it is good practice to remove the first flush.

4. Conclusion

The study compared the quality of rainfall with the run-off water collected from two types of roofs: green roofs and bitumen roofs.

Both types of roofs neutralize acidic precipitation below pH=4. However, there is a significant difference between the run-off from green roofs and that from bitumen roofs in terms of EC, turbidity, COD, P, and N. The samples collected from the green roofs showed the highest values of EC and turbidity compared to the rain and bitumen runoff. In some samples, the rain and bitumen runoff have higher values of turbidity, NH_4^+-N, and PO_4^{3-}-P, indicating that the green roof could reduce the pollution accumulated in the air during rainfall. In addition, the study found that while the green roof reduced runoff, it increased average concentrations of COD, the sum of ammonium and nitrate nitrogen, and P compared to the bitumen roof. As a result, the non-treated runoff from the green roof may contribute to higher nutrients and organic loads in the sewerage system, as well as not be suitable for non-potable water reuse, such as toilet flushing and clothes washing. However, due to its high levels of P and N, it may be suitable for irrigation or fertilization.

The bitumen roof runoff has a similar concentration to the monitored parameters, like other traditional materials like asphalt, ceramic tiles, concrete, asbestos, aluminum, and corrugated iron roofs, except for the COD, where the measure concentration is higher.

The study's findings suggest that there are unknown factors that can spontaneously and significantly affect concentrations in rain or runoff, as evidenced by the extreme concentrations detected in comparison to average values in this study and reported in the literature. There is a wide variety of green roofs, including different substrates, vegetation, vegetation cover, depth, and slope. All of these factors play a role in the runoff quality and can lead to significant variations in the monitored parameters. The study also investigated the effect of air pollution, specifically nitric and sulphur dioxides, as well as fine particles, on rainfall quality. No clear link between air pollution and rainwater quality was found. This is in line with the findings on the topic from previous studies. To better understand the relationship between air and rainfall quality, it would be necessary to monitor all precipitation events and acquire more data, as well as analyze the first flush, the fluctuations in the quality in the periods after it, and the rain quality of the first rain event after prolonged droughts.

5. Declarations

5.1. Author Contributions

Conceptualization, E.T., I.R., D.V., and G.D.; methodology, E.T. and I.R.; software, E.T. and D.V.; validation, E.T., I.R., D.V., and G.D.; data curation, E.T. and D.V.; writing—original draft preparation, E.T. and D.V.; writing—review and editing, I.R. and G.D.; visualization, E.T.; supervision, I.R.; project administration, G.D.; funding acquisition, I.R. and E.T. All authors have read and agreed to the published version of the manuscript.

5.2. Data Availability Statement

The data presented in this study are available on request from the corresponding author.

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5.5. Conflicts of Interest

The authors declare no conflict of interest.

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