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Article

Changes in Stormwater Quality and Heavy Metals Content along the Rainfall–Runoff Process in an Urban Catchment

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Abstract: Stormwater quality in an urban watershed can be influenced by several factors, including land use patterns, atmospheric deposition, and human activities. The objective of this study was to investigate spatial and temporal changes in stormwater quality and heavy metal content during the rainfall–runoff in an urban sub-catchment (30 ha) in the town of Olsztyn (NE Poland). Samples were collected from six locations along the rainfall–runoff pathway, including the following direct rainfall and runoff locations: roof runoff, surface runoff, storm collector, and the river. Parameters such as pH, specific conductivity, fluorescent dissolved organic matter (fDOM), total dissolved solids (TDS), and turbidity were measured in situ, while samples were analyzed for heavy metal content (Cu, Cr, Fe, Ni, Zn, and Pb) in the lab (ICP-OES). The results showed significant changes in water quality along the runoff. The highest concentrations of heavy metals were found in samples from a stormwater collector and surface runoff, particularly in winter and spring, due to the increased deposition of air pollutants and salt washout from roads. This study highlights the importance of monitoring stormwater quality and heavy metals in urban watersheds in terms of impacts on the river ecosystem as a recipient of stormwater. Solutions such as green infrastructure and stormwater management are proposed to mitigate the impacts of urbanization on water quality and protect the aquatic environment.

Keywords: runoff; urban catchment; rainwater; impermeability; blue–green infrastructure

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1. Introduction

Progressive urbanization is an inevitable process that accompanies the development of urban areas [1]. Intensive urbanization brings about a number of changes in shaping the environment [2]. One of them is the increase in impervious surfaces [1,3–5], which disrupts the water cycle [6] and thus the water balance [7]. In urban watersheds, the problem is also the increase in areas where mineral and organic pollutants are deposited [8,9]. As a result of rainfall, sediments are washed away and eventually enter surface water ecosystems, especially rivers and lakes, through stormwater drainage systems [10,11].

The physical parameters that characterize a watershed and determine the rainfall–runoff are mainly substrate permeability and land use. The quality is also affected by rainfall characteristics, especially intensity, duration, and the number of antecedent dry days [12].

In the rainfall–runoff process, it is important to know the path that stormwater takes before it flows into surface waters such as rivers and lakes. Rainwater already absorbs pollutants during the atmospheric phase of the hydrologic cycle [13]. After contact with the surface, it then forms a runoff in which the pollutant concentration gradually increases along its path, reaching a maximum value when the drainage system is connected to the receiving water. Under natural conditions, where most of the surface is permeable, the process of infiltration occurs. Infiltration is an essential process in the natural hydrological cycle and contributes to about 50% of the water balance [14]. The infiltration process is an essential factor that supports natural filtration by allowing the migration of pollutants and thus their purification [10]. The water cycle is disturbed in urban areas where impermeable surfaces predominate. Due to the limited infiltration (15%) and increased surface runoff (55%), the outflow of water from the catchment area through the storm sewer system directly into the water reservoir is accelerated and increased [14]. The natural process of water purification no longer occurs. Moreover, the sewer infrastructure cannot clean such an amount of surface runoff [10]. As a result, the pollutant load directly enters the ecosystem, where the biotic elements are vulnerable to acidification and pollution, especially by heavy metals [15–21]. Aquatic ecosystems are exposed to heavy metal pollution as pollutants are deposited on sealed surfaces due to increased vehicle traffic and industrial and agricultural activities. Elevated concentrations of heavy metals in the aquatic environment pose a disease risk to living organisms, damage the flora of aquatic habitats, and, in extreme cases, can lead to infections and human diseases. In watersheds where the impervious surface rate exceeds 25%, runoff is unstable and contributes to the degradation of watercourses that receive pollutants [22].

Under the climatic conditions of areas with distinct seasons, such as the temperate transitional climate in Central Europe (Dfb type according to the Köppen classification [23]), it should be emphasized that the increase in water pollution is seasonal. In the winter half-year (November–April), the environment is polluted mainly by substances released into the atmosphere with combustion (heating of houses with gas or coal stoves), salinization of road surfaces, and increased exhaust emissions. During the summer half-year (May–October), the amount of plant pollen on wash surfaces and in the atmosphere increases, as does the pollution of road surfaces due to direct contact of tires with the road surface.

Due to the increasing disruption of the water cycle and the associated environmental impacts, it is crucial to take measures that can increase the opportunity for stormwater infiltration. Blue–green infrastructure (BGI) solutions, the idea and principles of which have been presented in the European Commission documents [24–27], serve this purpose. BGI, recognized as a crucial component of sustainable stormwater management in cities [28], is a set of solutions and strategies that include natural solutions (wetlands, ponds, rivers) and engineered systems (underground systems, infiltration wells) that provide ecological, landscape, economic, social, and environmental benefits [29,30]. Nature-based solutions (NBS) are also recognized as a multidisciplinary elements that combine social benefits with nature [31]. In recent years, the interest in such solutions has increased [29]. As a result, the concepts of NBS and BGI solutions are being incorporated into educational programs, and local communities are being involved in projects (e.g., ATeNaS [32], REACHOUT [33], Clearing House [34]). To incorporate stormwater NBS into urban watershed management plans and convince decision-makers, the need for such actions must be justified. Therefore, it is necessary to analyze the changes in the physical and chemical properties of stormwater along the runoff route from the urban catchment.

The objective of this work is to present the changes in selected stormwater quality characteristics and to demonstrate changes in pollution levels in the rainfall–runoff system, considering direct rainfall, roof runoff, surface runoff, stormwater collector, and river water as direct recipients of stormwater. In this work, the following hypotheses were tested: (i) stormwater that is not pretreated poses a threat to river water quality and (ii) stormwater quality changes as a function of land use, rainfall frequency (number of dry days before rain), and season. This study provides information regarding the state of a medium-sized urban environment, which may serve as an initial step toward the establishment of a program aimed at enhancing hydrological relationships within the urbanized area.

2. Materials and Methods

2.1. Study Area and Sampling Sites Locations

The study was conducted in the urban sub-catchment of Olsztyn (NE Poland), a city located on the Łyna River, the largest river in the Masurian Lake District (Figure 1).

Olsztyn is a city with an area of 88.33 km^2 (Central Statistical Office). Olsztyn is located in a temperate climate zone, with no dry season and a warm summer (Dfb) [23]. During the study period, the average air temperature was 9.7 °C; July was the warmest month (21.9 °C), while December was the coldest month (−1.5 °C). The total sum of precipitation was 747 mm, and the average relative humidity was 85%. The highest air temperature measured during the study period was 35 °C (in June), and the lowest temperature was −14.1 °C (in December).

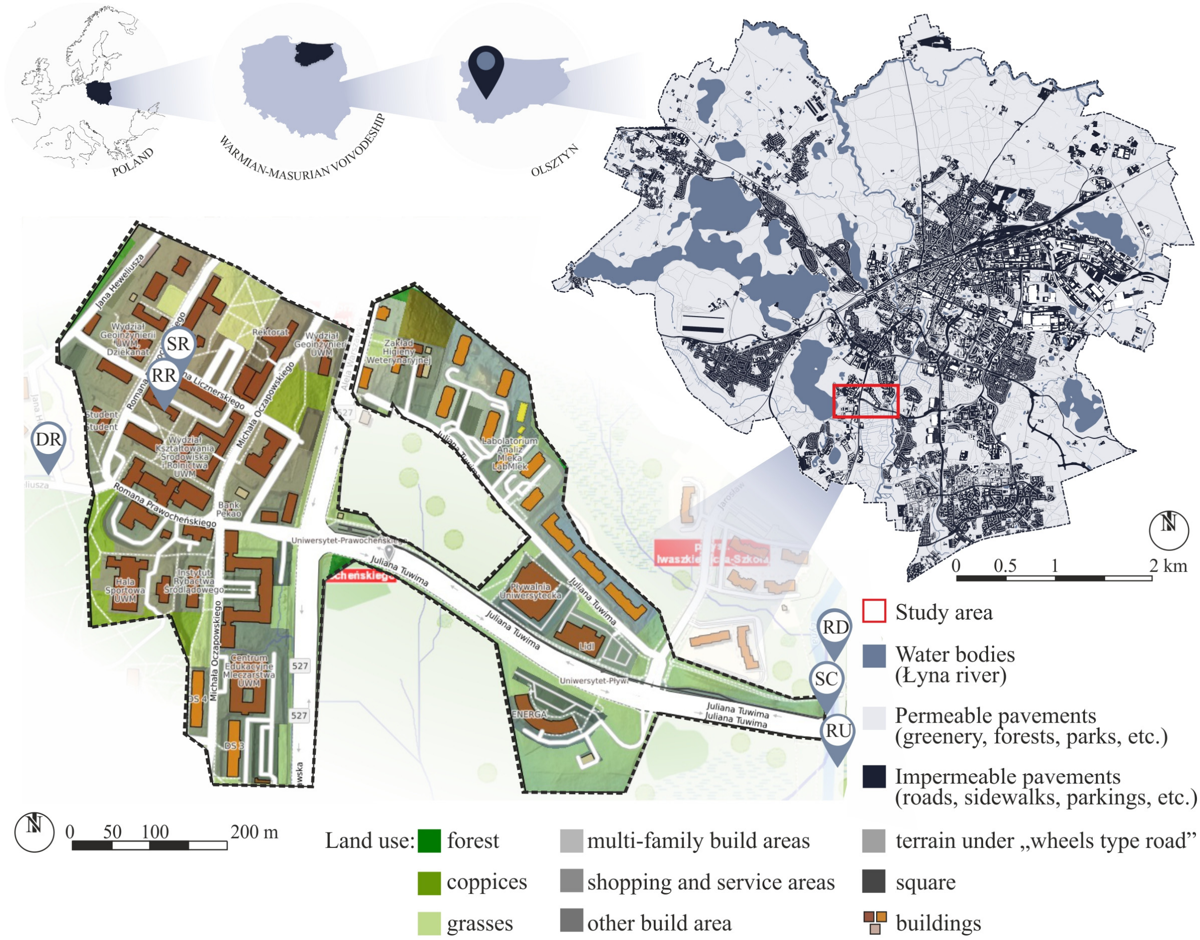

Figure 1. Location of the study area. Permeability structure of the city of Olsztyn and 30 ha study area. Own elaboration of authors based on SCALGO Live.

The mosaic of landforms, rich in moraine hills at an altitude of 88 to 154 m above sea level, and landscape depressions were formed after the Baltic Ice Age. The depressions are usually filled with water from lakes or wetlands or are dried up with drainage. The structure of land use in the city of Olsztyn is diverse: almost 45% of the area is anthropogenically used, 19% is agricultural, 28% is forest and woody vegetation, and 8% is covered by water bodies [35]. There are 15 lakes and 4 watercourses within the administrative boundaries of the city. The main recipient of rainwater from the city area is the Łyna River. The river is the most important watercourse in the region with a total length of 264 km and a catchment area of 7126 km^2. The city of Olsztyn is located in its upper part, about 45 km north of the headwater area. Due to the high retention rates of the catchment (sandy soils, forested areas, and lakes), the river is hydrologically stable and does not pose a flood hazard to the city [36]. The mean flow at the Olsztyn (Kortowo) site during 1971–2021 was 3.72 m^3/s, with a low mean flow of 3.12 m^3/s and a high mean flow of 4.40 m^3/s.

A stormwater drainage network with a catchment area of 30 ha was selected for this study. It is characterized by diversified land use, a predominance of built-up areas (58%), and traffic areas (13%). The northern part of the study area includes the university campus, while the central and southeastern part is dominated by traffic areas along the city's two main roads. The land use pattern of the studied area is shown in Figure 1. Impervious surfaces occupy approximately 76% of the study area. The permeability classification was based on a detailed map of land development and field views. Permeable surfaces included lawns, greenways, parks, and woodlands. Roads, sidewalks, parking lots, and buildings were classified as impervious [37–39].

Water samples for the analysis of quality parameters were collected from six locations in the southwestern part of Olsztyn (Kortowo). The following sampling sites are shown in the diagram (Figure 2): direct rainfall (DR); roof runoff (RR); surface runoff (SR); upstream (RU); storm collector (SC); and river downstream of the collector (RD). Table 1 provides an overview of the micro-catchments considered in this study.

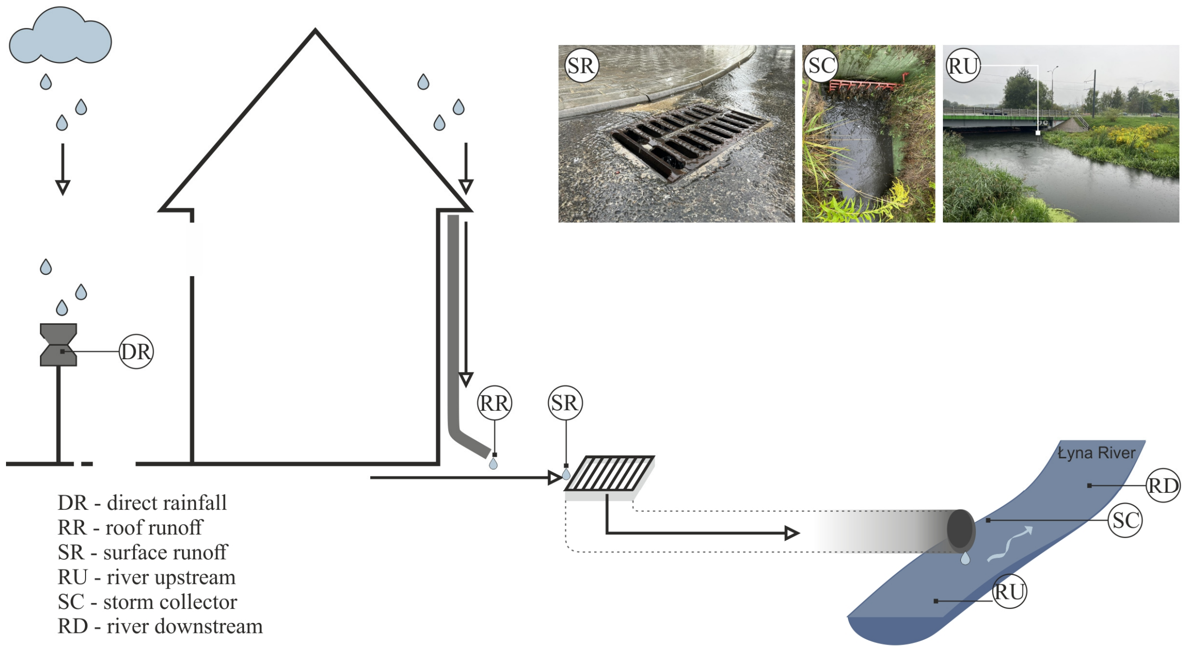

Figure 2. Scheme of sampling site location.

Table 1. Detailed information about sampling sites.

Sampling Site	Area of Urban Sub-Catchment (ha)	Materials/Land Use	Runoff Coefficient, C	Details
RR	0.012	Ceramic tile	0.90	Three gutters drain the roof area
SR	0.279	Asphalt and cobblestones	0.80–0.90	Includes internal roads within the campus area
SC	30.000	Diversified land use:		Storm collector outlet: ϕ630 mm
		Asphalt and cobblestones (47%)	0.80–0.90	Flat residential, with ca. 60% of impervious area
		Grass (20%)	0.30	Roadside green belts, lawns
		Roofs (16%)	0.75–0.95	Residential and service buildings
		Asphalt (13%), i.e., traffic areas	0.70–0.85	The main street (Tuwima, Warszawska) and side roads
		Parks and woodlands (4%)	0.10–0.30	Group of trees

2.2. Sampling and Analytical Procedures

All samples were collected from rainfalls from March 2021 to September 2022. Only rainfalls with a sum of >0.1 mm were included in this study. Samples of direct rainfall were collected at the meteorological station on the campus of the University of Warmia and Mazury (100 m from the study area). Runoff samples were collected at the edge of the gutter (RR), at the edge of the storm drain embedded in the road (SR), and at an outlet of the storm collector pipe (SC), from where the runoff was discharged directly into the river channel. For comparison purposes, river water was collected both downstream (RD) and upstream (RU) of the storm collector outlet at a distance of ca. 30 m, which was sufficient for mixing the discharge water with the river water. Table 2 provides a characteristic of the 12 rainfall events monitored throughout the study period.

Table 2. Characteristics of rainfall events during the study period.

Event No.	Date	Rainfall Amount (mm)	Average Rainfall Intensity (mm/h)	ADP (d)
1	12 March 2021	0.9	0.31	0.75
2	16 May 2021	2.5	2.58	5.50
3	22 June 2021	21.7	19.73	9.63
4	24 June 2021	3.8	3.80	1.50
5	2 July 2021	32.6	2.45	7.50
6	6 August 2021	54.9	2.44	1.54
7	30 September 2021	1.2	1.00	5.00
8	31 December 2021	5.5	0.54	6.25
9	9 February 2022	3.4	0.32	0.50
10	4 April 2022	1.1	0.97	40.25
11	9 June 2022	7.2	1.20	7.75
12	9 September 2022	8.5	2.36	10.70

Note: ADP—antecedent dry period.

Sampling was initiated as soon as roof runoff began (defined as time 0 min). Samples were collected at each of the 5 sites at 10 min intervals. Sample collection was discontinued after gathering water from all sampling points (70–80 min after the onset of roof runoff). A total of 4 samples were collected from the roof each time (at the start of roof runoff, at 10, 20, and 30 min). In addition, bulk samples of direct rainfall (DR) were collected during rainfall. A total of 108 samples were collected manually. Samples were collected in 1500 mL polyethylene (PE) bottles (APHA 2017), labeled, and transported to the laboratory for analysis within 1–12 h. At each sampling point, pH, specific conductance (SpCond), fluorescent dissolved organic matter (fDOM), total dissolved solids (TDS), and turbidity of water were measured using a calibrated YSI EXO2 multiparameter probe (YSI, a brand of Xylem, Yellow Springs, OH, USA). In the laboratory, water samples were digested in nitric acid using a Multiware 3000 microwave oven (Anton Paar, Graz, Austria) and filtered with membrane filters (0.45 μm). Heavy metal concentrations were determined with atomic emission spectrometry using ICP-OES (ThermoFisher, Waltham, MA, USA). The calibration procedure was performed using a multi-element standard (Merck KGaA, Darmstadt, Germany) [40].

2.3. Meteorological Data Source and Analyses

During the study period, meteorological data were collected from a calibrated meteorological (weather) station operated by the Department of Water Management and Climatology (the University of Warmia and Mazury in Olsztyn, Poland). The following meteorological parameters were used: rainfall intensity (mm), air temperature (°C), and humidity (%). As an explanatory variable, the length of the antecedent dry period (ADP) was considered as the number of days without rainfall events >0.1 mm (d) prior to analysis.

Rainfall events that have been analyzed according to the Chomicz classification [41] include moderate rain (8 events), heavy rain (2 event), and driving rain (2 events). The degree of unevenness was indicated based on the unevenness of the rainfall index (I_{un}) as follows:

$$I_{un} = \frac{\sum_{i=1}^{i=12} \left| R_i - \frac{R_r}{12} \right|}{R_r} \cdot 100, \quad (1)$$

where R_i is the monthly sum of rainfall [mm]; R_r is the annual rainfall [mm].

2.4. Statistical Analysis

The normal distribution of the physicochemical data and environmental variables were checked using the Shapiro–Wilk test ($p < 0.05$). Samples identified as extreme outliers were not included in further statistical analyses. Spearman's correlation coefficients and basic descriptive statistics were determined. Correlation was determined to test the relationship between heavy metal concentrations with the ADP. Nonparametric analysis of variance (Kruskal–Wallis test and Dunn's test as a post hoc procedure) was used to test differences in contaminant concentrations between sampling sites. Seasonal variability of roof runoff samples collected at 10 min intervals was also evaluated. The procedure was performed using Statistica 13 software (TIBCO Software Inc., Palo Alto, CA, USA).

3. Results

3.1. Rainwater Characteristics

The annual rainfall sum was 677 mm in 2021, while it was 487 mm in 2022 (Figure 3). During the study period, the total rainfall sum amounted to 747 mm. The highest recorded rainfall occurred in August 2021 (183 mm), while no rainfall was recorded in March 2022. Total rainfall was assessed as highly uneven (I_{un} = 73%) in 2021 and as moderately uneven (I_{un} = 51%) in 2022.

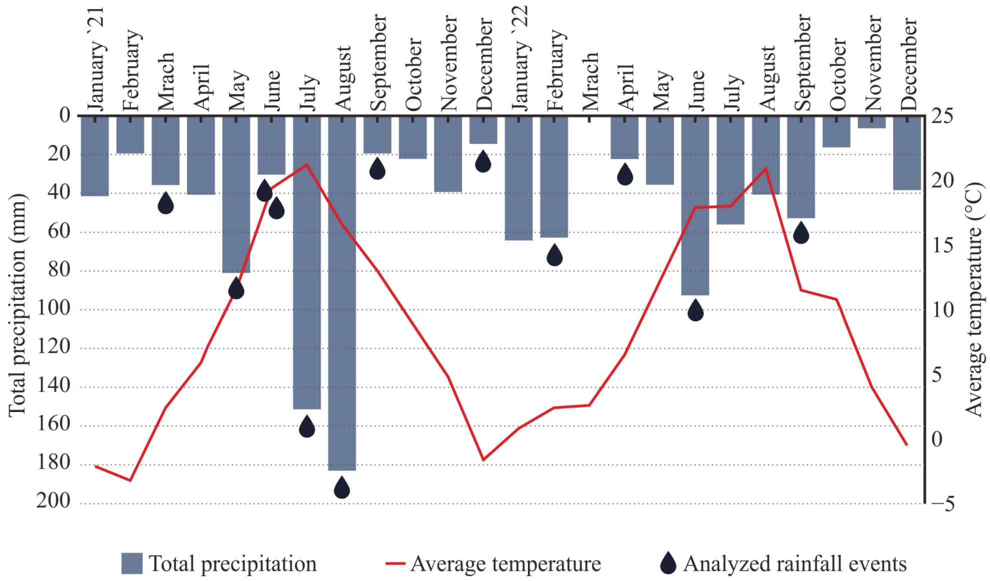

Figure 3. Monthly rainfall sums and average monthly air temperatures in 2021–2022 in Olsztyn, Poland.

3.2. Water Quality Parameters during Rainfall–Runoff Process

Significant differences (one-way ANOVA, Dunn's test at $p < 0.05$) in stormwater quality between natural sampling sites (direct rainfall (DR) and river upstream (RU)) and samples directly supplied from impervious surfaces or influenced by anthropogenic factors (roof runoff (RR), surface runoff (SR), storm collector (SC), river downstream (RD) were stated (Table 3). The lowest pH values were obtained for roof samples (RR), and the highest pH values were found in the samples from the SC. Due to the different weather conditions during rainfall events and the different sampling sites, the electrolytic conductivity covered a wide range of values from 4.36 to 5607.87 µS/cm (Table S1). The lowest value of TDS was found in the RR (3.25 mg/L), while the highest in the sample from the SC (3645 mg/L). Average values for this parameter tend to increase in the direction of stormwater outflow to the river. For turbidity, the lowest and highest values were measured in the samples from the RR and SR (0.57 NTU and 336.85 NTU, respectively). The average value was the lowest in RU samples and the highest in SR samples. The lowest average content of fDOM in effluent was found in the DR (14 QSU) and the highest in the SR (126.8 QSU).

Table 3. Physicochemical parameters (pH, SpCond, TDS, Turbidity, and fDOM) and concentrations of heavy metals (mean $\overline{x}$ (µg/L), ± standard deviation, *SD*) in the studied urban catchment. Differences between sampling sites according to one-way ANOVA. Various letter symbols denote groups of means differing significantly in Dunn's test ($p < 0.05$).

		DR (n = 12)	RR (n = 48)	SR (n = 12)	SC (n = 12)	RU (n = 12)	RD (n = 12)
pH	Median	5.72 ^{a}	6.22 ^{ab}	6.83 ^{b}	7.79 ^{b}	7.46 ^{b}	7.32 ^{b}
	±*SD*	0.72	0.58	0.44	0.44	0.39	0.38
SpCond	$\overline{x}$(µS/cm)	28.0 ^{ab}	73.0 ^{b}	244.3 ^{cd}	1439.5 ^{d}	342.1 ^{cd}	368.2 ^{cd}
	±*SD*	15.6	113.0	324.5	1604.3	27.1	76.6
TDS	$\overline{x}$ (mg/L)	20.5 ^{a}	48.9 ^{a}	197.3 ^{ab}	935.7 ^{c}	236.2 ^{b}	247.5 ^{b}
	±*SD*	9.8	72.9	297.9	1084.5	23.0	46.5
Turbidity	$\overline{x}$ (NTU)	6.8	13.3	83.4	76.7	6.0	9.2
	±*SD*	8.3	34.7	97.2	57.7	5.0	5.4
fDOM	$\overline{x}$ (QSU)	14.0	68.8	126.8	70.6	46.9	49.3
	±*SD*	19.1	103.0	81.5	52.9	16.2	22.3
Cu	$\overline{x}$	5.0	27.2	37.1	92.2	3.7	6.9
	±*SD*	5.6	41.7	45.2	85.9	2.6	4.3
Cr	$\overline{x}$	5.1	4.8	19.4	63.9	4.9	6.4
	±*SD*	3.6	3.8	30.9	62.8	3.8	3.6
Fe	$\overline{x}$	144.4 ^{a}	221.1 ^{abc}	5668 ^{cd}	11,835 ^{d}	665.2 ^{cd}	945.6 ^{cd}
	±*SD*	126.8	250.8	14,450	19,941	294.3	386.7
Ni	$\overline{x}$	4.7 ^{a}	4.9 ^{a}	12.3 ^{b}	36.7 ^{c}	2.4 ^{a}	4.4 ^{a}
	±*SD*	3.3	4.8	13.4	30.4	1.4	2.6
Zn	$\overline{x}$	108.8 ^{ab}	2330 ^{c}	231.4 ^{ab}	856.8 ^{abc}	7.3 ^{a}	11.7 ^{a}
	±*SD*	51.1	2992	484.4	1217	7.4	7.0
Pb	$\overline{x}$	7.4 ^{a}	8.3 ^{ab}	25.0 ^{cd}	35.4 ^{d}	5.6 ^{ab}	5.5 ^{ab}
	±*SD*	4.2	8.1	34.3	40.0	4.9	4.9

Notes: SpCond—specific conductance; TDS—total dissolved solids; fDOM—fluorescent dissolved organic matter.

The average concentration of metals in the samples of the studied locations on the runoff route is presented in Table 3. The lowest heavy metal concentrations were found in direct rainfall samples. Among the runoff-generating surfaces (roof runoff (RR), surface runoff (SR), storm collector (SC)), the lowest average concentrations of Cu, Cr, Fe, Ni, and Pb were found in the samples from the roof. The SC samples have the highest metal concentrations except for Zn. The highest Zn concentration was found in the RR samples, which may be related to the material the gutter is made of (galvanized pipe). The average concentrations of Cu and Ni were twice as high in samples from the storm collector (SC) as in the surface runoff (SR). At the same time, the concentration values for Cr, Fe, and Ni increased almost three-fold. Considering the possible influence of stormwater runoff on the water quality of the Łyna river, slightly higher values of the analyzed parameters were found downstream (RD) rather than upstream (RU) from the SC. However, no statistically significant differences were found.

3.3. The Impact of Antecedent Dry Period on Heavy Metal Concentrations

The frequency of rainfall affects the concentration of metals in an urban catchment. The surface from which the samples are taken is also important. Table 4 shows the relationship between the metal concentration and the length of the dry period using the samples from the RR as an example. The relationship between heavy metal concentrations and the ADP values ($p < 0.05$) showed that the concentration of metals on the roof surface increases with the length of the rain-free period. This dependence is most evident during the winter half-year. The highest correlation coefficients for roof runoff were stated for Ni (r = 0.89; $p < 0.01$), Zn (r = 0.88; $p < 0.01$), Cr (r = 0.73; $p < 0.01$), Fe (r = 0.68; $p < 0.01$), and Pb (r = 0.51; $p < 0.05$). In the summer half-year, the correlations between heavy metals and the ADP were significant in the case of Pb (r = 0.48; $p < 0.05$) and Ni (r = 0.44; $p < 0.05$).

Table 4. Correlation coefficients between metal concentrations (µg/L) and the number of dry days. ADP (d)—roof runoff in winter and summer half-year.

		Cu	Cr	Fe	Ni	Zn	Pb	ADP
Winter half-year	ADP	0.02	0.73 **	0.68 **	0.89 **	0.88 **	0.51 *	1.0
Summer half-year	ADP	0.24	0.23	−0.38	0.44 *	0.29	0.48 *	1.0

Notes: ADP—antecedent dry period (d); *—Spearman's correlation coefficient statistically significant ($p < 0.05$); **—Spearman's correlation coefficient statistically significant ($p < 0.01$).

3.4. The Impact of Seasons on Stormwater Quality

Rainwater samples from the roof collected at 10 min intervals were analyzed by season. The results of the ANOVA analysis (Figure 4) showed that the washout of settled particles by rainwater from the roof surface is the highest during the first 10 min of a rainfall event, regardless of the season. In the following time intervals, the roof runoff contains less and less pollutants (no statistically significant differences at $p < 0.05$). Mineralization of water, expressed by specific electrical conductivity, was the lowest in winter (average 47 µS/cm), when snowmelt and frequent rainfalls diluted the water. The highest SpCond values were found in roof runoff samples collected in the spring. Due to direct washout of dry deposition, especially after 40 days of rainless periods in March and April 2022, samples collected from the RR during the first 10 min were characterized with SpCond > 400 µS/cm, followed by samples collected between 10and 20 min with SpCond > 100 µS/cm.

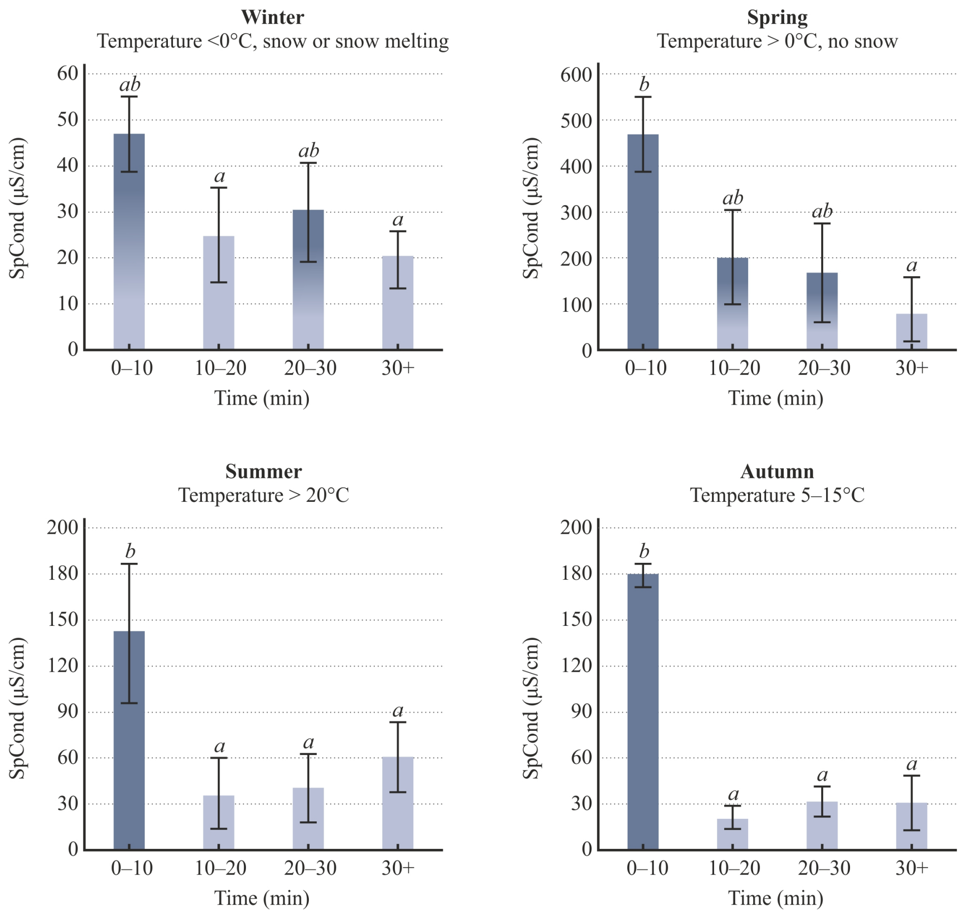

Figure 4. Seasonal variability (mean ± SEM) in electrical conductivity (µS/cm) in roof runoff (RR) as a function of rainfall duration. Statistically significant differences between time interval groups were determined using Dunn's post hoc test at $p < 0.05$. Various superscripts indicate groups of means that differ significantly from each other.

4. Discussion

Sampling location is of great importance in analyzing the pollution levels of water bodies along the stormwater runoff route. High concentrations of metals indicate moderate and heavy pollution at sampling sites (SR and SC), one can see the effect of urbanization on the quality of surface runoff in the city. The occurrence of Pb in surface runoff is due to road traffic [42], while Cu and Fe are present due to the corrosion of metal parts of cars [42,43].

Since the majority of water samples along the stormwater runoff route have high concentrations of the analyzed metals, the runoff from the studied areas of the SR and SC can be classified as heavily or even extremely polluted. In the case of the roof area, the runoff is less polluted. Therefore, runoff from surfaces with a high degree of sealing, especially those intended for vehicular traffic, can be considered a threat to the environment, especially if it is discharged directly into the river. Therefore, it is necessary to limit or eliminate the inflow of traffic-related pollution.

The results show that the concentration of metals in the water samples along the rainfall–runoff process increases with decreasing rainfall frequency. This relationship is confirmed by the interesting results of Soltaninia et al. [44]. The authors considered the type of land use and showed that the concentrations of Cu, Zn, and Pb increase along with the ADP. It was found that heavy metal concentrations increased significantly between 1 dry day and 115 dry days in areas with high development (Zn from 0.8 mg/L to 5.2 mg/L; Cu from 0.1 mg/L to 0.75 mg/L; Pb from 0.1 mg/L to 1.4 mg/L). In open areas with less infrastructure, Zn increased from 0.2 mg/L to 0.4 mg/L; Cu from 0.02 mg/L to 0.12 mg/L; and Pb from 0.02 mg/L to 0.6 mg/L. A study by Zhang et al. [45] also confirmed that land use and the ADP significantly affect the concentration of Zn and Cu in surface runoff. Ladislas et al. [46] showed that the variability of the heavy metal concentrations in surface runoff from highways depends on the ADP, among other factors. In support of this hypothesis, Zn concentrations in urban runoff range from 200 µg/L to 2800 µg/L, according to the literature [46]. It should be noted that the total concentration of heavy metals in street runoff is 2–15 times higher than the heavy metal concentrations in roof runoff [47–51]. The highest concentrations are measured in water samples from stormwater collectors [52,53]. Heavy metal concentrations in water samples from stormwater collectors are 3–1000 times higher than the permissible average concentration of heavy metals specified in the standards (2008/105/EC) [54]. Also, comparing heavy metal concentrations to irrigation water quality standards [55], tested water samples exceed these standards. Fe shows the highest levels of exceedance, whether considering water samples from the SR or SC. This is important, especially during the spring season, when cultivated fields rely on rainwater and roof runoff for irrigation and are exposed to surface runoff. There is a risk that the yields from these fields could pose health risks to people [44,56].

The results of our study in Olsztyn (Poland) generally confirm the findings of other researchers [48–52]. The diversity and variability of these factors lead to a wide range of metal concentration values in the literature. The high concentration of Cu and Pb in surface runoff in urban areas may be due to several factors, including emissions from transportation, industry, point sources, and water and wastewater systems. It should be noted that the increase in the intensity of these substances in space is the result of progressive urbanization and consequently the increase in population density. As Olsztyn is a relatively unpolluted city, it is understandable that the results fluctuate around the lower limits of the ranges indicated in the cited works, especially as far as the results of the rainwater collector (Cu, Pb) are concerned. It should be noted that several factors, including weather conditions, traffic intensity, rainfall frequency, and type of pavement, influence heavy metal concentrations in urban catchments. The diversity and variability of these factors result in a wide range of metal concentration values in the literature. This explains the fact that significantly higher values are measured in metropolitan areas (e.g., Beijing [57], Shanghai [58]) rather than in smaller cities (e.g., Aqaba [59]) or in Olsztyn, where this study was conducted. The obtained results are an argument for the need to reduce surface runoff pollution from urban areas. Thus far, engineered solutions have been the most common [60]. Stormwater separators and improved stormwater treatment facilities are effective engineered solutions. The authors point out that these methods are costly and time-consuming. However, NBS are increasingly used and are gaining social acceptance. Such solutions include elements that combine engineered and ecological functions, such as rain gardens or permeable surfaces [29]. The effectiveness of NBS in precleaning surface runoff is confirmed by studies conducted by [61–64]. Rain gardens can reduce the content of heavy metals in surface runoff by 80–90% [62]. Permeable pavements can reduce the presence of metals by 73% to 99% [61]. Rain gardens reduce surface runoff by 1.93% to 42% [65,66]. Permeable pavements improve water balance by reducing surface runoff by 1 to 40% [67]. Based on this study's results, NBS can be implemented. It will help to improve the water balance and limit surface runoff, reducing the pollution of rivers from urban sources.

Future directions of urban hydrologic studies should consider long-term monitoring and analysis of the rainfall–runoff process to ensure successful implementation of NBS or BGI solutions as a basis for sustainable development of the urban environment.

5. Conclusions

Our study, conducted in a 30 ha urban sub-catchment, showed that the rainfall–runoff process, consisting of direct precipitation, surface runoff from impervious surfaces, and recipients, exhibited a significant gradient of water quality degradation. The results showed that pollutants covering impervious surfaces (roads, sidewalks) in urban areas are easily washed away with surface runoff. The higher concentrations of heavy metals in surface runoffs and storm collectors may pose a significant threat for stormwater recipients, particularly in winter and spring, due to increased deposition of air pollutants and salt washout from roads. This study highlights the importance of monitoring stormwater quality and heavy metals in urban watersheds, in terms of impacts on the river ecosystem as a recipient of stormwater. Efforts should be made to increase permeable and biologically active areas in cities. Solutions such as green infrastructure and stormwater management are proposed to mitigate the impacts of urbanization on water quality and protect the aquatic environment. When properly adapted to local hydrological and meteorological conditions, engineered and biological solutions offer a range of benefits that can be effective long-term tools for water management in urban catchments.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15193505/s1, Table S1: Data from rainwater and stormwater monitoring.

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